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Ph.D. degree in Electrical Eng.

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temperature dependence of conductivity and mobility of β and a-sic for temperature sensors

By

Nayef Muhammed Abu-Ageel

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Electrical Engineering

1996

ABSTRACT

TEMPERATURE DEPENDENCE OF CONDUCTIVITY AND MOBILITY OF β -AND α -Sic for temperature sensors

By

Nayef Muhammed Abu-Ageel

Conductivity and Hall measurements of poly and monocrystalline β -SiC films prepared by laser ablation and commercial α -SiC wafers were conducted in a temperature range of 13-800 K. Polycrystalline β -SiC films and heavily doped α -SiC wafers showed mobilities in ranges of 0.3-3 cm²/Vs and 2-50 cm²/Vs and electron concentrations in ranges of 10¹⁹-4×10²⁰ cm⁻³ and 5×10¹⁷-5×10¹⁹ cm⁻³, respectively, whereas lightly doped α -SiC wafers showed higher mobilities (10-280 cm²/Vs) and lower electron concentrations (4×10¹²-1×10¹⁹ cm⁻³) throughout the entire temperature range.

Transport data of polycrystalline β -SiC films and heavily doped α -SiC wafers exhibited a shallow activation energy of ≤ 5 meV below 100 K. In this temperature range, polycrystalline β -SiC data was analyzed in terms of impurity/defect band and hopping models. At higher temperatures, two activation energies (9-20 meV and 75 meV) were obtained for polycrystalline β -SiC and one activation energy (80-84 meV) for α -SiC. In case of heteroepitaxial β -SiC films deposited on Si substrates, two models were presented to extract the conductivity and Hall data of β -SiC films from measurements on the β -SiC/Si structure.

Measurements of Seebeck coefficient were obtained for polycrystalline 3C-SiC films and monocrystalline α -SiC wafers in a temperature range of 300-533 K. The resistivity and Seebeck coefficient data were investigated to assess the potential of these SiC polytypes for thermal sensors such as temperature and heat flux measuring devices.

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ACKNOWLEDGEMENTS

I would like to extend my sincere appreciation to Professor Dean M. Aslam, the principle adviser of this thesis, for his excellent guidance and constant encouragement and to Dr. Lajous Rimai from Ford Motor Company for his excellent and valuable supervision of this work.

I would like to thank the members of my oral committee, Professor J. Asmussen, Professor D. Reinhard and Professor M. Thorpe for their time and comments.

I would also like to thank the group at the Scientific Research Laboratories of Ford Motor Company for the technical assistance. In particular I wish to thank: R. Ager, R. Soltis, W. Vassell, A. Samman, D. Kubinski and J. Visser.

Finally, I would like to extend my special appreciation to my parents, whom I have not seen for more than eight years, for their constant support since my early school days.

TABLE OF CONTENTS

LIST	OF T	ABLES	ix
LIST	OF FI	IGURES	x
1	Rese	1	
	1.1	Introduction	1
	1.2	Objective of this Work	3
	1.3	Organization of Dissertation	3
2	Back	ground	4
	2.1	Introduction	4
	2.2	SiC Properties	5
	2.3	SiC Technology	11
		2.3.1 Thin-Film Growth of SiC	11
		2.3.2 Doping	15
		2.3.3 Metallization	16
	2.4	Characterization of SiC Films	17
		2.4.1 Structural Characterization	17
		2.4.2 Electrical Properties	18
	2.5	SiC Films as Temperature Sensors	20
	2.6	Summary	21
3	Lase	r Ablation Technology	22
	3.1	Introduction	22
	3.2	Pulsed Laser Deposition Technique	23
	3.3	Sample Fabrication	23
		3.3.1 Deposition of SiC Film	23
		3.3.2 Deposition of Metal Contacts	26
	3.4	Summary	27

4	Meas	surement Techniques	28
	4.1	Introduction	28
	4.2	Van der Pauw's Measuring Procedure	28
	4.3	Seebeck Coefficient Measurement Technique	30
	4.4	Summary	33
5	Cond	luctivity and Mobility of SiC	34
	5.1	Introduction	34
	5.2	Polycrystalline Cubic SiC Films	35
		5.2.1 Experimental	35
		5.2.2 Conductivity and Hall Measurements	36
		5.2.3 Analysis of Intermediate and High Temperature Data	39
		5.2.4 Analysis of Low Temperature Data	50
		5.2.4.1 Hopping Conduction	51
		5.2.4.2 Impurity/Defect Band Conduction	59
	5.3	Monocrystalline SiC	64
		5.3.1 Monocrystalline α -SiC Substrates	65
		5.3.2 Monocrystalline β-SiC Films	70
	5.4	Summary	85
6	Seeb	eck Coefficient of SiC	87
	6.1	Introduction	87
	6.2	The Seebeck Coefficient	89
	6.3	Results and Discussion	93
	6.4	Applications	100
		6.4.1 Thermoelectric Temperature Sensor	100
		6.4.2 Heat Flux Sensor	102
		6.4.3 Thermoelectric Generator	106
	6.5	Summary	109
7	SiC '	Thermistors	110
	7.1	Introduction	110
	7.2	Resistivity of SiC	111
	7.3	Summary	121
8	Sum	mary and Future Research	122
	8.1	Future Work	123
Mul	tiple-La	yer Resistivity Model	124
BIB	LIOGR	APHY	135

LIST OF TABLES

2.1.	Comparison	of semicond	lucting pro	operties.		. 6
2 .1. V	Companson	or semicone	lucting pro	pernes.	•••	, v

2.2. Lattice constants, energy gaps at 300K, stacking sequences, and thermal conductivity of common SiC polytypes. ... 10

2.3. Electronic parameters of β -SiC⁸⁶. m_o is the electronic rest mass. ... 19

5.1. Activation energies: e_i (conductivity) and E_i (Hall data) and constants: a_i (conductivity) and A_i (Hall data) for five samples. ... 42

5.2. Thicknesses, deposition temperatures, deposition times, and pulse rates for five SiC films. ... 71

6.1. The electron concentration $n=1/qR_{\rm H}$, Fermi level location below E_c and effective mass estimated at 300 K for some polycrystalline β -SiC and α -SiC monocrystalline samples. ... 97

6.2. Properties of some materials for thermoelectric generation applications. η is calculated using T_{high} =600K and T_{low} =300K. ... 108

7.1. The temperature coefficient α at 300 K for some alloys, oxides, hexagonal SiC, and polycrystalline SiC films. ... 118

7.2. Temperature coefficients of resistivity (TCR) of some polycrystalline 3C-SiC samples evaluated over the corresponding temperature range. ... 119

7.3. Temperature coefficients of resistivity (TCR) of some polycrystalline and single crystalline 3C-SiC films and heteroepitaxial 6H- and 4H-SiC samples evaluated over the corresponding temperature range. Thicknesses and available carrier concentrations obtained at room temperatures are also provided. ... 120

LIST OF FIGURES

2.1. A close-packed layer of spheres with centers at points A. A second layer of spheres can be placed over this, with centers over the points marked B. A third layer can be placed over A and the resulting sequence is ABAB... (2H structure) or it can be placed over C and the resulting sequence is ABCABC... (3C structure). 7

2.2. Possible respective orientation of Si and C atoms in tetrahedral bonding.

- (a) Si-C group with adhering carbon and silicon atoms.
- (b) Si and C atoms in eclipsed position (2H).
- (c) Si and C atoms in staggered position (3C).
- (d) The axes-system and the base of the unit cell. ... 7

2.3. Positions of atoms in (1120) planes.

- (a) Relative position of Si and C atoms.
- (b) Position of Si in 3C.
- (c) Position of Si in 2H.
- (d) Position of Si in 6H.
- (e) Position of Si in 15R.
- (f) Position of Si in 4H.

3.1. A schematic diagram of the pulsed laser deposition system. ... 25

... 9

4.1. A sample of arbitrary shape with four metal contacts along the circumference for conductivity and Hall measurements. ... 30

4.2. Sample arrangement for Seebeck coefficient measurement. ... 31

5.1 Temperature dependence of conductivity of 3 polycrystalline β -SiC films with the fits shown as solid lines. ... 37

5.2 Temperature dependence of the inverse of measured Hall coefficient, $1/R_{\rm H}$, and the corresponding carrier concentration, $1/qR_{\rm H}$, of samples of Fig.5.1 with the fits shown as solid lines. ... 38

5.3 Temperature dependence of the mobility derived from the Hall and conductivity data as $\sigma R_{\rm H}$ for samples of Fig.5.1. ... 40

5.4 The measured conductivity (hollow symbols) of 152B and fits (solid lines) obtained in 3 different temperature ranges using Eq.5.4. Slopes and intercepts of these lines represent activation energies and corresponding constants: (a) e_1 and a_1 , (b) e_2 and a_2 , and (c) e_3 and a_3 43

5.5 The measured electron concentration (hollow symbols) of 152B and fits (solid lines) obtained in 3 different temperature ranges using Eq.5.3. Slopes and intercepts of these lines represent activation energies and corresponding constants: (a) E_1 and A_1 , (b) E_2 and A_2 , and (c) E_3 and A_3 44

5.6 Fermi level position computed using Fermi Statistics (Eqs.5.1-2) for 2 of the samples of Table 5.1. ... 47

5.7 Inverse of measured Hall coefficient, $1/R_{\rm H}$, for samples of Fig.5.6, with carrier concentration fits obtained by the charge neutrality condition assuming no compensation and considering 3 independent donor levels represented by activation energies shown in Table 5.1.

5.8 Fermi level position computed by fitting the measured electron concentration n of 2 polycrystalline samples using Eq.5.5. In these fits, N_a , N_{d1} and N_{d2} are treated as parameters and $(N_a/N_{d2})=33\%$ 54

5.9 Effective carrier concentration, $1/qR_{\rm H}$, for samples of Fig.5.8, with carrier concentration fits obtained by the charge neutrality condition assuming compensation ratio of 33% and considering two independent donor levels represented by activation energies E_1 and E_2 as shown in Table 5.1. 55

5.10 Fermi level position for sample 194A computed using the charge neutrality condition for compensation ratios of 10%, 33%, and 90% and considering two independent donor levels represented by activation energies E_1 and E_2 shown in Table 5.1. ... 56

5.11 Inverse of measured Hall coefficient, $1/R_{\rm H}$, for 194A with its fits using corresponding Fermi level locations for the 3 different compensation ratios of Fig.5.10. 57

5.12 Energy band of SiC with two donor levels located at E_1 and E_2 below the bottom of the conduction band E_c . The impurity/defect band is located at (E_2-E_3) below E_c . The energy levels in this figure are not drawn to scale and the intrinsic level E_i should not be exactly in the middle of the bandgap. ... 60

5.13 Inverse of measured Hall coefficient, $1/R_{\rm H}$, with corresponding electron concentration for some 4H- and 6H-SiC. The fits for samples A and H in the low temperature range are shown as solid lines. ... 66

5.14 The Hall mobility ($\mu=\sigma R_{\rm H}$) as computed from Fig.5.13 and Fig.5.15. ... 67

5.15 The temperature dependence of measured conductivity for 7 samples of 6H-SiC and one 4H-SiC sample. ... 69

5.16 The measured Hall voltage of sample 362 in two temperature ranges. These results are obtained using an input current of 0.1 mA and magnetic field of 8 kGauss. Interface-Si structure represents the Si under the peeled off β -SiC film. 73

5.17 The measured Hall voltage in the high and low temperature ranges of some samples of Table 5.3. These results are obtained using an input current of 0.1 mA and magnetic field of 8 kGauss. ... 74

5.18 The measured resistance of two highly resistive films in the low and high temperature ranges. The measurement was done on SiC/Si structure (solid symbols) and on interface-Si structure after the removal of the SiC film (hollow symbols).79

5.19 The measured resistance of 3 different films in the low and high temperature ranges. The solid symbols represent the data of the SiC/Si structure. The hollow symbols represent the data of interface-Si after removing the delaminated portion of the SiC film. The dotted line represents the data of the Si substrate that was underneath the shadow mask during deposition. ... 80

5.20 (a) A schematic of the sample used for Hall voltage measurement with 4 metal contacts at the corners of the sample. (b) Equivalent cicuit of (a). ... 82

6.1 (a) Top view of the sample under test showing the metal contacts and the thermocouples with T being the lower end temperature and ΔT being the temperature difference between the two ends. (b) A schematic of the band diagram of the sample showing the electrical field E and the Seebeck emf (i.e. qV). 91

6.2 Measured Seebeck coefficient for three polycrystalline 3C-SiC films (solid symbols) and three hexagonal samples (hollow symbols) 94

 6.4 The absolute value of the Seebeck emf for β -SiC (solid symbols) and α -SiC (hollow symbols) and a platinum thermocouple. ... 101

6.5 A schematic of n- and p-SiC cells connected serially. This schematic represents either a thermoelectric generator with T_{high} - T_{low} is large or a heat flux sensor with T_{high} - T_{low} = ΔT is very small. ... 105

7.1 The resistivity of some β -SiC (solid symbols) and α -SiC (hollow symbols). ... 112

7.2 Two cycles of the resistivity of some polycrystalline β -SiC films. ... 114

7.3 (a) The sensitivity coefficient α for samples of Fig.7.1. (b) An expansion of the data shown in (a). ... 116

A.1 A top view of the sample used in our model. The two metal contacts are shown in dark color. ... 125

A.2 A two dimensional plot of the imposed field in the Y direction at the surface (i.e. Z=0). ... 126

A.3 A two dimensional plot of the imposed field in the X direction at the surface (i.e. Z=0). ... 127

A.4 A three dimensional plot of the imposed field at the surface (i.e. Z=0). ... 128

A.5 A three dimensional plot of the potential at the surface (i.e. Z=0) assuming that the conductivity of the three layers is the same. ... 129

CHAPTER 1

RESEARCH MOTIVATION AND GOAL

1.1 Introduction

There is a growing research and interest in wide bandgap materials because of their potential use in high power, high temperature, and high frequency electronic device applications. Silicon-based devices have limited operating temperature (below 150°C) and their use for micromechanics is limited to temperatures below 600°C where Si starts to deform plastically^{1,2}. There is a need for a semiconductor, operable in a wide temperature range, with high thermal conductivity and breakdown voltage. Although there are several interesting wide bandgap materials such as diamond, SiC, GaAs, and other III-V compounds, of these SiC is the most promising one. GaAs is not suitable for high temperature applications since its bandgap is close to that of Si. Diamond technology is still being developed and n-type doping and heteroepitaxy are not very successful⁷. Technology of other wide bandgap materials is not well developed⁸. SiC technology is much more advanced due to major improvements in bulk and film growth of SiC, capability of n- and p-type doping, physical stability in an oxidizing atmosphere, the

possibility to grow relatively low-defect-density oxides on its surface² and some degree of compatibility with the existing Si technology^{5,9,10}.

SiC has strong potential for electronic devices and sensors operating at high temperatures and in chemically aggressive environments such as those prevailing in automotive and jet engines⁵. This is due to the unique physical, chemical and electrical properties of SiC such as its large band gap, large thermal conductivity and high breakdown voltage.

Chemical vapor deposition (CVD) is the most successful technique so far for (hetero and homo) epitaxial growth of SiC films onto Si, 4H-SiC and 6H-SiC substrates. This technique usually requires a high growth temperature (1400°C) which is incompatible with the existing Si technology and may lead to film contamination in addition to the hydrogen incorporation inherent to the process^{2,11}. Pulsed Laser Deposition (PLD) has been used recently to deposit polycrystalline^{12,13} and monocrystalline^{14,15} β -SiC films from ceramic SiC targets on Si substrates at 800°C and 900-1000°C, respectively, but these films have not been fully characterized.

In this research the temperature dependence of conductivity and Hall coefficient in the temperature ranges of 13-1275 K and 17-800 K, respectively, are reported for the first time for laser-deposited polycrystalline β -SiC films. The temperature dependence of Seebeck coefficient in the temperature range of 300-550 K is reported for the first time for β -SiC and α -SiC. Furthermore, measurements of the conductivity and Hall coefficient of monocrystalline β - and α -SiC in a temperature range of 13-800 K are also reported. These results are analyzed to determine the potential of β - and α -SiC for temperature sensor applications.

1.2 Objectives of this Work

The primary objectives of this research are to study the temperature dependence of conductivity, mobility and Seebeck coefficient of β - and α -SiC in a wide temperature range and to determine their potential for temperature sensor applications.

This requires deposition of the metal contacts needed for the measurements and construction of the measurement systems. The obtained results have to be analyzed using appropriate models, in order to assess the potential of SiC for thermal sensor applications such as temperature and heat flux measuring devices.

1.3 Organization of Dissertation

A review of SiC properties, technologies, and SiC use for temperature sensors is presented in chapter 2. The deposition process that we have used to prepare SiC films and their metal contacts is explained in chapter 3. A description of the conductivity, Hall, and thermoelectric measurements methods used in this research is presented in chapter 4. Chapter 5 presents the measured conductivity and Hall concentration for polycrystalline and heteroepitaxial 3C-SiC and monocrystalline α -SiC. Chapter 6 presents the measurement of the Seebeck coefficient for SiC in addition to a discussion of the potential application of SiC in thermoelectric sensors. Chapter 7 focusses on potential application of SiC as a thermistor. Chapters 3-7 deal with the work performed in the present research. Chapter 8 summarizes the results of this study.

CHAPTER 2

BACKGROUND

2.1 Introduction

The interest in SiC has been renewed since the introduction of the technology that allows the growth of SiC films on Si substrates in the 1980's. In the late 1980's, a major development in SiC technology was achieved as the commercial production of highquality 6H-SiC wafers started. Although there has been some success in preparing SiC electronic devices, SiC technology still suffers from problems related to crystal growth, doping and metallization. A review of the progress that has been made in SiC technology is needed in order to investigate such problems.

The SiC general properties such as physical, chemical, and structural properties compared to those of Si are discussed in section 2.2. In addition, this section contains a summary of the methods used for bulk growth of SiC crystals. In section 2.3, SiC thin film technology which includes thin film growth, doping, and metallization is discussed. Structural and electrical characterizations of SiC films are presented in section 2.4. The use of SiC films as temperature sensors is discussed in section 2.5.

2.2 SiC Properties

SiC is a wide-band-gap semiconductor with outstanding physical and chemical characteristics. Table 2.1 shows the properties of β - and 6H-SiC compared with those of diamond, Si, and GaAs. This material possesses high hardness, high thermal conductivity, superior resistance to fracture and deformation at elevated temperatures, excellent resistance to corrosion, thermal shock and radiation damage, and is chemically inert^{5,2,10}. Junction isolation problems limit the operation of silicon based devices to less than 150°C.² SiC based devices would remove this limitation. The electrical properties of β -SiC films compare favorably with Si for minority, as well as majority carrier device applications.

SiC is a stable compound of silicon and carbon. Each Si (or C) atom is surrounded by four C (or Si) atoms tetrahedrally with sp³ hybrid bonds (covalency is about 88%)¹⁶. Most of the valence electron-charge density in SiC is located near the carbon atom, because of this asymmetric charge density SiC looks like a polar compound. SiC exhibits a form of one-dimensional polymorphism called polytypism. Different stacking sequence of double layers of Si and C atoms results in different polytypes structures. Each double layer consists of a plane of close-packed Si atoms over a plane of close-packed C atoms; one Si atom lies directly over each C atom in a double layer. Each successive double layer is stacked on the previous double layer in a close-packed arrangement that allows for only three possible relative positions for the double layers as shown in Fig.2.1 and Fig.2.2. These positions are normally labeled A, B, and C. Cubic, hexagonal, or rhombohedral structures are produced as a result of different stacking sequence. According

Properties	3C-SiC	6H-SiC	Diamond	Si	GaAs
Lattice constant (Å)	4.358		3.567	5.430	5.65
Thermal expansion (×10 ⁻⁶⁰ C)	4.63		1.1	4.16	5.9
Density (g.cm ⁻³)	3.216		3.515	2.328	
Melting point (°C)	2540*	**	1420	1238	⟩1800
Bandgap (eV)	2.2	2.9	5.45	1.1	1.43
Saturated electron velocity V _s (×10 ⁷ cm s ⁻¹)	2.5		2.7	1.0	2.0
Mobility (cm ² V ⁻¹ s ⁻¹) Electron Hole	1000 40	600	2200 1600	1500 600	8500 400
Breakdown voltage E _B (×10 ⁵ V cm)	40		100	3	40
Dielectric constant K	9.7		5.5	11.8	12.8
Thermal conductivity $\sigma_T(W \text{ cm}^{-1}K^{-1})$	5	4.9	20	1.5	0.46
Absorption edge (µm)	0.4		0.2	1.4	
Refractive index	2.65		2.42	3.5	3.4
Hardness (kg mm ⁻²)	3500		10000	1000	600
Z_{J} (×10 ²³ W Ω s ⁻²)	10240		73856	9.0	62.5
$Z_{\rm K}$ (×10 ² W cm ⁻¹ s ⁻¹ °C)	90.3		444	13.8	6.3
Physical stability	excellent	excellent	very good	good	fair
Bandgap type	indirect	indirect	indirect	indirect	direct

Table 2.1. Comparison of semiconducting properties^{5,6}.

Sublimes *

** Phase change $Z_J = (E_B V_S / \pi)^2$ $Z_K = \sigma_T (V_S / K)^{1/2}$



Fig.2.1. A close-packed layer of spheres with centers at points A. A second layer of spheres can be placed over this, with centers over the points marked B. A third layer can be placed over A and the resulting sequence is ABCAB... (2H structure) or it can be placed over C and the resulting sequence is ABCABC... (3C structure).



Fig.2.2. Possible respective orientation of Si and C atoms in tetrahedral bonding¹⁷.

- (a) Si-C group with adhering carbon and silicon atoms.
- (b) Si and C atoms in eclipsed position (2H).
- (c) Si and C atoms in staggered position (3C).
- (d) The axes-system and the base of the unit cell.

to Ramsdell the different polytypes can be characterized by their local symmetry (C=cubic, H=hexagonal or R=rhombohedral) and the number of double-layers after which the layer sequence is repeated. Thus, we have 3C for cubic SiC (known as β -SiC) and all of the other polytypes are known as α -SiC. In these structures all atoms lie on symmetry axes, and all symmetry axes lie in (1120) planes (in this notation the c (cubic 111) axis is (0001)) as shown in Fig.2.2(d). A (1120) plane therefore represents these structures as shown in Fig.2.3(a). The different crystallographic polytypes of SiC are formed by different zig-zag sequences of Si-C double layers as shown in Fig.2.3.

The band structure, and thus important electronic and optical properties vary significantly from one polytype to another. The most important polytypes for applications are 3C-, 4H-, and 6H-SiC due to layer production in pure form. Cubic SiC has the zincblende lattice arrangement of GaAs⁵. Table 2.2 shows Ramsdell notation, lattice constants, stacking sequences and energy gaps of some polytypes.

Acheson's method was the first process to produce bulk crystals of silicon carbide (for grinding and cutting purposes). In this process a mixture of silica and carbon (sand and coal) is heated according to a definite temperature-time cycle in air to produce silicon carbide¹⁷. The development of a sublimation process for growing higher purity α -SiC single crystals was reported by Lely in 1955. This process as it had been developed by the early 1970's involves the heating of a polycrystalline SiC charge to about 2500 °C to sublime the SiC which condensed on the slightly cooler parts of an inner hollow graphite cavity. This cavity was formed initially inside the charge and lined with a porous graphite tube.



Fig.2.3. Positions of atoms in (1120) planes¹⁷.

- (a) Relative position of Si and C atoms.
- (b) Position of Si in 3C.
- (c) Position of Si in 2H.
- (d) Position of Si in 6H.
- (e) Position of Si in 15R.
- (f) Position of Si in 4H.

Table 2.2. Lattice constants, energy gaps at 300K, stacking sequences, and thermal conductivity of common SiC polytypes.^{5,18}

Туре	Constants (Å)		Gap	Stacking sequence	Conductivity
	a	С	(eV)		(W/cm.K)
2H	3.076	5.048	3.3	ABAB	4.9
4H	3.073	10.053	3.3	ABACABAC	4.9
6H	3.081	15.117	2.9	ABCACBABCACB	4.9
3C	4.360		2.2	ABCABC	5.0

Nucleation of individual crystals was uncontrolled, and the resulting crystals were randomly-sized hexagonally-shaped α -SiC platelets. The platelets often exhibited a layered structure of various α polytypes with the stacking direction of the atomic planes of these polytypes being along the {0001} directions. Transition region of random stacking of double layers (one-dimensional disorder) occurred between polytypes. Since these polytypes have different energy bandgaps, undesirable heterojunctions were produced in the crystals^{5,9}. A seeded-growth sublimation process developed by Tairov et al.^{19,20}, Ziegler et al.²¹, and Carter et al.²² produced bulk crystals of a single polytype of SiC at temperatures of the order of 2200°C. The size of the crystals is limited not by the technique, but by the ability to cut large diameters of this very hard material⁹.

This sublimation process has been taken over by the groups at Siemens AG²³ and by a group at the North Carolina State University from which an industrial activity at Cree Research was derived. Highly doped n-type 25 mm wafers of 6H-SiC and 4H-SiC are now commercially available¹¹. Since this sublimation growth technique produces highly doped (up to 10^{19} cm⁻³) n-type wafers, an epitaxial layer has to be grown onto them in order to realize active microelectronic devices. Recently, growth of bulk crystals of β -SiC by the sublimation technique has been reported^{24,25}. The seeds for the sublimation process were 6H-SiC substrates (Acheson- and Lely-grown) and free-standing monocrystalline β -SiC films. Chemical vapor deposition technique was used initially to grow monocrystalline β -SiC films on Si(100) substrates and subsequently the Si substrate was removed.

2.3 SiC Technology

2.3.1 Thin-Film Growth of SiC

Because controllable quality SiC substrates are not available, the growth of SiC thin films on foreign substrates in amorphous (a-), polycrystalline (pc-) as well as in heteroepitaxial (c-) forms has been investigated extensively. Polycrystalline and amorphous SiC have been grown on Si, thermally oxidized Si, glass and sapphire substrates. Heteroepitaxial growth of β -SiC has been achieved on Si as well as on TiC_x. Single crystal growth of β - and 6H-SiC was achieved on 6H-SiC substrates (Acheson, Lely and boule wafers)⁵.

Silicon substrates have been most frequently used as the substrate of choice for the heteroepitaxial growth of β -SiC thin films because of the availability of the former in well characterized and reproducible defect free and large area forms of controlled purity⁹. Another interesting feature of Si substrates is that in spite of the large lattice mismatch (20%) the cubic structure of the Si lattice automatically selects the cubic polytype β -SiC. The heteroepitaxial growth of SiC on Si still has the following major problems.

(1) The high defect density, which includes misfit dislocations, twins, stacking faults, and antiphase boundaries (APB's), is present. The APB's are created because of the growth of a non centrosymmetric (β -SiC) onto a centrosymmetric substrate (Si) from a random distribution of nucleation sites. The density of defects is higher at the interface where misfit dislocations and twins are usually found and might extend to few μ m from the interface. On the other hand the stacking faults as well as APB's generally extend all the way to the film surface. These defects might be caused by the mismatches in the coefficients of lattice parameters (20%) and thermal expansion (8%) between the Si and SiC, or probably by the nucleation process²⁶⁻²⁸.

(2) The high concentration of residual donors and compensating acceptors. Hall measurements indicate that while the net electron carrier concentration in unintentionally doped material could be as low as 5×10^{16} cm⁻³, the actual donor and acceptor impurity concentrations are often as high as 10^{18} cm⁻³ (i.e. there is greater than 90% compensation of the donors by acceptors). So far the evidence regarding the origin of the donors and the source of the compensating acceptors points to nitrogen and point defects in the material, respectively^{29,30}.

(3) Chemical vapor deposition (CVD) growth of β -SiC films on Si often requires very high substrate temperatures (1360°C in many cases) which can lead to film

contamination by other impurities. Also some hydrogen incorporation inherent to the process. The high substrate temperatures are close to the melting temperature of Si (1412°C). Thus the compatibility with the existing Si technology is hard to fulfill.

There have been numerous studies regarding the elimination of the above problems. In order to reduce the high defect density caused by the lattice mismatch, TiC_x (less than 1% mismatch) substrates were investigated. Somewhat improved growth was achieved, but great difficulties (3140°C growth temperature at pressure greater than 10 atmospheres) in producing defect-free single-crystal TiC_x has hindered its use as a substrate for SiC growth³¹.

Another way attempted to overcome the large lattice mismatch between SiC and Si is to convert the Si surface layer of the substrate to a thin β -SiC layer by flowing a dilute mixture of a hydrocarbon in H₂ over the substrate as its temperature is ramped from room temperature to the growth temperature (near 1400°C). This carbonization step (buffer layer) is followed by the film growth using a flowing mixture of silane and a hydrocarbon carried in hydrogen. This two-step β -SiC CVD process has been initially reported by Nishino et al.^{32,33} and subsequently by numerous authors³⁴⁻³⁷. Heteroepitaxial growth of β -SiC at 1100°C on Si(111) and Si(100) has been recently reported by Takahashi et al¹⁸. Golecki et al.³⁸ have recently reported heteroepitaxial growth of β -SiC using a single stoichiometric precursor (H₃SiCH₃) in their thermal CVD process.

New deposition techniques of β -SiC films are now being investigated to determine

if the film quality can be improved. Fuyuki et al.³⁹ have reported atomic layer-by-layer control using gas source molecular beam epitaxy (Gas-source MBE) of the deposition of β -SiC within the temperature range 1250-1320K on β -SiC(100) substrates previously prepared on Si(100) by the two-step CVD process. Sugii et al.⁴⁰ have reported the growth of β -SiC(111) on Si(111) oriented 4° toward <211> using gas-source MBE at 1173K. Photostimulated epitaxial deposition of β -SiC on sapphire (α -Al₂O₃)(0001) has been achieved by Nakamatsu and coworkers^{41,42} using an ArF laser, C₂H₂, and Si₂H₆ within the temperature range of 1253-1425K, and a pressure of 10⁻² Pa. Deposition of polycrystalline β -SiC films on Si using an electron cyclotron resonance (EAR) plasma (v=2.45 Hz) discharge in a gas mixture of Sh₄, C₄, and H₂ in the temperature range 680-K have been reported by Cohere et al.⁴³. Electron beam evaporation of α -SiC has been used to deposit polycrystalline SiC films on [111] Si and sapphire substrates, within a temperature range of 600-900°C, but these films contain α -SiC^{44,45}. Other techniques such as sputtering can also produce SiC films on Si or some other substrates, at lower temperatures than those used in the CVD process, but the films are usually amorphous or microcrystalline⁴⁶. The laser ablation technique more recently has been used to deposit polycrystalline^{12,13} and epitaxial^{14,15} SiC films from ceramic SiC targets on Si substrates at 800°C and 900-1150°C, respectively.

In an attempt to substantially reduce the concentrations of all defects simultaneously, growth of β -SiC(111) on the Si(0001) and C(0001) faces of commercial (Acheson-derived) 6H-SiC single crystals substrates has been investigated within the temperature range of 1683-K at 1 aim total pressure⁴⁷⁻⁵⁰. In contrast to films grown on Si

substrates, few defects were observed in these films when examined by cross sectional transmission electron microscopy (XTEM), however, examination in plan view revealed the presence of double positioning boundaries (DPB's). DPB's are usually created when the orientation of the film growth is not the same at all nucleation points. High quality 6H-SiC films have been grown on "off-axis" 6H-SiC wafers that were produced from sublimation-grown boules⁵¹⁻⁵⁵. The low defect density was verified by extensive plan view TEM⁵¹.

2.3.2 Doping

The capability of shallow n- and p-type dopings of SiC is essential if the material is to reach its full potential for electronic device applications. SiC film growth by various techniques including chemical vapor deposition (CVD) leads usually to highly n-type doped films with no intentional introduction of dopants. Analysis of the temperature dependence of the experimental Hall data shows an activation energy of 15-22 meV. Some authors have suggested that the residual shallow donor is nitrogen⁵⁶ and others related the presence of the shallow activation energy to structural defects that behave as shallow donors⁹.

Although SiC films are unintentionally doped, controlled n- and p-type dopings can be achieved by in situ doping (gas phase during growth or diffusion sources) or ion implantation. Al and P are usually used to dope SiC p-type and n-type, respectively. Nitrogen is used also to obtain n-type conductivity by replacing a C-site. For 6H-SiC the shallowest acceptor observed is Al on Si-site with an activation energy of 200 meV⁷. For 3C-SiC the activation energies for Al acceptors³⁰ and nitrogen donors⁵⁷ are 160 and 34-37 meV, respectively.

2.3.3 Metallization

High temperature stable and low resistive contact structures are essential for development of SiC devices. Several contact structures have been investigated to date, however most results point at difficulties to fabricate low resistivity ohmic contacts with good adhesion. Although diffusion of the metal and chemical reaction produces good mechanical adhesion, excessive diffusion at the high temperatures results in spiking and might cause electrical shorting of the device⁵⁸.

Evaporation and sputtering techniques are usually used to metallize SiC^{59.64}. Ni is widely used to form ohmic contacts to SiC upon high temperature annealing (900°C). This results in formation of Ni silicides⁶⁵. Ni, Au-Ta, Ti, Mo and Cr form ohmic contacts on n-type β -SiC upon annealing. Mo/ β -SiC contact has been reported to be thermally stable up to 970°C with contact resistivity of $4.02 \times 10^{-2} \Omega$ cm² after annealing at 970°C⁶⁶. For p-type β -SiC, Al,⁶⁴ Al-TaSi₂ and Ni form ohmic contacts upon annealing with contact resistivity of Ni/ β -SiC contact of $3.19 \times 10^{-2} \Omega$ cm² after annealing⁶⁶. Several metallic elements (e.g. Ta, Ti, Mo), refractory silicides (e.g. TaSi₂, TiSi₂, MoSi₂), and interstitial compounds (i.e. carbides, nitrides, and borides) have been developed as ohmic contacts for 6H-SiC with somewhat high specific contact resistivity (10^{-3} - $10^{-4} \Omega$.cm²)⁶⁷. Ti-W alloy makes a good high temperature low resistance ohmic contact to n-type Si face of 6H-SiC⁶⁸. MeSi₂/n-6H-SiC contact has been reported⁶⁹ to be stable at high temperatures with contact resistance less than $10^{-4} \Omega.cm^2$.

2.4 Characterization of SiC Films

2.4.1 Structural Characterization

There are several methods to identify polytypes in SiC. One simple method is to observe the luminescence under ultraviolet light at liquid nitrogen temperature and then again as the sample warms up. Although this method determines only the predominant polytype in a mixed polytype crystal, it is useful as a quick way to examine a large number of films in a short time. Electron and x-ray diffraction methods can be used to identify a single polytype and provide more exact information about the presence of multiple polytypes in a film. X-ray and reflection electron diffraction techniques are used to obtain information about the surface being examined. Transmission electron microscopy (TEM) is used to study and identify the buried layers of the material. Furthermore, TEM is used to provide information about the epitaxial relation between film and substrate in case of heteroepitaxial growth. However, TEM, x-ray and electron diffraction techniques give little or no information about the non-crystalline phases that might be present in the material⁷⁰.

Further information about the non-crystalline phases can be obtained from Raman spectroscopy. Cubic (3C) SiC film shows the characteristic Raman peak position of the transverse-optic (TO) and longitudinal-optic (LO) at relative wave numbers of 796 and 973 cm⁻¹, respectively. Well ordered graphitic material has only one Raman peak at ≈ 1600 cm⁻¹ and the presence of disorder or small crystallite size gives rise to peak at 1355 cm⁻¹

¹.^{14,71-74} Although TEM, Raman spectroscopy, and x-ray and electron diffraction techniques are used to study the crystalline nature of the films and to identify polytypes, they are not useful for studying the morphology of SiC films. Scanning electron microscopy (SAM) is a very useful tool for morphology and visual analysis and provides information about films in terms of voids, cracks, dislocations, uniformity of surface, and film-substrate interface, etc. Optical-absorption spectra can be used to estimate the lowest indirect gap of the material being studied and thus to identify polytypes⁷⁵.

2.4.2 Electrical Properties

Although epitaxial and amorphous films have been the focus of many studies^{76-79,29-30}, less work has been reported on polycrystalline SiC^{45,80-83}. Polycrystalline SiC is easy to prepare at lower temperatures than epitaxial SiC, and is more stable than amorphous SiC²⁹. In earlier studies of electrical properties of polycrystalline SiC, the films were deposited directly on insulating substrates^{45,81,82}. The reported parameters are conductivities, charge carrier concentrations and Hall mobilities.

The carrier concentrations are generally computed assuming one type of carriers in the conduction band that contributes to the electrical transport. Polycrystalline n-type SiC films with no intentional doping, grown on thermal oxidized SaO₂ and fused quartz glasses by plasma enhanced chemical vapor deposition (PECVD)⁸¹, showed Hall mobility, carrier concentration and conductivity in the ranges of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, 10^{16} - 10^{18} cm^{-3} and 0.1-1 Ω^{-1} -cm⁻¹, respectively. Hall mobility showed a weak dependence on deposition temperature from 600 to 900 C, but the deposition temperature had no effect on the room temperature carrier concentration. In another study, polycrystalline SiC films deposited on sapphire by electron beam evaporation⁴⁵, showed n-type conduction with no impurities added intentionally. Carrier concentrations and Hall mobilities were in the ranges of $5.0x10^{16}-5.0x10^{17}$ cm⁻³ and 2-20 cm²V⁻¹s⁻¹, respectively. The Hall mobility and room temperature carrier concentration increased with the deposition temperature for deposition at 700-900°C and were independent of temperature for deposition at 600 - 700 °C^{45,82}. The conduction mechanism in polycrystalline SiC and the temperature dependence of conductivity and Hall coefficient have not been reported.

Single crystalline β -SiC has electron mobility of 1000 cm²V⁻¹s⁻¹ in spite of its wide-bandgap energy (2.3 eV)⁸⁴, and a calculated saturation drift velocity of 2.7×10⁷ cm.s⁻¹ (at 2×10⁵ V.cm⁻¹) for electrons⁸⁵. Table 2.3 shows the electronic parameters of β -SiC.

Table 2.3. Electronic parameters of β -SiC⁸⁶. m_o is the electronic rest mass.

Transverse mass of electrons (m ₁)	0.247m _o
Longitudinal mass of electrons (m ₁)	0.677m _o
Density of states effective mass of electrons $[m_e^{+}=(m_tm_l)^{1/3}]$	0.346m _o
Number of equivalent minima in the conduction band (M _c)	3
Effective mass of holes (m _h [•])	unknown

The electrical properties of single crystalline β -SiC were reported by many authors^{29,30,45,58,87,88}. For single crystalline β -SiC films grown on Si substrates by chemical

vapor deposition, formation of an impurity band was observed. These films are highly compensated and show electron concentration, Hall mobility and conductivity at room temperature in the ranges of 10^{16} - 10^{17} cm⁻³, 200-600 cm²V⁻¹s⁻¹ and 1-10 Ω ⁻¹cm⁻¹, respectively. The reported activation energies computed from Hall data are in the range of 0.014-0.025 eV^{58,87,88}. The values reported for conductivity data are in the range of 0.025-0.032 eV⁸⁷. The activation energy associated with the hopping conduction was not observed.

2.5 SiC Films as Temperature Sensors

SiC single-crystal thermistors were developed by the Carborundum Company as a high-temperature sensor. These thermistors exhibit high electrical stability under conditions of continuous 1000-h exposure to 450°C and repeated thermal shocking from -100 to 450°C. SiC thin films are considered to be applicable for manufacturing SiC thermistors as a high-temperature sensor while the silicon carbide thermistors are not easy to manufacture because the silicon carbide single crystals cannot be precisely cut and polished due to their hardness⁸⁹. A thermistor using an RF-sputtered SiC film has been developed as a temperature sensor for cooking products with stable thermistor properties over a temperature range of 0-500C^{89.92}. There have been no reports about SiC-based heat flux sensors and thermoelectric generators.

2.6 Summary

Laser ablation technique has been recently used to deposit β -SiC films. Studying the electrical properties of these films is essential to determine their potential for temperature sensor and electronic device applications. Consequently, this study may indicate the potential of the laser ablation technique for deposition of high quality β -SiC films.

CHAPTER 3

LASER ABLATION TECHNOLOGY

3.1 Introduction

Pulsed-laser deposition (PLD) technique has been used to produce high-quality films of high-T_c superconducting oxides and a number of other materials such as metals, piezoelectrics and ferroelectrics^{93,94}. However, deposition of epitaxial layers of semiconductors by PLD has not received the same attention, although there is potential for growth of high-quality (hetero)epitaxial films at moderately lower temperatures (near 1000°C) than those of other techniques^{15,95}. The laser ablation technique has been used to deposit polycrystalline^{12,13} and epitaxial^{14,15} SiC films from ceramic SiC targets on Si substrates at substrate temperatures lower than those generally used in the CVD process. Since this technique has been employed for the deposition of thin SiC films in this research, features of this technique and details of the deposition system are discussed in this chapter.

The characteristics of laser ablation technique for thin film deposition are explained in section 3.2. Deposition and metallization of SiC films and sample
fabrication are presented in section 3.3.

3.2 Pulsed-Laser Deposition Technique

PLD is an attractive technique for thin film deposition because it has the following advantages over other standard techniques:

(a) The localization of the ablation process at the target surface due to the very short pulse duration (nanosecond) and to the very small size of the laser spot $(2\times3 \text{ mm}^2)^{13}$ provides a well controlled ablation of the material and high growth rate $(0.2 \text{ nm/pulse})^{14}$. (b) This technique has the advantage of producing highly energetic species that can lead to (hetero)epitaxial growth of high-quality films^{15,95,96} and provides control over the kinetic energy of the evaporated particles (10-200 eV) by changing the laser parameters and the external bias. This large kinetic energy of ablated species is comparable to that of charged particles obtained by the ion beam technique. Compared with other thermal growth techniques such as molecular beam epitaxy (MBE), this one produces species with kinetic energies 2-3 orders of magnitude larger^{97,98}.

(c) This technique is suitable for growth of multicomponent and multilayered thin films and for in-situ deposition and metallization of semiconductors^{94,99}.

3.3 Sample Fabrication

3.3.1 Deposition of SiC Films

A schematic diagram of the PLD system for the growth of SiC thin films is shown in Fig.3.1. A stainless steel vacuum system is equipped to prevent cratering of the target surface by allowing the rotation of the target. The vacuum chamber is evacuated by a turbomolecular pump to a base pressure of 5×10^{-6} Torr before starting the deposition process. The surface of the target is illuminated by the laser beam over areas ranging from 2×10 to 1×5 mm² at a variable angle of 0-90° from an excimer laser of wavelength 193 nm (ArF) or 351 nm (XeF). The pulse energy at the target can be adjusted between 100 and 400 mJ corresponding to fluences from 2 to 8 J/cm². The angle between the target and the substrate normal can be adjusted in a range of 0-90°. The distance between the target and the substrate is another variable to be optimized. The ablation targets are 99.5% pure SiC stoichiometric ceramics (Angstrom Corp.). The substrates are Si wafers, fused quartz microscope slides approximately 0.5 mm thick, and slightly thicker sapphire R-cut plates. Immediately before use they are ultrasonically cleaned for 15 min each in (i) distilled water with detergent (liquinox); (ii) distilled water; (iii) 2-propanol, and finally dried in flowing nitrogen. The substrate and a boron-nitride-coated graphite resistive heater (trade name Boralectric, from Union Carbide) are enclosed in a tantalum radiation shield with a square opening, 2.5 cm on the side for plume access¹⁵.

Temperature during deposition is monitored with near-IR (Ircon model V-15C10) through a sapphire access window to the vacuum system. The pyrometer has a relatively narrow wavelength passband, from 1.0-0.9 μ m. It views a circle of less than 1 mm diameter, over which one expects relatively constant film thickness. The viewing aperture is small (F≈150) implying small beam divergence. Under these conditions oscillations corresponding to standing waves in the growing film can be clearly observed in the pyrometer reading. Such oscillations allow the monitoring of the film growth rate,^{15,100} but

- H: Heater
- **R:** Radiation Shield
- S : Growing Film
- M: Shadow mask



Fig.3.1. A schematic diagram of the pulsed laser deposition system.

alter the interpretation of the signal in terms of temperature. Thus, the temperatures are taken from the readings just prior to start of deposition. Whereas for Si substrates, which is optically thick, this initial pyrometer reading (using the appropriate emissivity of Si) yields the actual substrate temperature for the optically thin quartz and sapphire substrates, after correction for the substrate reflectivity and using the emissivity of boron nitride it yields the heater temperature. A tantalum shadow mask can be placed on top of the substrate to pattern the deposited film.

3.3.2 Deposition of Metal Contacts

The in-situ deposition of SiC films and metal contacts by pulsed laser deposition method eliminates the required cleaning steps prior to deposition of the ohmic contacts and might lead to a better adhesion to SiC films due to the large kinetic energy of the ablated atoms and molecules upon arrival at the film surface. This attractive method is described as follows. Once the SiC film is deposited the metal contacts can be deposited either in the pulsed laser deposition system described above. The ablation targets are high purity metals and are irradiated from an ArF or XeF excimer laser. Radiation is focused near the surface of the target. The substrate rests on a boron-nitride-coated graphite resistive heater (or a flat alumina heater) and the substrate normal is either at 0° or 45° to the target surface. A shadow mask is placed on substrate surface to allow selective deposition of the contacts. Ni and Pt are deposited (base pressure 5×10⁻⁶ Torr) in a range of deposition temperatures between room temperature and 500°C. Cleaning of the films is not needed as long as the replacement of the targets and the placement of a shadow mask is done in a short period of time. The temperature is monitored either with a thermocouple attached to the alumina heater or with near-IR pyrometer as described earlier.

3.4 Summary

The potential of the pulsed-laser ablation technique for deposition of high-quality SiC films is great. In addition, the deposition system and SiC sample fabrication process are simple.

CHAPTER 4

MEASUREMENT TECHNIQUES

4.1 Introduction

This chapter deals with the experimental techniques used in this research to measure conductivity, Hall coefficient, and Seebeck coefficient of SiC. In section 4.2, van der Pauw's procedure for conductivity and Hall coefficient measurement is explained. In section 4.3, the methods that are usually used for Seebeck coefficient measurement are explained.

4.2 Van der Pauw's Measuring Procedure

It was shown by van der Pauw in 1958 that four electrodes are needed along the circumference of a plane-parallel sample with arbitrary shape to perform conductivity and Hall measurements. Two transfer resistances R_1 and R_2 can be evaluated in the following way. If a current I_{12} is applied between electrodes 1 and 2, a voltage V_{34} will appear between electrodes 3 and 4 (see Fig. 4.1).

In a similar way, applying a current $I_{\scriptscriptstyle 23}$ between electrodes 2 and 3, a voltage $V_{\scriptscriptstyle 14}$

will appear between electrodes 1 and 4. This leads to $R_1 = V_{34}/I_{12}$ and $R_2 = V_{14}/I_{23}$. According to van der Pauw the resistivity ρ is given by¹⁰¹

$$\rho = \frac{1}{\sigma} = \left(\frac{\pi d}{\ln 2}\right) \left(\frac{R_1 + R_2}{2}\right) f\left(\frac{R_1}{R_2}\right), \qquad \dots (4.1)$$

where d is the sample thickness in cm; σ is the conductivity in Ω^{-1} .cm⁻¹; R₁ and R₂ are in Ω ; and f(R₁/R₂) is a dimensionless and monotonically decreasing function with the increasing R₁/R₂. f(R₁/R₂) values range between 0 and 1 depending on R₁/R₂ where f(1)=1 and f(∞)=0. If the sample has a square shape and homogeneous, f(R₁/R₂) will be equal to 1. The same electrodes can be used to evaluate the Hall coefficient R_H. If a current I₁₃ is passed between 1 and 3, a voltage V₂₄ appears between 2 and 4. Considering this situation if a magnetic field perpendicular to the sample is applied, an additional voltage V_H between 2 and 4 appears.

The total voltage between 2 and 4 with the presence of magnetic field is $V^+=V_{24}\pm V_{H}$. When the magnetic field is reversed, the same voltage V_H appears between 2 and 4 with opposite polarity. The total voltage between 2 and 4 with the presence of opposite magnetic field is $V^-=V_{24}\mp V_H$. This voltage V_H , the Hall voltage, can be expressed as $V_H=(V^+-V^-)/2$. The Hall coefficient R_H is related to the current I_{13} and the magnetic induction B by

$$R_{H} = 10^{8} \frac{dV_{H}}{BI_{13}}, \qquad \dots (4.2)$$

where d is in cm, V_{H} is in volts, B is in Gauss, R_{H} is in cm³Coulomb⁻¹ and I_{13} is in Amps.

29



Fig.4.1. A sample of arbitrary shape with four metal contacts along the circumference for conductivity and Hall measurements.

4.3 Seebeck Coefficient Measurement Technique

There are two methods for measurement of Seebeck coefficient. In one technique, one end of the sample under test is held at a certain temperature such as boiling helium or nitrogen during the measurement. The temperature of the other junction is changed to the required temperature T and the Seebeck emf E(T) is measured. The Seebeck coefficient Q(T) is calculated as $\partial E(T)/\partial T^{-102}$. The other technique is the so called differential technique.

In our work, we used the differential technique¹⁰². In this case, both ends are first

brought to the required temperature T and then the temperature of one end is further increased by a small increment $\Delta T \sim 1 K$. Measurement of the small Seebeck emf ΔE between the two ends leads to the Seebeck coefficient Q at T+($\Delta T/2$)which is given by

$$Q(T+\frac{\Delta T}{2})=\frac{\Delta E}{\Delta T}, \qquad \dots (4.3)$$

The first technique requires only the measurement of T and E(T) whereas T, Δ T, and Δ E are to be determined in the second one. On the other hand, the first technique requires more data processing to obtain Q(T).



Fig.4.2. Sample arrangement for Seebeck coefficient measurement¹⁰².

One experimental arrangement to obtain T, Δ T, and Δ E is shown in Fig.4.2. Two thermocouples (e.g. Pt and Pt+13%Rh) are connected to the two ends of the sample through metal contacts. The metal contacts have negligible effect on the measurements since the Seebeck coefficient of metals is one order of magnitude lower than that of semiconductors. A small heater can be used to raise the temperature of one end of the sample by Δ T relative to that of the other end. The temperature of the entire sample can be brought to T by inserting the sample into a low or high temperature measurement system.

T and $(T+\Delta T)$ can be obtained using the thermocouples A-D and B-C, respectively, while holding their outside junctions at a constant temperature. This leads to an estimate of ΔT . The Seebeck emf ΔE between the two junctions can be measured directly using a voltmeter. The Seebeck coefficient can be evaluated using Eq.4.3.

T, ΔT , and ΔE can be obtained in another way where two Seebeck emfs can be measured between the two ends of the sample (i.e. ΔE_{AB} and ΔE_{DC}). The difference between these two measurements leads to

$$\Delta E_{AB} - \Delta E_{DC} = [(Q_{Pt} - Q_X) - (Q_{Pt+13\&Rh} - Q_X)] \Delta T,$$

= $[Q_{Pt} - Q_{Pt+13\&Rh}] \Delta T,$
= $Q_{Pt, Pt+13\&Rh} \Delta T,$... (4.4)

where, $Q_{Pt+13\%Rh}$, and Q_X are the absolute Seebeck coefficients of Pt, Pt+13%Rh, and sample X, respectively. Since the relative Seebeck coefficient of Pt and Pt+13%Rh (i.e. $Q_{Pt,Pt+13\%Rh}$) is available, ΔT can be evaluated using Eq.4.4. Q_X can be obtained using

$$\Delta E_{AB} = \Delta E_{X,Pt} = (Q_{Pt} - Q_X) \Delta T, \qquad \dots (4.5)$$

since $Q_{\mbox{\scriptsize Pt}}$ is also available in standard charts.

4.4 Summary

The measurement techniques used in this research are explained in this chapter. The measurement of the conductivity and Hall coefficient allows the calculation of the mobility and carrier concentration using a suitable model. The Seebeck coefficient measurements coupled with the Hall measurements are used to explain the conduction process in SiC and thus to determine the potential of SiC for temperature sensor applications.

CHAPTER 5

CONDUCTIVITY AND MOBILITY OF SiC

5.1 Introduction

Measurements of fundamental electrical properties, such as carrier concentration, conductivity, mobility, etc., of SiC are essential in evaluating its potential for electronic device applications. Low temperature measurements are useful in determining types and precise locations of shallow impurity levels. High temperature measurements are needed in locating deep impurity levels and studying conduction process at such temperatures.

Electrical properties of β -SiC (i.e. cubic SiC) films deposited on either Si or insulating substrates by laser ablation of ceramic stoichiometric SiC targets have not been reported. On the other hand, there have been many reports about conductivity and Hall carrier concentration of monocrystalline α -SiC.

In this chapter, measurements of conductivity and Hall voltage of polycrystalline β -SiC and monocrystalline β - and α -SiC are discussed. For polycrystalline β -SiC films deposited on insulating substrates and for α -SiC (6H and 4H) wafers, carrier concentrations and mobilities are evaluated from the measured data assuming that carriers in a

single band are responsible for electrical transport. For monocrystalline β -SiC films deposited on Si substrates, the measured conductivity and Hall voltage represent the combined structure of the β -SiC film, interface and Si substrate. Multiple-layer conductivity and Hall voltage models are used to obtain a simple understanding of the relation between the conductivity and Hall data of the β -SiC film and those of the Si substrate.

5.2 Polycrystalline Cubic SiC Films

5.2.1 Experimental

Polycrystalline β -SiC films were deposited on 3x2 cm² quartz substrates using laser deposition method as described in chapter 4. The film thicknesses and deposition temperatures ranges are 1000-4500Å and 1189-1298°C, respectively.

These polycrystalline films show the optical properties characteristic of the 3C polytype of SiC (i.e. β -SiC). Analysis of optical transmission spectra of these films shows a lowest-energy gap near 2.2 eV which is the value for cubic SiC. The films deposited above 800°C show (111) and (222) x-ray-diffraction bands from crystal planes parallel to the substrate. Selected-area electron-diffraction transmission patterns of these films show predominant crystallite orientation with the 111 axis normal to the substrate. The crystallite dimension for the films deposited at ~1150°C is in the order of 50 nm¹⁰⁶.

Samples were cut in 1×1 cm² sizes and cleaned with acetone, isopropanol and deionized water. Using a shadow mask, 2000Å thick layers of Ni and Pt were sequentially sputtered as 1.6 mm diameter circles, at the four corners to provide the contacts. The Pt

layer was needed to protect the Ni against oxidation and to allow wire bonding. No annealing was done as low contact resistance was not critical for Van der Pauw procedures.

The measurements in the 13-300K range were done in a closed-loop helium cryostat, whereas above 300K a stainless-steel chamber evacuated by a turbomolecular pump to 8x10⁻⁶torr was used. The sample was attached to a flat alumina resistive heater using ceramic paste. The sample temperature was monitored by a chromel-alumel thermocouple. An electromagnet provided a magnetic field of 8 kGauss for the Hall measurements, which were obtained by averaging the 8 readings corresponding to the switching of contacts and the direction of magnetic field and current.

5.2.2 Conductivity and Hall Measurements

Fig.5.1 illustrates the temperature dependence of the conductivity of laser deposited films for 3 samples. The film thickness and deposition temperature ranges are 1000-4500 Å and 1189-1298°C, respectively. The conductivities increase monotonically with temperature and are an order of magnitude larger than those reported for polycrystalline SiC films prepared by plasma enhanced chemical vapor deposition and electron beam evaporation ^{44,45}.

The Hall coefficient R_H was measured in a temperature range of 17-729 K. The effective carrier concentration n and mobility μ were calculated assuming that electrons are the sole carriers. Fig.5.2 shows the temperature dependence of $1/R_H$ and n for samples of Fig.5.1. The inverse Hall coefficient $1/R_H$ increases monotonically with temperature



Fig.5.1 Temperature dependence of conductivity of 3 polycrystalline β -SiC films with the fits shown as solid lines.



Fig.5.2 Temperature dependence of the inverse of measured Hall coefficient, $1/R_{\rm H}$, and the corresponding carrier concentration, $1/qR_{\rm H}$, of samples of Fig.5.1 with the fits shown as solid lines.

and ranges between 3 and 65 cm⁻³Coulomb. As seen in Fig.5.3, μ varies slowly with T and only occasionally (as for 194A) it shows a clear T dependence (below 200K). There is no correlation between this temperature dependence and deposition temperature or film thickness. Due to short mean free paths (discussed below), surface scattering is negligible even for such thin sample (1000 Å) and thus cannot explain such lack of temperature dependence.

5.2.3 Analysis of Intermediate and High Temperature Data

Assuming that there is a number of donor (ground) states N_{di} per unit volume of degeneracies β_i at energy levels E_i , within the bandgap, the charge neutrality condition gives^{9,119}.

$$n = \sum_{i} \frac{N_{di}}{1 + \beta_{i}^{-1} \exp(\eta + \epsilon_{i})} \qquad \dots (5.1)$$

where n, the electron concentration in the conduction band, is given by

$$n = \frac{2N_c}{\sqrt{\pi}} \int_0^{\infty} \frac{\epsilon^{1/2} d\epsilon}{1 + \exp(\epsilon - \eta)}, \qquad \dots (5.2)$$

 $\varepsilon_i = E_i/kT$, $\eta = (E_f - E_c)/kT$, E_f is the Fermi energy level, E_c is the bottom edge of the conduction band, $k=0.86174 \times 10^{-4} eV/^{\circ}K$, T is temperature, and N_c is the density of states in the conduction band. The number of terms in the sum of Eq.5.1 is equal to the number of the donor energy levels. Each term gives the number of ionized donors at the corresponding energy level.



Fig.5.3 Temperature dependence of the mobility derived from the Hall and conductivity data as $\sigma R_{\rm H}$ for samples of Fig.5.1.

For a nondegenerate semiconductor with $(\eta + \epsilon_i) \ge 2$, a special case of Eq.(5.1) can be written as¹¹⁶

$$n = \sum_{i} A_{i} \exp(-\frac{E_{i}}{kT})$$
, ... (5.3)

where $A_i = \beta_i N_{di} \exp(-\eta)$. Thus a set of activation energies E_i can be obtained by fitting the measured carrier concentration with Eq.(5.3) if we assume that A_i are temperature independent.

If we could define a temperature independent effective mobility μ , the same set of activation energies e_i should be obtained by fitting the measured conductivity data with¹³²

$$\sigma = \sum_{i} a_{i} \exp\left(-\frac{e_{i}}{kT}\right), \qquad \dots (5.4)$$

where $\sigma = q\mu n$, $a_i = q\mu A_i$ and $e_i = E_i$.

Three exponentials were needed to fit the measured effective Hall carrier concentrations and conductivities using equations 5.3 and 5.4, respectively, leading to three sets of values for E_i , A_i , e_i and a_i as shown in Table 5.1. The activation energies e_i and constants a_i are obtained as follows. The smallest activation energy e_3 and the constant a_3 are obtained from the slope and intercept of $log(\sigma)$ versus 1/T in the temperature range of 17-40 K as shown in Fig.5.4(a) for sample 152B. Next, the calculated values of $\sigma_3=a_3exp(-e_3/kT)$ are subtracted from the actual experimental conductivities at corresponding temperatures, and the slope and intercept of $log(\sigma-\sigma_3)$ versus 1/T in the 50 to 150K temperature range yield e_2 and a_2 (see Fig.5.4(b)). Repeating this once more

Sample	Activation energies (meV)						Constants					
							(dimensionless)			(Coulomb)		
	e ₁	e ₂	e ₃	E ₁	E ₂	E ₃	aı	a ₂	a ₃	$\mathbf{q}\mathbf{A}_1$	qA ₂	qA3
140A	76	8	0.8	75	7	0.8	40	9	12	45	3.7	8
152B	80	9	0.4	80	9	0.9	42	8.5	18	65	9.5	28
194A	74	14	1.5	74	11	1.4	30	14	11	11	2	5
164B	69	12	1.7	69	12	2.5	45	11	10	70	7	20
193A	69	19	1.9	69	20	3.8	30	17	13	15	7	9

Table 5.1. Activation energies: e_i (conductivity) and E_i (Hall data) and constants: a_i (conductivity) and A_i (Hall data) for five samples.

yields e_1 and a_1 for the conductivity component activated above 250K as shown in Fig.5.4(c). The activation energies E_i and constants A_i are obtained in the same way. The corresponding slopes and intercepts are shown in Fig.5.5 for sample 152B. With three terms Eq.5.4 yielded the fit shown by the solid line in Fig.5.1. The data could not be fitted with two terms and no clear improvements was seen with more than three terms. Hall data are also fitted in the same way using Eq.5.3 and yielded three pairs of constants A_i and E_i . The fits of the Hall data are not as good as those of the conductivity data, but still they are acceptable as shown by solid lines in Fig.5.2.

These fits, shown by solid lines, are valid if it is assumed that the density of states is temperature independent. Within the data accuracy, $E_1=e_1=74.5\pm5.5$ meV for all films and the quality of the fits is quite good. This result indicates that at the higher temperatures electrons in the conduction band with temperature independent mobility are



Fig.5.4 The measured conductivity (hollow symbols) of 152B and fits (solid lines) obtained in 3 different temperature ranges using Eq.5.4. Slopes and intercepts of these lines represent activation energies and corresponding constants: (a) e_1 and a_1 , (b) e_2 and a_2 , and (c) e_3 and a_3 .



Fig.5.5 The measured electron concentration (hollow symbols) of 152B and fits (solid lines) obtained in 3 different temperature ranges using Eq.5.3. Slopes and intercepts of these lines represent activation energies and corresponding constants: (a) E_1 and A_1 , (b) E_2 and A_2 , and (c) E_3 and A_3 .

mainly responsible for the conductivity.

Polycrystalline films deposited by different techniques^{45,80,81} had mobilities below 10 cm²/Vs even at carrier concentrations below 10¹⁸ cm⁻³. The low mobility and large carrier concentration in our samples even at temperatures as low as 17 K, seem to imply large concentrations of electrically active impurities or defects leading to concentrations in the range of 10¹⁹-10²⁰ cm⁻³ and a short carrier mean free path. For example, at 800 K, Rutherford scattering by such densities of singly charged centers¹⁰⁷ yields mean free paths in the range of 6-20 Å, which become even shorter at temperatures below 800 K. Surface states associated with the grain boundaries change the bulk properties of the grains to depths of 4 to 27 Å (Debye screening length) at effective carrier concentrations found in these films. Therefore, in our films with grain sizes¹⁰⁶ of 150 to 500 Å the effect of surface scatterring on bulk transport may be negligible. However, our results do not rule out the possibility of grain boundary conduction.

The energy E_1 which activates conduction above 250K might be related to transitions from donors to conduction band. This being the case, before extracting E_1 using Eq.5.3, the data should be corrected for the T^{3/2} dependence of the density of states. The data corrected for this yields $E_1=55\pm5$ meV. As SIMS analysis of our films showed a density of nitrogen donors in excess of 10¹⁹ cm⁻³, this activation energy may be related to nitrogen donors. Activation energies in the range of 53-54 meV have been seen in the transport and electron paramagnetic resonance (EPR) data of high mobility monocrystalline SiC^{9,112,132}, even at nitrogen donor concentrations in the range of 10¹⁷-10¹⁹ cm⁻³. Our E₁ values are also comparable to the values obtained by photoluminescence spectroscopy for nitrogen donors in single crystals¹¹⁴ and to those obtained from Seebeck coefficient measurements (see chapter 6).

The activation energies E_2 and e_2 , although the same for each film except 194A, exhibit some variation among the films and the quality of the fits is not as good as those of $E_1=e_1$. For 194A, $E_2\neq e_2$, which might be due to the dependence of its mobility on temperature in this range. E_3 and e_3 differ from each other and vary appreciably from film to film, ranging from 0.4 to 3.8 meV. These results indicate that conduction at low temperatures may not predominantly take place in the conduction band and the mobility may not be temperature independent and therefore the assumptions made in the above analysis may not be valid in this temperature range.

To investigate the validity of the assumption of single band conduction, the location of Fermi level was determined through out the entire temperature range by fitting measured effective carrier concentration with Eq.5.1. Fermi statistics was used since the lowest activation energy is in the order of 1 meV and, thus, degeneracy is expected at least at low temperatures. Fig.5.6 shows that the computed Fermi level E_f is located within the conduction band, indicating degeneracy, even at the lowest temperature, and E_f moves deeper in the conduction band as temperature increases. The strong temperature dependence of measured n and σ especially at high temperatures is hard to explain if our films become strongly degenerate as temperature increases suggesting that the fitted n might be exaggerated.

Using the obtained locations of E_r , the measured effective carrier concentration was fitted with Eq.5.1 assuming that 3 independent impurity levels exist. A degeneracy



Fig.5.6 Fermi level position computed using Fermi Statistics (Eqs.5.1-2) for 2 of the samples of Table 5.1.

of 2 was used for each of the energy levels given by the activation energies of Table 5.1 and the donor densities were treated as parameters. The resulting fits are only good in the high temperature range as shown in Fig.5.7 and require very high donor densities $(N_{d1}=N_{d2}=10^{21} \text{ cm}^{-3} \text{ and } N_{d3} \text{ in the order of } 10^{22} \text{ cm}^{-3} \text{ for both } 164B \text{ and } 152B)$ for the heavily doped films, with the total donor density of the 3 donor levels being in the range of 10²² cm⁻³. These donor densities seem to be comparable to the densities of atoms in SiC (9.7×10²² cm⁻³) as the x-ray-diffraction studies indicate a crystalline structure within the grains of our SiC films¹⁰⁶, such high donor densities are unreasonable and might indicate that the measured carrier concentrations are too high. On the other hand, the fits for the films with lower electron concentrations yield reasonable donor densities in the order of 10^{20} cm⁻³ (N_{d1}=N_{d2}=10²⁰ cm⁻³ and N_{d3}=2.8×10²⁰ cm⁻³ for 194A). Generally, the fits are best in the high temperature range (See Fig.5.7, sample 194A) indicating that the contributing carriers are in the conduction band. The low temperature fits are generally unacceptable and attempts to increase the donor density N_{d3} do not alleviate this problem indicating that single band conduction assumption is not valid in the low temperature range. For example, in case of 194A, taking $N_{d3}=4\times10^{22}$ cm⁻³ leads to a carrier concentration of 5.2×10^{18} cm⁻³ at T=23K which is one order of magnitude less than that derived from the Hall constant.

The low temperature data seem to indicate more complicated conduction processes such as impurity/defect band formation and hopping¹¹⁹. Hopping conduction requires compensation to occur whereas impurity/defect band conduction does not. In what follows we present our analysis of the low temperature data for both of these mechanisms.



Fig.5.7 Inverse of measured Hall coefficient, $1/R_{\rm H}$, for samples of Fig.5.6, with carrier concentration fits obtained by the charge neutrality condition assuming no compensation and considering 3 independent donor levels represented by activation energies shown in Table 5.1.

5.2.4 Analysis of Low Temperature Data

The phenomenological analysis introduced above was implicitly based on the assumptions of temperature independent mobility and single band conduction. The inconsistency of low temperature results shows that these assumptions might not be valid in the low temperature range. Assuming that 3 independent impurity levels exist, the location of Fermi level and thus the corresponding carrier concentration in the conduction band can be determined for any set of donor densities, activation energies and degeneracy factors using the charge neutrality condition. A degeneracy of 2 was used for each of the energy levels represented by the activation energies of Table 5.1. The donor densities were treated as parameters in order to fit the measured carrier concentrations.

Boltzmann statistics can be used only if the Fermi level E_r is several kT below the bottom of the conduction band E_c . Since the lowest activation energy is in the order of 1 meV, degeneracy is expected at least at low temperatures. Using Fermi statistics, a fit to the effective carrier concentrations obtained from the Hall data of some of the films requires very high donor densities ($N_{d1}=N_{d2}=10^{21}$ cm⁻³ and N_{d3} in the order of 10^{22} cm⁻³ for both 164B and 152B) for the heavily doped films, with the total donor density of the 3 donor levels being in the order of 10^{22} cm⁻³. These donors are either impurities or electrically active defects and should be less than the densities of atoms in the host crystal in order to preserve the crystalline structure. The atomic density in a SiC crystal is 9.7×10^{22} cm⁻³ and x-ray-diffraction studies indicated the crystalline structure of our polycrystalline SiC films within the grains¹⁰⁶.

Therefore, such high donor densities are unreasonable and might indicate that the

measured carrier concentrations are too high. Even with such high donor densities the obtained fits are only good in the high temperature range. On the other hand, the fits for the other films yield more reasonable donor densities ($N_{d1}=N_{d2}=10^{20}$ cm⁻³ and $N_{d3}=2.8\times10^{20}$ cm⁻³ for 194A), with their total being in the order of 10^{20} cm⁻³. Generally, the fits are best in the high temperature range as shown in Fig.5.7 indicating that there the contributing carriers are in the conduction band. The corresponding Fermi level E_f is located within the conduction band, indicating degeneracy, even at the lowest temperature and increases monotonically with temperature as shown in Fig.5.6 for samples 152B and 194A.

The low temperature fits are generally unacceptable and attempts to increase the donor density N_{d3} do not alleviate this problem (For 194A, taking $N_{d3}=4\times10^{22}$ cm⁻³ leads to a carrier concentration of 5.2×10^{18} cm⁻³ at T=23K which is one order of magnitude less than that derived from the Hall constant) indicating that single band conduction assumption is not valid in the low temperature range. The possibility of impurity/defect conduction either by hopping or impurity/defect band formation is considered below.

5.2.4.1 Hopping Conduction

Hopping conduction might proceed by direct or thermally activated tunneling. Thermally activated hopping occurs when an electron tunnels from one localized and occupied state to another localized and unoccupied state which has a different energy by exchanging energy with the lattice vibrations. In direct hopping, an electron will tunnel from an occupied state to an unoccupied state of some energy with no need for assisting phonons. If hopping is thermally activated, conductivity tends to zero at very low temperatures. In our measurements, it was not possible to go to such low temperatures to check this condition and thus the scatter in the low temperature data prevents an unambiguous conclusion about the type of hopping that might exist. The presence of empty donors is a necessary condition for hopping conduction. At low temperatures this condition can be fulfilled only by compensation. As the concentration of compensating sites goes to zero, so does the concentration of empty sites leading to zero conductivity at the lowest temperature.

Hopping conduction does not occur unless Fermi level is in the vicinity of the impurity/defect band or hopping level. Therefore, one way to exclude some of these possibilities without getting involved in details of the conduction process is by determining the location of Fermi level^{107,108}.

Assume that in addition to E_1 a level E_2 of lower activation energy exist, with the smallest activation energy E_3 being responsible for hopping. Since we do not have any information about the density of compensating acceptors, we investigate the effect of acceptor concentration on the location of Fermi level. Probability of hopping from full to empty sites depends on densities of both full and empty sites, being highest when full and empty sites have, approximately, equal occupations ($E_2 \sim E_f$).

The charge neutrality condition now has to include as a parameter an acceptor concentration N_a as follows:

$$n = \sum_{i} \frac{N_{di}}{1 + \beta_{i}^{-1} \exp(\eta + \epsilon_{i})} + N_{a} \qquad \dots (5.5)$$

This acceptor level will be occupied by electrons from the donor states or the valence band requiring an increase in the donor density to fit the measured carrier concentration in the high temperature range. Fermi level E_t locations are determined by fitting the measured carrier concentration using Eq.5.5. N_e , N_{d1} , and N_{d2} are treated as parameters. E_3 contributes to conduction in the hopping band but not in the conduction band. The obtained Fermi level locations E_f and the corresponding fits of the measured carrier concentration for two samples are shown in Fig.5.8 and Fig.5.9, respectively. Both samples show degeneracy above 100 K where E_t goes deeper within the conduction band. For T≤100K, the Fermi level stays in the vicinity, in terms of kT, of the intermediate energy level E_2 for compensation ratio N_e/N_{d2} near 33%. As temperature increases above 100K, Fermi level moves away from E_2 .

For sample 194A, the effect of the compensation ratio on E_f is shown in Fig.5.10. The obtained fits which correspond to these Fermi level locations are shown in Fig.5.11. As the compensation ratio moves away from 33% the pinning of the Fermi level at E_2 disappears. As compensation ratio increases more electrons fall into the acceptor states from the conduction band or the donor states requiring an increase in the donor density to fit the high temperature effective carrier concentrations.

The pinning of E_f even at 100K shows that donor sites at E_2 are, approximately, half empty indicating that in this model even at this high temperature there is significant



Fig.5.8 Fermi level position computed by fitting the measured electron concentration n of 2 polycrystalline samples using Eq.5.5. In these fits, N_a , N_{d1} and N_{d2} are treated as parameters and $(N_a/N_{d2})=33\%$.



Fig.5.9 Effective carrier concentration, $1/qR_{\rm H}$, for samples of Fig.5.8, with carrier concentration fits obtained by the charge neutrality condition assuming compensation ratio of 33% and considering two independent donor levels represented by activation energies E_1 and E_2 as shown in Table 5.1.



Fig.5.10 Fermi level position for sample 194A computed using the charge neutrality condition for compensation ratios of 10%, 33%, and 90% and considering two independent donor levels represented by activation energies E_1 and E_2 shown in Table 5.1.



Fig.5.11 Inverse of measured Hall coefficient, $1/R_{\rm H}$, for 194A with its fits using corresponding Fermi level locations for the 3 different compensation ratios of Fig.5.10.

contribution to conduction from this level. The exact location of the acceptors energy level below midgap has no significant effect on the Fermi level location.

The donor density N_{d1} at energy level E_1 has to be in the order of 10^{22} cm⁻³ and 10^{21} cm⁻³ for 140A, 152B, and 164B and for both of 193A and 194A, respectively. The donor density N_{d2} at E_2 has to be in the range of 4×10^{19} - 1×10^{20} cm⁻³ for all samples. Such high donor densities are unreasonable (10^{22} cm⁻³) or exaggerated (10^{21} cm⁻³) probably indicating that the carrier concentration can not be directly derived from Hall effect in the hopping region. In the high temperature range the fits of the effective carrier concentrations were acceptable as shown in Fig.5.11 whereas in the low temperature range the discrepancy is much larger than the previous case shown in Fig.5.7 due to the introduction of compensation and elimination of the smallest energy level E_3 .

Thus, for the lightly doped samples, 193A and 194A, hopping conduction might account for the discrepancy between measured and calculated carrier concentrations at T \leq 100K with a compensation ratio of about 33%. Whereas as in the high temperature range the data can be explained by single band conduction of carriers mainly activated from E₁ and E₂ energy levels with donor densities being in the range of 10²¹ cm⁻³. For the other films, a fit to the high temperature data with two energy levels requires unreasonably large donor densities on the range of 10²² cm⁻³ and thus single band conduction in this case is ambiguous.

The carrier concentrations in the conduction band at low temperatures might be much lower than those calculated from the measured Hall coefficient as $1/qR_{H}$ if hopping conduction is taking place. Calculation of hopping electrical parameters such as Hall
coefficient and mobility is not possible since hopping theory provides only a qualitative description of the conduction mechanism. A quantitative model requires the development of the Hall coefficient considering the effect of magnetic field on carrier wave functions as they tunnel from occupied sites to empty ones^{115,119}.

5.2.4.2 Impurity/Defect Band Conduction

Impurity or defect band conduction is an alternative mechanism to hopping without the requirement of compensation. Impurity/defect band formation requires sufficient overlap of the localized electron wave functions of the defect or impurity centers to cause significant energy broadening. It may be assumed that the excited states of impurities/defects form this impurity/defect band. At absolute zero, this band and the conduction band are assumed to be empty. In this band the density of states including degeneracy of excited states should be large enough to accommodate the excited carriers so they can move with finite mobility.

Although we assume that the impurity/defect band is located between E_c and E_2 as shown in Fig.5.12, it may also be between E_2 and E_1 . In the former case electrons can be excited from E_1 and E_2 into the impurity/defect band whereas in the latter case only electrons at E_1 can be excited into the impurity/defect band. In both cases electrons can be excited into the conduction band from both E_1 and E_2 levels. The smallest activation energy E_3 is assumed to be the activation energy needed to excite carriers from E_2 (considering the former assumption) or E_1 (considering the latter assumption) into the lower edge of the impurity/defect band. According to our measurements, the largest



Fig.5.12 Energy band of SiC with two donor levels located at E_1 and E_2 below the bottom of the conduction band E_c . The impurity/defect band is located at (E_2-E_3) below E_c . The energy levels in this figure are not drawn to scale and the intrinsic level E_i should not be exactly in the middle of the bandgap.

60

activation energy E_1 is equal to 74.5±5.5 meV. The intermediate E_2 and smallest E_3 ones are in ranges of 7-20 meV and 0.8-3.8 meV, respectively. In order to study the two cases mentioned above, the measured electron concentration n=1/qR_H has to be fitted with the following equation as obtained using the charge neutrality condition^{9,119}:

$$n = \frac{N_{d1}}{1 + \beta_1^{-1} \exp(\eta + \epsilon_{d1}) + \beta_{23}^{-1} \exp(\eta + \epsilon_{d23})} + \frac{N_{d2}}{1 + \beta_2^{-1} \exp(\eta + \epsilon_{d2}) + \beta_{23}^{-1} \exp(\eta + \epsilon_{d23})}, \quad \dots (5.6)$$

where

$$n = \frac{2N_c}{\sqrt{\pi}} \int_0^{\infty} \frac{\epsilon^{1/2} d\epsilon}{1 + \exp(\epsilon - \eta)} \qquad \dots (5.7)$$

is the carrier concentration in the conduction band and $\eta = (E_f - E_e)/kT$. N_e is the density of states in the conduction band. There are N_{d1} and N_{d2} donor (ground) states per unit volume of degeneracies β_1 and β_2 at $E_1 = \varepsilon_{d1} kT$ and $E_2 = \varepsilon_{d2} kT$, respectively. The energy separation between the ground state of E_2 and the impurity/defect band (or the excited state of E_2) is given by $E_3 = \varepsilon_{d3} kT$. Thus, the impurity/defect band is located at $E_{23} = (\varepsilon_{d2} - \varepsilon_{d3})kT = \varepsilon_{d23}kT$ below E_e with its degeneracy being β_{23} . The Fermi level may be any where above midgap. N_{d1} and N_{d2} are used as parameters to fit the measured carrier concentration.

The density of electrons in the impurity/defect band is equal to the density of donors with electrons trapped in the excited state E_{23} , which is given by¹¹⁹:

$$n_{d} = \frac{[\beta_{23}^{-1} \exp(\eta + \epsilon_{d23}] N_{d1}}{1 + \beta_{1}^{-1} \exp(\eta + \epsilon_{d1}) + \beta_{23}^{-1} \exp(\eta + \epsilon_{d23})} + \frac{[\beta_{23}^{-1} \exp(\eta + \epsilon_{d23})] N_{d_{2}}}{1 + \beta_{2}^{-1} \exp(\eta + \epsilon_{d2}) + \beta_{23}^{-1} \exp(\eta + \epsilon_{d23})} \dots (5.8)$$

The impurity/defect band will contribute to conduction only if Fermi level is in the vicinity of this band. The location of the Fermi level can be calculated using the charge neutrality condition (i.e. Eq.5.6) with the donor density and degeneracy factor β_{23} being used as parameters. As the donor density increases the degeneracy factor has to be increased also in order to have the Fermi level in the vicinity of the impurity/defect band (e.g. for donor density N_d in the order of 10^{15} cm⁻³, $\beta_{23} \ge 8$ whereas for N_d ~ 10^{19} cm⁻³, $\beta_{23} \ge 1000$).

Considering that the impurity/defect band is above E_2 , fitting the effective carrier concentrations of samples 152B, 164B and 140A (N_d is in the range of 10^{20} - 10^{22} cm⁻³) leads to E_f far from the location of the impurity/defect band at low temperatures unless degeneracy of the excited state is extremely high and unreasonable. Furthermore, it was not possible to fit the measured carrier concentration at high temperatures (even if $\beta_{23} \ge 1000$) since most of the excited carriers tend to stay in the impurity/defect band even at high temperatures. For samples 194A and 193A, fitting the carrier concentration at the lowest temperatures resulted in N_{d1} in the order of 10^{20} cm⁻³ and carrier concentrations in the impurity/defect and conduction bands at high temperatures in the order of 10^{20} cm⁻³ and 10^{19} cm⁻³, respectively, with the effective carrier concentration $1/qR_H$ at high temperatures being several times larger than the one calculated using Eqs. 5.6-8. Thus, this case is ruled out.

Considering that the impurity/defect band is between E_2 and E_1 , fitting the effective carrier concentrations is not possible with donor densities N_{d1} and N_{d2} in the range of the atomic density in SiC (9.7×10²²cm⁻³) even at high temperatures. Therefore, impurity/defect band model does not explain our results.

Impurity/defect band conduction requires high degeneracy to provide enough empty states for the carriers so they can move with finite mobility whereas hopping conduction requires compensation to produce such empty states. The existence of either conduction mechanism in our case depends on the compensation and donor density. Impurity/defect band mechanism leads to an unreasonably large degeneracy and seems to indicate that the effective carrier concentration is exaggerated. Hopping mechanism does provide a reasonable explanation of part of our data but with exaggerated donor densities indicating the need for a quantitative analysis to obtain the actual carrier concentration from the measured Hall coefficient in the hopping range.

Measured Hall coefficient of highly compensated semiconductors might lead to an exaggerated estimate of the carrier concentration. Therefore, this case is considered here. When both electrons and holes contribute to conduction, the Hall coefficient $R_{\rm H}$ can be expressed as

$$R_{H} = \frac{1}{q} \frac{p \mu_{h}^{2} - n \mu_{\theta}^{2}}{(p \mu_{h} + n \mu_{\theta})^{2}}, \qquad \dots (5.9)$$

where μ_e and μ_h are the electrons and holes mobilities, respectively, and n and p are the

electron and hole concentrations, respectively. According to the above equation the Hall coefficient will be smaller than 1/qn if $p\mu_h^2$ is comparable to $n\mu_e^2$. Therefore, the Hall coefficient associated with highly compensated films (i.e. the Fermi level is near the intrinsic level and accordingly electron concentration is, approximately, equal to the concentration of intrinsic carriers) leads usually to an exaggerated carrier concentration if estimated as $1/qR_{\rm H}^{116}$. If electron and hole concentrations are near the intrinsic concentration, fitting the measured conductivities of our films with $\sigma=q(\mu_en+\mu_hp)$ will require unreasonably large mobilities ($\geq 10^6$ cm² V⁻¹s⁻¹). Therefore, this phenomenon does not explain the existence of high effective carrier concentration.

5.3 Monocrystalline SiC

In addition to depositing polycrystalline β -SiC films, laser ablation technique was used to grow monocrystalline β -SiC films on Si substrates. As these monocrystalline films (thickness $\leq 1 \mu m$)¹⁴⁴ have wide potential device applications, measurements of their conductivity, mobility and carrier concentration is needed to assess that potential.

Since the polycrystalline β -SiC films were deposited on insulating substrates, their electrical properties were measured with no need for separating the film from the substrate. Usually β -SiC films (0.7-50 μ m thick) grown on Si by chemical vapor deposition (CVD) are prepared for electrical characterization by chemically etching the Si substrate^{30,87}. However, etching the substrate is not needed in case of laser-deposited monocrystalline β -SiC on Si since these films seem to be isolated from the substrate by a highly resistive (porous) interface¹⁴⁴.

Since the quality of monocrystalline α -SiC substrate wafers is good, studying their electrical properties might shed some light on the results obtained for polycrystalline β -SiC and the potential of both poly and monocrystalline β -SiC prepared by laser ablation for certain applications such as temperature sensors. In the next section, measurements of conductivity, mobility and carrier concentration of both of these monocrystalline SiC polytypes are presented.

5.3.1 Monocrystalline α-SiC Substrates

Van der Pauw measurements were conducted on commercially available 6H- and 4H-SiC wafers. The wafers were cut in 1×1 cm² sizes to obtain square samples suitable for the available measurements systems. The thickness of these samples is in a range of 0.0569-0.1143 cm. The measurement systems and method of measurement were similar to those described earlier in 5.2.1. Fig.5.13 shows the temperature dependence of the inverse Hall coefficient $1/R_{\rm H}$ and electron concentration (n=1/qR_H) of one 4H-SiC sample and some 6H-SiC samples in a temperature range of 50-300K. The electron concentration increases monotonically with temperature and ranges between 10^{12} and 10^{20} cm⁻³. As shown in Fig.5.14, the mobility of these samples ($\mu=\sigma R_{\rm H}$) increases with temperature reaching its maximum then goes down as temperature increases due to lattice scattering. The maximum of the mobility for all samples ranges between 25 and 280 cm²V⁻¹s⁻¹ and occur in a temperature range of 150-300K. It is obvious that the mobility



Fig.5.13 Inverse of measured Hall coefficient, $1/R_{\rm H}$, with corresponding electron concentration for some 4H- and 6H-SiC. The fits for samples A and H in the low temperature range are shown as solid lines.

G (6H)

H (6H)

Fits

D (6H)

O E (4H)

△ F (6H)

A (6H)

B (6H)

C (6H)



Fig.5.14 The Hall mobility (μ = $\sigma R_{\rm H}$) as computed from Fig.5.13 and Fig.5.15.

D (6H)

E (4H)

F (6H)

Ο

0

Δ

G (6H)

H (6H)

A (6H)

B (6H)

С (6Н)

values decrease as the donor density increases due to the increase in impurity scattering. For example, sample A has the lowest mobility and highest donor density compared to other samples.

The temperature dependence of the conductivity σ for samples of Fig.5.13 is shown in Fig.5.15. σ increases with the increasing temperature for T \leq 300K and starts decreasing as temperature exceeds 300K due to the sharp decrease in mobility at those temperatures.

The activation energy for these substrates can be obtained by fitting the data using Eq.5.3 with two activation energies for samples A and B or one activation energy for the rest of the samples. The obtained fits shown as solid lines for samples A and H in Fig.5.13 are good except at very low (below 60K for sample H) temperatures which might be due to impurity/defect conduction. The shallow activation energy E_2 for samples A and B is 5 meV which is comparable to the shallow activation energy of the polycrystalline β -SiC films reported in this chapter. These polycrystalline films have high carrier concentrations and low mobilities with values comparable to those of samples A and B especially at low temperatures. The deep activation energy E, for all samples is in a range of 80-84 meV assuming temperature independent density of states. Recalculating this deep activation energy assuming $T^{3/2}$ dependence of the density of states leads to values in a range of 58-60 meV. The activation energies calculated using Hall measurements in a temperature range of 90-1000K are 81-84 meV and 52.1 meV for 6H-SiC and 4H-SiC, respectively^{28,29,88} whereas photoluminescence (PL) studies indicated a higher value of 170 meV¹⁴⁵. Activation energy of 81-84 meV was obtained from Hall electron concentration



Fig.5.15 The temperature dependence of measured conductivity for 7 samples of 6H-SiC and one 4H-SiC sample.

of $\langle 10^{17}$ cm⁻³ at 100K⁸⁸. In our case, wafers (samples C to H) that showed a single activation energy (80-84 meV) have comparable electron concentration of $\langle 10^{17}$ cm⁻³ in the same temperature range. On the other hand, samples A and B that showed a shallow activation energy have electron concentration of at least one order of magnitude larger than that of other samples especially at T \leq 100K. It seems that the shallow activation energy is associated with impurity conduction at low temperatures as it was found for polycrystalline β -SiC earlier in this chapter. This impurity conduction is noticed at T \leq 60K in case of sample H (low donor density) and extends to 120K for samples A and B (large donor density). Impurity conduction and dependence of activation energy on the donor density have been reported in earlier studies of β -SiC^{87,114}.

5.3.2 Monocrystalline β-SiC Films

Epitaxial β -SiC films were deposited on single-crystal Si wafers by laser ablation of ceramic stoichiometric SiC, carbon, or alternating silicon and carbon targets described elsewhere^{103,144}. X-ray diffraction spectroscopy and transmission electron microscopy indicated the crystalline cubic structure (i.e. β -SiC) of these films and alignment with the Si substrate¹⁴⁴. The film thicknesses, deposition temperatures and times, and pulse rates are shown in Table 5.2.

Even though the deposition time of 177 is approximately one order of magnitude larger than that of other samples, the thickness of 177 is comparable to the thickness of

Sample	Thickness (Å)	Dep. Temperature (°C)	Dep. Time (min)	Pulse Rate (Hz)
177	10000	1166	60	5
306	5500	1188	7	20
307	6000	1193	4	20
315	5500	1195	5.5	20
362	6500	1216	2.5	20

Table 5.2. Thicknesses, deposition temperatures, deposition times, and pulse rates for five SiC films.

other samples. This discrepancy might be due to the lower pulse rate (5 Hz) and deposition temperature (1166°C) of 177 compared to those (20 Hz and \geq 1188°C) of other samples.

Since shadow masks were used for selective area deposition, SiC growth occurred only within the openings of the shadow mask. The portion of the Si substrate underneath the mask did not receive any of the ablated material (i.e. the plume) and no SiC growth was noticed on the surface of this portion. The initial stages of epitaxial growth of SiC on Si seem to proceed by the reaction of carbon in the plume with Si outdiffusing from the substrate. As the growth of the film on top of the Si substrate continues, voids are left behind and the contact between the growing SiC film and the substrate is maintained over a progressively reduced area. Thus, some thick portions of the SiC film peel off due to the loss of contact surface with the substrate¹⁴⁴ leaving part of the film-substrate interface on top of the Si substrate. Three different samples of each Si substrate were prepared for resistance and Hall measurements. First sample was cut from the part of the substrate that was exposed to the plume. This sample has the sandwich structure, SiC-interface-Si, with the metal contacts being on the surface of the SiC film. A second sample was prepared from the part of the Si substrate that was underneath the shadow mask during deposition. A third sample was prepared from the remaining Si after the removal of the delaminated SiC film from the top. This SiC film broke into small pieces and was too thin to be used for the measurement. In our discussion, we will refer to these 3 samples as SiC/Si, interface-Si and Si, respectively.

Samples were cut in 1×1 cm² sizes and the preparation of the metal contacts and samples for van der Pauw measurements were done as described in 5.2.1. The measurements in the low (13-300K) and high (T \geq 300K) temperature ranges were done in the measurement systems described in 5.2.1.

Figs.5.16-17 show the measured Hall voltage of the SiC/Si, interface-Si and Si structures for samples of Table 5.2 in the low (below 300K) and high temperature (above 300K) ranges. The magnitude of the Hall voltage in the low temperature range is much larger than that in the high temperature range for most samples. For temperatures below 300K, the Hall voltage of the SiC/Si structure is at least one order of magnitude lower than that of the interface-Si structure for all samples except 306. This might be due to a lower interface resistivity (i.e. less voids with smaller size) which results from either lower deposition temperature (1188°C for 306 compared to 1193-1216°C for other samples) or lower deposition time (7 min for 306 compared to 60 min for 177).



Fig.5.16 The measured Hall voltage of sample 362 in two temperature ranges. These results are obtained using an input current of 0.1 mA and magnetic field of 8 kGauss. Interface-Si structure represents the Si under the peeled off β -SiC film.



Fig.5.17 The measured Hall voltage in the high and low temperature ranges of some samples of Table 5.3. These results are obtained using an input current of 0.1 mA and magnetic field of 8 kGauss.

As temperature increases above 300K, the Hall voltage values decrease and become negative (n-type conductivity) at temperatures given by Table 5.3. For both the interface-Si and SiC/Si structures of samples 362 and 307, these negative values exhibit a minimum with the lower values (larger magnitude) being those of the interface-Si structure. As temperature increases above 500°C, Hall voltage values for both structures approach the same value (-10μ V).

Even though the Si substrate had n-type conductivity, after deposition the conductivity of the SiC/Si, interface-Si and Si (front and back sides) was p-type for temperatures below 345 K and above 35 K (see Table 5.3). This indicates the formation of a p-type layer on the outer surface of the n-Si substrate. The formation of this p-type layer on the front and back sides of the n-Si substrate might be due either to loosing enough phosphorous from the outer surface of the substrate so that the native acceptor concentration becomes relatively larger or to doping the substrate with an acceptor available in the deposition system. This acceptor might be coming out of the resistive boron-nitride-coated graphite heater used in the deposition system to heat the n-Si substrate. Since the diffusion coefficient of boron and phosphorous in Si is very small $(2.51 \times 10^{-12} \text{ cm}^2/\text{s}$ at 1200° C), this p-type Si layer is expected to be very thin (few 1000 Å).

As temperature decreases below 300K, the positive Hall voltage shows a maximum then decreases for all samples and becomes negative at T \leq 35K for some samples. Usually, the Hall voltage increases as the carrier concentration decreases with the decreasing temperature. Therefore, the decrease in the Hall voltage at low temperatures might be due
 Table 5.3. Temperature range of n-type conductivity for samples of Table 5.2.

Sample	Temperature range	
177A [SiC/Si]	T≥631K , 100K ≤T≤ 130K and T≤34K	
177B [interface-Si]	T≥544K	
177C [Si]	low temperature data shows p-type*	
306A [SiC/Si]	low temperature data shows p-type*	
306B [interface-Si]	at T=28K*	
307A [SiC/Si]	T≥393K	
307B [interface-Si]	T≥393K and T≤35K	
315A [interface-Si]	T≥363K and T≤31K	
315B [SiC/Si]	T≥363K	
362A [SiC/Si]	T≥379K and T=23K	
362C [interface-Si]	T≥345K	

* No high temperature data is available.

to an increasing contribution to conduction from the n-Si substrate as the thickness of the depletion layer of the p-n junction decreases with the decreasing temperature. The change of the conduction type from p to n at temperatures \leq 35K might be due either to predominant contribution to conduction from the n-Si substrate or to impurity/defect band conduction within the p-SiC film and the p-Si thin layer.

It seems that predominant conduction takes place in the n-type Si substrate at high temperatures (above 300K) as the steep decrease in the Hall voltage shows in Figs.5.16-17. For temperatures below 300K, more conduction seems to occur in the SiC film as a result of the existing pn junction and the highly resistive interface between the SiC film and the n-Si substrate. The SiC/Si structure of sample 177 shows lower Hall voltage values compared to those values of the same structure of other samples for T \leq 300 K. This might indicate that the SiC film of 177 is more isolated from the substrate compared to other samples and thus the measured low Hall voltage values of the SiC/Si (177A) is mainly that of the SiC film for T \leq 300K. Table 5.3 shows that only for sample 177, the change from p- to n-type conductivity for the SiC/Si structure occurs at a higher temperature compared to that for the interface-Si structure (631K and 544K for 177A and 177B, respectively) supporting the view that the SiC film is well isolated from the substrate.

A better isolation between the film and substrate is obtained for longer deposition times as the contact surface between the SiC film and Si substrate reduces and the thickness of the p-n junction increases with deposition time, respectively. Thus, this isolation might be due to a longer deposition time of 60 minutes for 177 compared to that of \leq 7 minutes for other samples (Table 5.2). The low values of the measured Hall voltage of 177A indicate that this SiC film is highly compensated and therefore shows n-type conductivity in a temperature range of 100-130K whereas the interface-Si shows p-type conductivity in this temperature range.

The transfer resistance was measured using van der Pauw method as described in chapter 4. Figs.5.18-19 show the measured resistances of the SiC/Si (solid symbols) and interface-Si (hollow symbols) structures for samples of Table 5.3 in addition to the measured resistance of the Si structure for sample 177 (dotted line). The measured resistance of both the SiC/Si and interface-Si structures is at least one order of magnitude larger than that of the Si structure at temperatures below 300 K which might be due to defects and voids that exist in the SiC film and the interface, respectively. These voids in turn lead to an increase in the resistance of interface-Si structure compared to that of the SiC/Si structure (few times) for all samples at T \leq 300K. Above 300K, the SiC/Si and interface-Si resistances for all samples show sharp decrease with temperature and approach the same value.

The resistance data coupled with the Hall voltage data indicate that conduction takes place predominately in the n-type Si substrate above 300K. At lower temperatures, SiC film contributes more than both the p-type interface and the n-Si substrate to conduction. Therefore, the low temperature data of the SiC film needs to be extracted from the combined measured data of the SiC/Si structure using appropriate resistivity and Hall coefficient models. Multiple-layer models for Hall coefficient and resistivity are discussed below.



Fig.5.18 The measured resistance of two highly resistive films in the low and high temperature ranges. The measurement was done on SiC/Si structure (solid symbols) and on interface-Si structure after the removal of the SiC film (hollow symbols).



Fig.5.19 The measured resistance of 3 different films in the low and high temperature ranges. The solid symbols represent the data of the SiC/Si structure. The hollow symbols represent the data of interface-Si after removing the delaminated portion of the SiC film. The dotted line represents the data of the Si substrate that was underneath the shadow mask during deposition.

When the Hall voltage of two-layer structure such as SiC/Si is measured, the Hall voltage of the SiC film need to be extracted from the measured data. This section presents a model that deals with two layers with a resistive interface between them.

Fig.5.20(a) shows a schematic diagram of a symmetrical two-layer sample prepared for Hall voltage measurement using van der Pauw method. The equivalent circuit of this sample during the application of a magnetic field perpendicularly to the surface of the sample. The input current I_{AC} is applied between A and C. The effective Hall voltage of both layers is measured between B and D. As shown in Fig.5.20(b), R_1 and V_1 represent the resistance and Hall voltage of the upper layer, respectively, whereas R_2 and V_2 represent those of the lower layer. The interface resistance coupling the two layers together is represented by R_3 and R_4 . If the interface is homogeneous, R_3 will be equal to R_4 .

If the two layers are not identical, the Hall voltages developed within each layer will be different (i.e. $V_1 \neq V_2$) leading to a current flow between the upper and lower layers through the interface. This current is negligible for very large values of R_3 and R_4 compared to R_1 representing a case of well isolation of the upper layer (p-type and n-type layers with nonleaky p-n junction). Large current flows through the interface if R_3 and R_4 are very small compared to R_1 representing a case of a conducting interface (two n-type layers with different resistivities). Intermediate current flows through the interface if R_3 and R_4 are comparable to R_1 corresponding to a case of leaky p-n junction when it is reverse-biased. This p-n junction becomes conducting if it is forward-biased.





Fig.5.20 (a) A schematic of the sample used for Hall voltage measurement with 4 metal contacts at the corners of the sample. (b) Equivalent circuit of (a).

Using the equivalent circuit of Fig.5.20(b), the effective Hall voltage is given by

$$V_{DB} = \frac{V_1 \left[R_2 + R_3 + R_4 \right] - V_2 \left[R_1 \right]}{R_1 + R_2 + R_3 + R_4} . \qquad (5.10)$$

The applied current I_{AC} splits between the upper and lower layers as I_1 and I_2 , respectively, with their values being dependent on the resistance of both layers and that of the interface. The ratio of these currents can be obtained using the equivalent circuit of Fig.5.20(b) with zero magnetic field ($V_1=V_2=0$) as

$$\lambda = \frac{I_1}{I_2} = \frac{R_2 + R_3 + R_4}{R_1}, \qquad \dots (5.11)$$

The Hall voltages of the upper and lower layers are given by

$$V_1 = \frac{BI}{d_1} \frac{\lambda}{\lambda + 1} R_{H1}, \qquad \dots \quad (5.12)$$

and

$$V_2 = \frac{BI}{d_2} \frac{\lambda}{\lambda+1} R_{H2}, \qquad \dots (5.13)$$

where B is the applied magnetic field. d_1 and d_2 are the thicknesses of the upper and lower layers, respectively. R_{H1} and R_{H2} are the corresponding Hall coefficients.

Substituting Eqs.5.11-13 into Eq.5.10 leads to

$$V_{DD} = B I \frac{\frac{R_{H1}}{d_1} \lambda^2 - \frac{R_{H2}}{d_2}}{(1+\lambda)^2} \dots \dots (5.14)$$

Since the thickness and Hall coefficient of n-type Si and the thickness of the β -SiC film are known, the measured Hall voltage can be fitted with Eq.5.14 to obtain the Hall coefficient R_{H1} of the β -SiC film. It was not possible to fit the measured data using this model. This might be due to using a temperature independent interface resistance (R_3 and R_4) and ignoring the p-type silicon thin-layer on top of the n-Si substrate. This model needs to be developed in order to include voltage and temperature dependent resistance to represent the nonlinearity of the p-n junction.

The possibility of extracting SiC data from sandwich measurements is enhanced by considering "spreading resistance" effects. These effects require model like that in appendix which provides a more accurate estimate of λ .

The measured resistance of a multiple-layer structure can be calculated using van der Pauw method (see chapter 4 for details) as

$$\rho = \gamma \left(\frac{R_1 + R_2}{2} \right) f\left(\frac{R_2}{R_1} \right), \qquad \dots (5.15)$$

where γ is the thickness correction factor, R_1 and R_2 are the measured transfer resistances, and $f(R_2/R_1)$ is a known correction factor for symmetry. For single layer structures, $\gamma = (\pi d/ln2)$ where d is the film thickness.

As shown in the appendix, this correction is given by:

$$\gamma = \frac{V}{E}, \quad \dots \quad (5.16)$$

where E is the applied potential at two adjacent contacts (E=I/ σ where I is the applied current and σ is the conductivity) and V is the potential at the other two contacts calculated using the model in the appendix.

In case of SiC/Si structure, the resistance (or resistivity) of the Si substrate is known and that of the interface can be treated as a parameter. One way to model the resistivity of this interface is to consider it as an intrinsic or doped layer of a semiconductor. By varying the bandgap and doping level of this layer, the interface resistivity varies. The measured resistance of the SiC/Si structure can be fitted now to obtain the resistance of the SiC layer. The results of the fit show that the resistance of the SiC film dominates ($R_{siC} \ll R_{si}$) below room temperature whereas the Si substrate dominates above room temperature.

5.4 Summary

Measured conductivity and Hall coefficient of polycrystalline SiC films deposited on quartz by laser ablation of SiC targets showed strong temperature dependence even at carrier concentrations in excess of 10^{20} cm⁻³. Phenomenological analysis produced three well separated activation energies, high carrier concentration and low mobility over the whole temperature range. Fits of the high temperature data of the films that show effective carrier concentrations in the order of 10^{20} cm⁻³ at high temperatures require unacceptable donor densities (i.e. $\sim 10^{22}$ cm⁻³). Hopping mechanism does provide a reasonable explanation for films that show effective carrier concentration in the order of 10^{19} cm⁻³ but with exaggerated donor densities. For those films hopping process seems to be associated with the intermediate energy level E₂ with the smallest activation energy E₃ being the hopping activation. 86

The resistance and Hall voltage data of the 3C-SiC heteroepitaxial films grown on Si substrates show that the Si substrate dominates conduction for temperatures larger than room temperature. The electron concentration of α -SiC substrates varies between 10^{12} cm⁻³ and 2×10^{18} cm⁻³ in a temperature range of 50-800 K. Our Hall measurements of α -SiC showed for the first time a very shallow activation energy of 5 meV which seems to be responsible for impurity conduction.

CHAPTER 6

SEEBECK COEFFICIENT OF SiC

6.1 Introduction

SiC has strong potential for sensors operating at high temperatures and in chemically aggressive environments such as those prevailing in automotive and jet engines⁸. The progress that has been achieved in bulk and thin-film SiC preparations, n-and p-type doping, and SiO₂ growth coupled with some degree of compatibility between SiC and Si technologies makes SiC an attractive material for microsensor applications. In particular, thermal microsensors which utilize the Seebeck effect to measure nonthermal signals are very promising due to both their reliability and functional simplicity. In this case, a nonthermal signal such as heat transfer rate, gas flow velocity, pressure, kinetic energy and radiant energy is first converted into an on-chip temperature gradient inducing an electrical signal that can finally be measured¹²³.

Metal or alloy thermocouples and thermistors are most frequently used to measure the temperature. Metal or alloy thermocouples¹³² have large temperature range (-240 to 2300°C), linear response, and low sensitivity whereas thermistors^{90-92,133-134} have lower temperature range (-100 to 900°C), nonlinear response, and high sensitivity. Semiconductor thermistors such as diamond also have been investigated. Although diamond thin film thermistors have high sensitivity and fast response time, they suffer from oxidation problem at temperatures above $600^{\circ}C^{120}$. Other types of temperature sensors show either poor sensitivity (resistance temperature detectors) or very limited temperature range (IC sensors).

Most of the surface heat flux measurement techniques suffer from slow response times which do not allow the measurements of transient heat fluxes. In addition, heat flux gages might cause surface disruptions leading to significant flow and thermal disturbances. These disturbances are compounded when gage cooling is required at high temperatures.

Higher response times and less surface disruptions have been obtained using thin film technology. In this case, a thin metal film is deposited on a material surface where the transient heat flux is measured by measuring either the dissipated power in or the resistivity of the film. To measure the dissipated power, an external current is passed through the thin film which is maintained at a constant temperature using a feedback control system such as a constant temperature anemometer controller. This technique suffers from a limited frequency response (i.e. below 100Hz)¹²⁸. In addition, the transient response of the gage might be degraded if the resistance of the gage does not cover the entire gage surface¹²⁹. Using thin film technology a layered heat flux microsensor has been recently developed¹³⁵. The total thickness of this gage is less than 2 µm and its time response is, approximately, 20 µsec¹³⁶. Therefore, this microsensor can be used to measure both transient and steady components of the heat flux.

There is current interest in developing temperature and heat flux sensors that have large temperature range, linear response, high sensitivity, fast response time, and high chemical stability. As the Seebeck emf of semiconductors is higher and the response time for thin-film temperature sensors is faster than that of metal and alloy combination, it is important to determine the possible advantages of using SiC thin films as the active material for thermoelectric temperature sensors. There have been some reports about SiC temperature sensors based on the measurement of SiC resistance⁹⁰⁻⁹² but there have been no reports about the measurement of SiC Seebeck coefficient versus temperature.

In this chapter, measurements of the Seebeck coefficient of polycrystalline β -SiC films and monocrystalline α -SiC substrates in a temperature range of 300-533 K are presented for the first time. It is found that Seebeck emf of the β - and α -SiC is larger than that of the standard platinum thermocouple. Application to temperature and heat flux sensors and thermoelectric generators is investigated.

6.2 The Seebeck Coefficient

When a temperature gradient is established along an extrinsic semiconductor slab (film), corresponding gradients in the carrier concentration and diffusion coefficient usually appear in the same direction. Carriers (either electrons or holes) in the presence of this temperature gradient will diffuse from the hot to the cold ends under open circuit and will establish an electric field which tends to force carriers motion in the opposite direction. At equilibrium, the flux of carriers caused by this field is equal to that caused by the diffusion process. Although the number of carriers passing through any crosssection of the semiconductor in a unit time in both directions are equal, carriers coming from the hot end will have higher energies than those coming from the cold end.

Phonons and charge carriers contribute to the continuous transfer of heat from the hot end to the cold one. However, heat is mainly transferred by phonons in SiC in the temperature range of interest due to its high thermal conductivity¹³⁸. Since measurement of the Seebeck emf is a steady state measurement, heat conductivity does not matter. However, phonons may contribute to the Seebeck emf by dragging a larger number of electrons from the hot end to the cold end. This drag effect was discovered by Gurevich in metals¹³⁷. In semiconductors, phonon contribution to the Seebeck emf is negligible in the transition and intrinsic ranges compared to the electronic contribution. This drag effect has very large values below room temperature at least in Si and Ge^{141,142}. For example, the contribution of this effect to Seebeck coefficient in Si at temperatures of 100K and 300K is as large as 6 mV/K and 0.43 mV/K, respectively.

If an intrinsic semiconductor (concentrations of electrons and holes are equal) is subjected to temperature gradient, still an electrical field will be established due to differences in the effective masses, energies and mobilities of electrons and holes, respectively. In this case, more electrons than holes diffuse toward the cold end due to the higher electrons mobility establishing an electrical field that accelerates the holes and decelerates electrons. This process continues until the drift and diffusion currents of holes and of electrons all add up to zero leading to equilibrium. As shown in Fig.6.1, the potential (Seebeck emf) that appears between the hot and cold ends is equal to qV where



Fig.6.1 (a) Top view of the sample under test showing the metal contacts and the thermocouples with T being the lower end temperature and ΔT being the temperature difference between the two ends. (b) A schematic of the band diagram of the sample showing the electrical field E and the Seebeck emf (i.e. qV).

q is the electron charge. The Seebeck coefficient is defined as the potential difference between the two ends per 1°C.

Assuming that electrons are the sole carriers that contribute to the Seebeck emf (n-type semiconductor) and the mean free time between carrier collisions τ can be expressed as $\tau \sim E^{-s}$ where E is the carrier energy, and s=1/2 for phonon scattering and s=-3/2 for ionized impurity scattering¹²², the Seebeck coefficient Q can be evaluated as^{122,123}

$$Q = -\frac{\pi^2 k}{q} \left(\frac{kT}{E_F} \right) \left(\frac{1}{2} - \frac{1}{3} s \right), \qquad \dots (6.1)$$

and

$$Q = -\frac{k}{q} \left[\frac{5}{2} - s + \ln \left(N_c / n \right) \right] = -\frac{k}{q} \left[\frac{5}{2} - s - \frac{E_F}{kT} \right], \quad \dots \quad (6.2)$$

for degenerate and nondegenerate cases, respectively. n and μ_n are the concentration and mobility, respectively, of electrons in the conduction. E_F is the Fermi level location relative to the bottom of the conduction band edge E_c with the assumed condition of (E_F/kT))0 for Eq.6.1 and the Boltzmann distribution for Eq.6.2. T is the absolute temperature, h is the Planck constant, k is the Boltzmann constant and q is the electronic charge. The density of states in the conduction band is given by¹²²

$$N_c = 2 \left(\frac{2 \pi m_n k T}{h^2} \right)^{3/2} M_c \qquad \dots (6.3)$$

where m_n is the density-of-state effective mass for electrons and M_c is the number of equivalent minima in the conduction band which is equal to 3 for SiC. If holes in addition

to electrons contribute to conduction, Eq.6.2 has to be modified in order to obtain the net contribution of electrons and holes to the Seebeck coefficient. The measured Q can be used to determine the Fermi level location E_F relative to the bottom edge of the conduction band E_c and consequently the carrier concentration in the conduction band can be determined.

The sign of the measured Seebeck coefficient can be used to determine the conduction type of a semiconductor. However, if the semiconductor is highly compensated, there is a possibility of obtaining the incorrect sign of Q within a certain range of temperature depending on the effective masses, mobilities and relative concentrations of holes and electrons. The Seebeck coefficient for metals and degenerate semiconductors is highly reduced compared to nondegenerate semiconductors since it is assumed that (E_F/kT) »1. When mobility of electrons is much larger than that of holes as it is in SiC, electrons become the major contributor to the Seebeck emf with its value being dependent on the concentration and effective mass of electrons.

6.3 Results and Discussion

The measurement technique of the Seebeck coefficient is explained in chapter 4. Fig.6.2 shows measured Seebeck coefficient versus temperature for some polycrystalline 3C-SiC (hollow symbols) and some monocrystalline 4H-SiC and 6H-SiC samples (solid symbols) in a range of 27-260°C. These values of the Seebeck coefficient range from -9 to -30 μ V/°C for the cubic samples and from -108 to -20 μ V/°C for the hexagonal samples. The Seebeck coefficient shows n-type conduction for all samples which is in



Fig.6.2 Measured Seebeck coefficient for three polycrystalline 3C-SiC films (solid symbols) and three hexagonal samples (hollow symbols).
agreement with the conduction type obtained from Hall measurements in this temperature range.

The Seebeck coefficient of the monocrystalline hexagonal samples is higher than that of the polycrystalline 3C-SiC samples near room temperature. However, as temperature increases the absolute value of the Seebeck coefficient of the hexagonal samples decreases due to the increase in the electron concentration and approaches that of the polycrystalline samples. The hexagonal sample A with the highest electron concentration (~10¹⁹ cm⁻³ at 23°C) has the lowest Seebeck coefficient of -30 μ V/K compared to -80 μ V/K and -108 μ V/K for samples E (~10¹⁷ cm⁻³ at 23°C) and D (~10¹⁶ cm⁻³ at 23°C), respectively.

Analysis of the measured Seebeck coefficient data coupled with the analysis of the Hall data is crucial in understanding the electronic properties of SiC for sensor applications. The phonon drag effect is negligible in our case since as we will see the measured Seebeck coefficient can be fitted assuming only electronic contribution (using Eq.6.2 with n being the measured Hall electron concentration).

Since the electron concentration of the polycrystalline β -SiC films is as large as 10^{18} cm⁻³ even at 20 K, these films might be degenerate. If this case, so. Eq.6.1 can be used to obtain the location of E_F. As the measured Q ranges from -9 to -30 μ V/K, Eq.6.1 leads to (E_F-E_c) in a range of 17-50 kT for phonon scattering and 33-100 kT for ionized impurity scattering.

Using Fermi distribution, the carrier concentrations in the conduction band n for the above locations of the Fermi level are found to be in the range of $(1 - 4) \times 10^{21}$ cm⁻³

and $(4 - 10) \times 10^{21}$ cm⁻³ for phonon scattering and ionized impurity scattering, respectively, in a temperature range of 300-550 K. These values of carrier concentration are one order of magnitude larger than the ones obtained from the Hall data and they require donor densities in the range of the atomic density of SiC (i.e. 9.7×10^{22} cm⁻³). As the conduction process seems to be predominately within the grains (chapter 5) and since x-ray-diffraction studies indicate the crystalline structure of our films within the grains, the possibility of having degenerate SiC films has to be excluded¹⁰⁶.

The Fermi level E_F location for samples of Fig.6.2 is estimated at 300 K using Eq.6.2 with s=1/2. For the polycrystalline samples, E_F - E_c ranges from -1.7 kT to -1.9 kT (~-45 meV at 300 K) whereas for the hexagonal samples it ranges from -1.42 kT to -1.92 kT (from -27.6 meV to -42.9 meV at 300 K) as shown in Table 6.1. Boltzmann approximation can be used as long as (E_c-E_F) »kT. For the polycrystalline samples, Boltzmann and Fermi statistics were used with the obtained results in both cases being very close. The values of E_F obtained from the measured Seebeck coefficient and the electron concentration n obtained from the measured Hall coefficient R_H as $1/qR_H$ can be used to estimate the quantity m_n/m_o , where m_n is the density-of-states effective mass and m_o is the free electron mass, by fitting n with N_cexp(- E_F/kT). For sample D, E_F-E_c ranges from -0.74 kT to -1.92 kT in a temperature range of 300-533K and thus Fermi statistics is used in the fitting.

At 300 K, the obtained values of m_n/m_o are shown in Table 6.1. These values are different from the ones determined by cyclotron resonance measurements for single crystalline β -SiC ($m_n/m_o=0.346$) and α -SiC ($m_n/m_o=0.45$)⁸⁸. For β -SiC samples and 6H-

Table 6.1. The electron concentration $n=1/qR_{H}$, Fermi level location below E_{c} and effective mass estimated at 300 K for some polycrystalline β -SiC and α -SiC monocrystalline samples.

Sample		n (cm ⁻³)	E _F -E _c (meV)	m _n /m _o
α-SiC:	sample 1 (6H)	1×10 ¹⁹	-42.9	0.787
	sample 5 (6H)	6×10 ¹⁶	-19.2	0.0156
	sample 6 (4H)	2×10 ¹⁷	-27.6	0.0391
β-SiC:	140 B	1×10 ¹⁹	-48.6	0.912
	164A	1×10 ¹⁹	-43.2	0.794
	194 C	1×10 ¹⁹	-45	0.831

SiC (sample A), having a large effective mass $(m_n/m_o=0.787 \text{ to } 0.912)$ might be due to the very large donor/defect concentration ($>10^{20} \text{ cm}^{-3}$). In addition, the anisotropy of the α -SiC crystals might lead to variations in the measured values of the effective mass.

For sample 1 (6H-SiC) and sample 6 (4H-SiC), the estimated effective mass values m_n/m_o are 0.0156 and 0.0391, respectively. These values are much lower than the measured one for α -SiC ($m_n/m_o=0.45$) and this might be caused by the anisotropic α -SiC crystal where the effective mass varies between the basal plane of the crystal and the c-axis^{139,140}. This means that the angle between the temperature gradient along the sample and the c-axis affects the values of the measured Seebeck coefficient and the effective mass.

The analysis of the Hall data of the polycrystalline 3C-SiC films (see chapter 5) shows that the electron concentration obtained as $1/qR_{H}$ might be exaggerated. Therefore,

using such electron concentrations in fitting the measured Seebeck coefficient will lead to a high estimate of the effective mass ($m_n/m_o=0.79$ to 0.91) as shown in Table 6.1. In this situation, the measured Seebeck data can be used to estimate the electron concentration assuming that the electron effective mass is known. Fig.6.3 shows the estimated electron concentration for some polycrystalline 3C-SiC films using Eq.6.2 assuming that the effective mass of electrons is equal to that of single crystalline β -SiC ($m_n=0.346m_o$) and phonon scattering is predominant (s=1/2). The obtained electron concentration increases monotonically with temperature and is in the range of 2×10^{18} - 7×10^{18} cm⁻³.

The activation energy E_d obtained from the calculated electron concentration of Fig.6.3 is, approximately, equal to 54 meV. Correcting the data of Fig.3 for the T^{3/2} dependence of the density of states leads to an $E_d \approx 50$ meV. This activation energy agrees with the obtained value of E_1 from Hall data (chapter 5) and is very close to the binding energy of nitrogen (i.e. 53-54 meV) reported in earlier studies of monocrystalline SiC^{5,14}. This result might indicate that measured Seebeck coefficient can be used to obtain the carrier concentration in the conduction band in cases where Hall data provides an exaggerated one.



Fig.6.3 The measured (solid symbols) and calculated (hollow symbols) electron concentration of 3 polycrystalline SiC samples. The calculated electron concentrations are obtained from the measured values of Seebeck coefficient using Eq.6.2.

6.4 Applications

6.4.1 Thermoelectric Temperature Sensor

Metal-alloy thermocouples measure temperature by measuring the Seebeck emf between two junctions where one junction is held at a known reference temperature such as room temperature and the other junction is exposed to the unknown temperature. Each junction consists of two metals (or alloys) that have different Seebeck emf values. If the Seebeck emf values of the two metals are the same, both emfs generated between the two measuring leads will cancel out and the net emf detected will be zero. This means that the difference in the work functions of the two metals at one junction relative to that at the reference junction ($\Delta \phi(T) - \Delta \phi(T_{ref})$) is used to measure the Seebeck emf. The measured Seebeck emf between two ends coupled with a reference temperature such as the temperature of the cold end can be used to obtain the unknown temperature of the other end.

The Seebeck emf E(T) of thermocouples and semiconductors reflects their potential for temperature sensors. Fig.6.4 shows the obtained output voltage E(T) of some polycrystalline β -SiC and monocrystalline α -SiC and that of a platinum thermocouple (Pt-10Ir versus Pt¹²⁴). The Seebeck voltage E(T) of SiC is obtained by integrating the Seebeck coefficient Q(T) over the corresponding temperature range assuming T_{ref}=300 K.

 α -SiC has higher Seebeck emf compared to β -SiC and platinum. Two β -SiC samples show higher Seebeck emf than that of the platinum thermocouple. This indicates that SiC has a good potential for temperature sensing at least in a temperature range of 300-533 K.



Fig.6.4 The absolute value of the Seebeck emf for β -SiC (solid symbols) and α -SiC (hollow symbols) and a platinum thermocouple¹²⁴.

6.4.2 Heat Flux Sensor

Heat Flux sensors measure the heat transfer per unit area that usually takes place between two materials if their temperatures are different. The application of this sensor is limited to the case where one material is a solid body such as a metal plate and the other one is a fluid material such as water or air. The sensor is usually placed at the surface of the solid material. Measuring the gradient of temperature at the surface provides information about the heat flux if the appropriate analytical model is used. Therefore, the resistivity or Seebeck effect of SiC can be used to obtain the temperature and thus the heat flux.

There are three modes of heat transfer: radiation, conduction, and convection. Radiation heat transfer occurs when heat is transferred through electromagnetic radiation with no need for a material medium. Heat transfer by conduction occurs when a temperature gradient exists within a material. The heat flows from the high-temperature region to the low-temperature region. Convection heat transfer takes place when a moving fluid contacts the surface of another material. In this case the rate of heat transfer depends on the velocity of the fluid. The velocity of the fluid is reduced to zero at the surface of the material due to viscousity. Thus the heat is transferred only by conduction at the surface. Since heat transfer rate and temperature gradient below the surface depend on the velocity of the fluid, measurement of the heat transfer at the surface gives not only the conduction heat transfer but the overall convection heat transfer. The overall heat flux is given by Newton's law:

$$q = h (T_s - T_f) + q_{rad}, \qquad \dots (6.4)$$

where h is the convection heat-transfer coefficient. (T_s-T_f) is the temperature difference between the surface and the fluid. The radiation heat flux q_{rad} is usually negligible compared to convection heat flux and can be ignored. A direct measurement of the heat flux requires measurement of the temperature difference (T_s-T_f) . Measuring the temperature only at the surface leads to indirect measurement of the heat flux using the appropriate analytical model.

A layered heat flux microsensor with a fast response time has been recently developed¹³⁵. Heat flux is obtained directly by measuring the temperature difference between the surface and the flowing fluid above it (T_s-T_f) . This microsensor consists of a thin thermal resistance layer sandwiched between two temperature sensors. Each temperature sensor consists of two thin metal strips which overlap at the middle of the resistor's width forming one thermocouple. These two thermocouples (i.e. above and below the resistor) are connected in series outside the resistor to obtain the temperature difference difference across the resistor.

The layered heat flux microsensor suffers from some problems. This microsensor consists of five layers, one thin film resistor layer sandwiched between two thermocouples where each thermocouple consists of two layers. Since the heat flux passes through the gage itself into the surface of the material, flow and thermal disruptions result. These disruptions can not be eliminated completely but can be minimized significantly by reducing the thickness of the sensor which in turn improves the time response. For thicknesses above 25 μ m, the time response of the layered heat flux microsensor is larger than 20 ms¹³¹ and for thicknesses less than 1 μ m, the time response is less than 100 μ s¹³⁰.

Since SiC can be used for high temperature applications, its thin film technology is well developed and its Seebeck coefficient is higher than that of metal thermocouples, investigating simpler structure of this microsensor to improve its performance utilizing thin film SiC technology is of interest. Our proposed structure has not been fabricated, however, it is discussed here in order to highlight its potential for a better performance.

The new structure uses many pairs of n- and p-type SiC cells connected serially as shown in Fig.6.5 in order to obtain a larger output signal. This is also the structure of a thermoelectric generator (see next section). In this structure only three layers are needed compared to five layers in the original structure. Having only 3 layers leads to a smaller thickness and thus thermal and flow disturbances are reduced. In addition, a thin layer of an insulating material that has a high thermal conductivity such as undoped polycrystalline diamond¹⁴³ can be deposited on the bottom and the top of this microsensor. This leads to homogeneous distribution of the temperatures T_s and T_f on the top and the bottom of the microsensor, respectively, and thus to a more accurate measurement.

The fabrication of this proposed structure requires only 4 major steps using laser ablation technology (see chapter 5). Firstly, a patterned metal layer is deposited using a shadow mask. Secondly, p- and n-SiC layers are deposited in sequence using appropriate shadow masks to obtain the p-type and the n-type cells. Thirdly, an insulating layer is deposited between the n- and p-type cells. SiC is insulating if deposited at room temperature and thus can be used for deposition between cells. Finally, a patterned metal



Fig.6.5 A schematic of n- and p-SiC cells connected serially. This schematic represents either a thermoelectric generator with T_{high} - T_{low} is large or a heat flux sensor with T_{high} - T_{low} = ΔT is very small.

layer is deposited on the top of the structure.

The fabrication process of this structure is easier than that of the original structure since the former has less number of layers. Laser ablation technology, in particular, can be used for in-situ deposition of the metal layers and the SiC layer. In this case, the high energy of the ablated plume usually leads to better adhesion between the deposited metals and the SiC film compared to other techniques. Moreover, the Seebeck emf signal of SiC films is usually larger than that of alloys and metals at least at high temperatures.

6.4.3 Thermoelectric Generator

A thermoelectric generator utilizes the fact that the Seebeck effect allows the generation of electrical power from thermal power. A thermoelectric device consists of a serial connection of cells as these of Fig.6.5. These cells might be made of similar or different semiconducting material. A metal contact at the top connects both cells. At the bottom, a metal contact is attached to each cell separately as shown in Fig.6.6. This device can work as a current generator or as a cooling couple. If a temperature difference $(T_{high}-T_{low})$ is maintained between the two ends of the device, this device will function as a voltage generator. On the other hand, if a current is externally supplied through this device, this device will function as a cooling couple.

The ratio M of the optimum load resistance R_o to the internal resistance R_i of the device will be given by¹²⁶

$$\frac{R_o}{R_i} = M = \left[1 + \frac{Z}{2} \left(T_{high} - T_{low}\right)\right]^{1/2}, \qquad \dots \quad (6.5)$$

where $Z=Q^2\sigma/\kappa$, σ is the electrical conductivity, κ is the thermal conductivity and Q is the Seebeck coefficient. If load resistance is equal to R_o , a current I flows in the circuit leading to maximum transfer of electrical power ($I^2 R_o$).

The ratio of electrical power lost in the optimum resistance R_o to the thermal power supplied at the heated end is defined as the efficiency. Assuming that both cells have the same properties (i.e. σ , κ , and |Q|), the efficiency of a thermoelectric generator is given by^{126,127}

$$\eta = \frac{T_{high} - T_{low}}{T_{high}} \frac{M - 1}{M + [T_{low} / T_{high}]}, \qquad \dots \quad (6.6)$$

The efficiency η of a thermoelectric generator increases as the Seebeck coefficient and the ratio of electrical to thermal conductivities (i.e. σ/κ) of the material increase. Since the ratio σ/κ for metals is five orders of magnitude higher than that for SiC, the potential of having an efficient SiC thermoelectric generator is weak.

Table 6.2 shows σ , Q, κ , Z, and η of monocrystalline 4H- and 6H-SiC, polycrystalline 3C-SiC and some other materials that are used for thermoelectric generation. Since κ for our polycrystalline SiC films has not been measured, the efficiency of these films is calculated using the thermal conductivity of monocrystalline SiC. This might lead to a smaller efficiency since thermal conductivity of monocrystalline

Material	σ (Ω ⁻¹ cm ⁻¹)	Q (μV/K)	к (w/cm K)	Z (K ⁻¹)	η
Metals ¹²⁵	10 ⁵ -10 ⁶	10	0.2-4.0	≤5×10 ⁻⁴	<1.2%
Boron Carbide ¹²⁶	400	320	0.05	8.2×10 ⁻⁴	1.9%
4H-SiC	1	80	5	1.28×10 ⁻⁹	3.2×10 ⁻⁶ %
6H-SiC	1-100	110	5	2.42×10 ⁻⁷	6.1×10 ⁻⁴ %
3C-SiC	30	10-30	5	5.4×10 ⁻⁹	1.4×10 ⁻⁵ %

Table 6.2. Properties of some materials for thermoelectric generation applications. η is calculated using T_{high} =600K and T_{low} =300K.

materials is usually higher than that of polycrystalline materials. However, even if thermal conductivity of polycrystalline 3C-SiC films is two orders of magnitude lower than that of monocrystalline films, the efficiency of our 3C-SiC films will be 3 orders of magnitude lower than that of metals.

The efficiency of 6H-SiC is larger than that of 4H-SiC and 3C-SiC by at least two orders of magnitude due to its high electrical conductivity and Seebeck coefficient. However, this high efficiency is still two orders of magnitude less than that of metals. Therefore, the potential of SiC for thermoelectric generators is not promising compared to the other materials that are currently used (e.g. metals) or investigated (e.g. semiconductors).

6.5 Summary

As the Seebeck coefficient of β - and α -SiC in temperature range of 300-533 K is large their potential for temperature and heat flux sensor applications is excellent. Further investigation of the Seebeck coefficient of SiC in a larger temperature range is needed especially for applications at high temperatures. In addition, studying the effect of anisotropy of α -SiC on the Seebeck coefficient will permit its maximization.

CHAPTER 7

SiC THERMISTORS

7.1 Introduction

The change of resistivity with temperature of semiconductors can effectively be used for temperature sensing through devices known as thermally sensitive resistors (i.e. thermistors). Materials that are usually used to sense temperatures include metals, alloys, insulators, and semiconducting materials such as compressed metal oxides, Si, diamond, ... etc. The magnitude of the sensitivity of metal oxides is larger by approximately an order of magnitude than that of metals or alloys. Alloys usually have higher resistivities and better physical properties compared to metals but these improvements are usually achieved at the expense of reduced sensitivity. The platinum resistance thermometer is still a temperature standard in range of $0-600^{\circ}C^{123}$.

Thermistors (i.e. semiconductor-based temperature sensors) have a limited use as compared to alloys-based temperature sensors in spite of their higher sensitivity. This is due to some disadvantages related to the properties of the host material of the thermistor compared to those of alloys. Those disadvantages include a limited temperature range (e.g. Si), oxidation of the host material which prevents reproducibility of resistivity (e.g. Diamond at T \geq 600°C), and not withstanding high pressure that might change the structure and thus the resistivity of the material (e.g. compressed metal oxides). Although the resistance range of insulators is very high (i.e. $\geq 10^{10} \Omega$), it is possible to use them as temperature sensors at very high temperatures (T \geq 600°C) as their resistance becomes practically measurable. Since the available temperature sensors operate over limited temperature ranges, it is of interest to investigate some other materials such as SiC that can operate in harsh environments and over a wider temperature range.

In this chapter, the resistivities of polycrystalline and single crystalline 3C-SiC and heteroepitaxial 4H- and 6H-SiC are discussed to determine the potential of these SiC polytypes for temperature sensors. Among those materials, polycrystalline 3C-SiC films showed a unique potential for temperature sensing over a wide temperature range of 13-1277 K.

7.2 Resistivity of SiC

The resistivity of SiC is measured using van der Pauw method (see chapter 4). Fig. 7.1 shows the measured resistivity of polycrystalline and single crystalline 3C-SiC and monocrystalline α -SiC in a temperature range of 20-900 K. The single crystalline 3C-SiC film (6000 Å thick) was deposited on Si substrate using laser ablation technique (see chapter 5 for more details). The measured resistance of the combined structure SiC/Si is an effective resistance of both the SiC film and the Si substrate. The resistivity of this SiC/Si structure is calculated from the measured resistance assuming that the thickness



Fig.7.1 The resistivity of some β -SiC (solid symbols) and α -SiC (hollow symbols).

is equal to the sum of the SiC film and Si substrate thicknesses (~0.04 cm).

The resistivity of polycrystalline β -SiC decreases monotonically with the increasing temperature over the entire temperature range whereas the resistivity of the single crystalline β -SiC decreases with temperature in general but sometimes increases slightly with temperature over short temperature ranges. The resistivity of α -SiC decreases with the increasing temperature for T \leq 300 K and increases as temperature goes above 300 K. In the low temperature range (i.e. below room temperature), α -SiC resistivity varies over a wider range (10⁻¹-10⁶ Ω .cm) compared to single crystalline β -SiC (~10¹ Ω .cm) and polycrystalline β -SiC (~10⁻¹ Ω .cm). In the high temperature range, single crystalline β -SiC (307B) has strong temperature dependence (10⁻¹-10² Ω .cm) whereas all other samples have weak temperature dependence. This might be due to the low resistivity of the Si substrate which shorts the SiC film at high temperatures.

The resistivity of all α -SiC samples shows strong temperature dependence below room temperature whereas weak temperature dependence is obvious above room temperature. Sample B, in particular, shows weaker temperature dependence than the other two samples. This might be due to the large carrier concentration (~10¹⁸ cm⁻³ at 300 K) of this sample compared to that of the other two samples (10¹⁶ and 10¹⁷ cm⁻³ for samples H and E, respectively, at 300 K).

Fig.7.2 shows two cycles of the resistivity of some polycrystalline β -SiC films in a temperature range of 13-1277K. The hollow symbols show the cycle that starts from the low temperature and goes to the high temperature whereas the solid symbols show the cycle that goes from high to low temperatures. The resistivity of these films has stronger



Fig.7.2 Two cycles of the resistivity of some polycrystalline β -SiC films.

temperature dependence at T≤200K. Their resistivity is very low (0.01-0.4 Ω .cm) compared to the single crystalline β -SiC and α -SiC samples especially at temperatures below 200 K. This might be due to the large carrier concentration of these films even at very low temperatures (\rangle 10¹⁸ cm⁻³). Even though some films were not initially annealed, the results were reproducible. The resistivity of the single crystalline β -SiC and α -SiC is also reproducible in the entire temperature range.

Resistivity of SiC can be used in temperature sensing. An important figure-of-merit of temperature sensors is their sensitivity to temperature change. This sensitivity can be studied in terms of the temperature coefficient α defined as¹²⁰

$$\alpha = \frac{1}{\rho} \frac{\delta \rho}{\delta T}, \qquad \dots (7.1)$$

where ρ is the resistivity and T is the temperature. The temperature coefficient α is suitable for sensitivity comparison of materials that have comparable resistance R values. Otherwise, the quantity $\Delta R/\Delta T$ can be used as a figure-of-merit.

Fig.7.3(a) shows the temperature coefficient α for the samples of Fig.7.1. All polycrystalline and single crystalline β -SiC samples exhibit a negative α through out the entire temperature range whereas α -SiC shows a negative α at low temperatures and exhibits a change of sign near room temperature. This is not a desirable characteristic of a temperature sensor since it limits its use to either the positive or negative temperature range of α to insure obtaining a single calculated value of temperature for a single value of measured resistivity.



Fig.7.3 (a) The sensitivity coefficient α for samples of Fig.7.1. (b) An expansion of the data shown in (a).

In general, all samples show higher sensitivities at lower temperatures due to the steep change in their resistivity at those temperatures. These sensitivities do not show any scattering throughout the whole temperature range except for single crystalline β -SiC. This scattering in sensitivity is not desirable and might be due to changes in resistivity values of SiC-Si interface.

Fig.7.3(b) shows that the temperature coefficient for α -SiC at T≥300K (0.002-0.004K⁻¹ for samples B and E) has a larger magnitude than that of polycrystalline β -SiC (0.0005-0.002K⁻¹). Since α for the former material becomes very small and approaches zero within a temperature range of 200-300K, the use of this material for temperature sensing in this temperature range should be avoided.

Table 7.1 shows that α -SiC and β -SiC have temperature coefficients comparable to those of platinum and tungsten. Therefore our polycrystalline SiC films can be a potential alternative for the commercially available platinum and tungsten temperature sensors since they have comparable sensitivity, negligible oxidation rate even at 1000°C, chemical inertness to corrosive atmospheres, radiation immunity and excellent mechanical properties. Hexagonal SiC suffers from a limited temperature range compared with our polycrystalline SiC films which have negative α through out the temperature range.

Material	α (/°K)	Material	α (/°K)
Platinum	+0.0037	4H-SiC (sample E)	-0.0015
Tungsten	+0.0052	6H-SiC (sample B)	-0.004
Nickel oxide	-0.044	β-SiC (307B)	-0.0144
Manganese oxide	-0.044	193A (poly. β-SiC)	-0.0026
6H-SiC (sample H)	+0.00014	152B (poly. β-SiC)	-0.0028

Table 7.1. The temperature coefficient α at 300 K for some alloys, oxides, hexagonal SiC, and polycrystalline SiC films.

For comparison of sensitivity of other semiconductor temperature sensors, the temperature coefficient of resistivity TCR is usually used. TCR is basically a crude average of α over the specified temperature range (i.e. T_{ref} T) and defined as¹²¹

$$TCR = \frac{1}{\rho(T_{ref})} \frac{\rho(T) - \rho(T_{ref})}{(T - T_{ref})}, \qquad ...(7.2)$$

where $\rho(T_{ref})$ is the measured resistivity at a reference temperature, usually taken as the lowest temperature in the operating temperature range of the sensor. $\rho(T)$ is the measured resistivity at the highest temperature T in that range.

Table 7.2 shows TCR for some polycrystalline 3C-SiC films over the entire temperature range. The sensitivity of sample 152B is one order of magnitude smaller than that of 193A and 160A as shown in Table 7.2. Samples 152B and 193A have comparable carrier concentrations in the entire temperature range, comparable thicknesses (Table 7.3)

and large difference in their sensitivities (one order of magnitude). For sample 193A, evaluating TCR over a narrower temperature range of 13-774 K leads to higher TCR values since the sensitivity of polycrystalline β -SiC films decreases with temperature.

Since TCR exhibits a change of sign with temperature for α -SiC samples, it is necessary to evaluate TCR in this case over a temperature range where sensitivity has no sign change. Taking this range to be the high temperature range (i.e. above room temperature) provides a possibility for us to compare our results with the published data which is only available in this temperature range. Table 7.3 shows TCR for the polycrystalline and single crystalline 3C-SiC, heteroepitaxial 4H- and 6H-SiC, and Si with the corresponding temperature range and carrier concentration.

Table 7.2. Temperature coefficients of resistivity (TCR) of some polycrystalline 3C-SiC samples evaluated over the corresponding temperature range.

Sample	TCR (%/K)	Temperature (K)	
1 52B (poly. β-SiC)	0.069	13-1277	
160A (poly. β-SiC)	0.111	295-1016	
193A (poly. β-SiC)	0.130	13-774	

Table 7.3 shows that above room temperature the sensitivity of our polycrystalline 3C-SiC films is comparable (160A) or one order of magnitude less (152B and 193A) than that of Si. This difference in sensitivity might be due to an approximately three orders of

Table 7.3. Temperature coefficients of resistivity (TCR) of some polycrystalline and single crystalline 3C-SiC films and heteroepitaxial 6H- and 4H-SiC samples evaluated over the corresponding temperature range. Thicknesses and available carrier concentrations obtained at room temperatures are also provided.

Sample	TCR (%/K)	Thickness (Å)	Concentration (cm ⁻³)	Range (K)
152B (poly. β-SiC)	0.049	3500	10 ²⁰	295-1277
160A (poly. β-SiC)	0.111	1200		295-1016
193A (poly. β-SiC)	0.092	3000	10 ²⁰	293-774
H (6H-SiC)	0.202	1121×10 ⁴	5×10 ¹⁶	294-757
B (6H-SiC)	0.084	845.82×10 ⁴	6.8×10 ¹⁸	498-738
E (4H-SiC)	0.227	568.96×10⁴	3.2×10 ¹⁷	314-735
3C-SiC*	0.091	105	»10 ¹⁷	623-823
Si* substrate	0.72		10 ¹⁷	300-923

*[121]

magnitude variation in the carrier concentrations. These polycrystalline films have comparable (152B and 193A) or larger (160A) sensitivities than the single crystalline 3C-SiC as shown in Table 7.3. In addition, they have a major advantage over Si and single crystalline 3C-SiC since they can be used as temperature sensors over a much wider temperature range with an acceptable sensitivity. The hexagonal samples show the same potential but over a smaller temperature range compared to the polycrystalline 3C-SiC films.

7.3 Summary

Polycrystalline 3C-SiC shows a negative temperature coefficient α over the entire temperature range which permits its use for temperature sensing over a wide temperature range (13-1277 K) with a single sensor. α -SiC exhibits a sign change in α in a temperature range of 200-300 K which limits its use to either high or low temperature range. The temperature coefficient of the single crystalline 3C-SiC shows some scattering in a temperature range of 200-600 K which prevents its use as a temperature sensor in that range.

CHAPTER 8

SUMMARY AND FUTURE RESEARCH

The objective of this research was to provide an understanding of the transport properties of SiC films deposited by Pulsed Laser Deposition technique and to study the potential of these films for temperature and heat flux sensors.

Conductivity and Hall measurements were conducted in a temperature range of 13-800K. In case of polycrystalline 3C-SiC films deposited on insulating substrates, Hall mobilities, carrier concentrations, and activation energies were obtained from these experimental measurements using a phenomenological model. Furthermore, the low transport data for polycrystalline 3C-SiC films were analyzed in terms of impurity/defect band and hopping models were used for the first time. In case of heteroepitaxial 3C-SiC films deposited on Si substrates, conductivity and Hall voltage models were used to extract the conductivity and Hall voltage of 3C-SiC films from measurements on the 3C-SiC/Si structure. In addition, data and analysis are also presented in chapter 5 for commercially available 6H- and 4H-SiC substrate wafers.

The Seebeck coefficient was also investigated for polycrystalline 3C-SiC films and

monocrystalline 4H- and 6H-SiC wafers to determine the potential of these SiC polytypes for thermoelectric generators and temperature and heat flux sensors. The measured Seebeck emf of our polycrystalline SiC films is comparable or larger than that of platinum thermocouple and thus has a good potential for temperature sensing as well as surface heat flux sensing. However, polycrystalline SiC films show a weak potential for thermoelectric generation compared to other materials.

8.1 Future Work

The Seebeck coefficient of polycrystalline 3C-SiC and monocrystalline α -SiC was obtained over a limited temperature range and the results showed good potential for temperature and heat flux sensors. Therefore, it would be interesting to measure the Seebeck coefficient of SiC over a wider temperature range including investigation of anisotropy for α -SiC polytypes. In addition, fabricating the proposed heat flux sensor using SiC technology is of interest. Further development of the presented conductivity and Hall coefficient models considering the nonlinearity of the p-n junction is needed to extract accurately the conductivity and Hall data of the β -SiC thin film from the SiC/Si structure. APPENDIX

APPENDIX

Multiple-Layer Resistivity Model

In this model, it is assumed that we have a three-layer rectangular sample with $2\delta_x \times 2\delta_y$ size. The thicknesses and conductivities of the top, intermediate, and bottom layers are t_1 , t_2 , and t_3 , and σ_0 , σ_1 , and σ_2 , respectively. The current I is applied into the top layer through rectangular contacts with $2c \times 2d$ size as shown in Fig.A1.

A two dimensional plots of the imposed field in the y and x directions are shown in Figs.A2 and A3, respectively. A three dimensional plot of the same field is shown in Fig.A4. Fig.A5 shows the potential $\phi(X,Y,Z=0)$ for the applied field of Fig.A4. The amplitude of this potential varies between -0.1 and 0.1 for $\sigma_0 = \sigma_1 = \sigma_2$ and from -0.9 to 0.9 for $\sigma_1 = \sigma_2$ and $(\sigma_1/\sigma_0) = 0.1$, respectively.



Fig.A.1 A top view of the sample used in our model. The two metal contacts are shown in dark color.

The imposed field $E_i(X,Y)$ through the contacts at the top layer can be expressed in terms of Fourier series in two dimensions as $E_i(X,Y)=F(Y)G(X)$. In the Y direction the applied field F(Y) is an even function at both contacts whereas this field in the X direction G(X) is an odd function at both contacts. Fig.A2 and Fig.A3 show Fourier expansion of the imposed field in the Y and X directions, respectively, using 200 terms. The imposed field $E_i(X,Y)$ is shown in Fig.A4.



Fig.A.2 A two dimensional plot of the imposed field in the Y direction at the surface (i.e. Z=0).



Fig.A.3 A two dimensional plot of the imposed field in the X direction at the surface (i.e. Z=0).



Fig.A.4 A three dimensional plot of the imposed field at the surface (i.e. Z=0).



Fig.A.5 A three dimensional plot of the potential at the surface (i.e. Z=0) assuming that the conductivity of the three layers is the same.
Since the space charge is assumed to be zero, Poisson's equation reduces to Laplace's equation:

$$\nabla^2 \mathbf{\Phi} (X, Y, Z) = 0, \qquad \dots (1)$$

where $\phi(X,Y,Z)$ is the potential at any point, $X=x/\delta_x$, $Y=y/\delta_y$, and $Z=z/\delta_x$. Solving this differential equation by separation of variables leads to:

$$\begin{aligned} & \phi_1(X) = a_1 \sin(\kappa X) + b_1 \cos(\kappa X), & \dots (2a) \\ & \phi_2(Y) = a_2 \sin(\lambda Y) + b_2 \cos(\lambda Y), & \dots (2b) \\ & \phi_3(Z) = a_3 \exp(-\gamma Z) + b_3 \cos(\gamma Z), & \dots (2c) \end{aligned}$$

where κ, λ , and γ are constants with $\gamma^2 = \kappa^2 + \lambda^2$. Since the current is applied through one contact and comes out of the other one, $\phi_1(X)$ and $\phi_2(Y)$ are odd and even functions of X and Y, respectively, leading to $b_1 = a_2 = 0$. Imposing zero current at the boundaries of the sample (i.e. $\nabla_X \phi_1(\pm 2\delta_x) = 0$ and $\nabla_Y \phi_2(\pm 2\delta_y) = 0$) leads to:

$$\kappa = (2m+1) \frac{\pi}{2} \frac{1}{\delta_{x}}, \qquad \dots (3a)$$

$$\lambda = n \frac{\pi}{2} \frac{1}{\delta_{y}}, \qquad \dots (3b)$$

$$\gamma^{2} = \left[\frac{(2m+1)^{2}}{(2\delta_{x})^{2}} + \frac{n^{2}}{\delta_{y}^{2}}\right] \pi^{2}, \qquad \dots (3c)$$

where m and n are integers ≥ 0 . The general solution of Laplace's equation can be written as:

$$\Phi(X, Y, Z) = \sum_{m} \sum_{n} F_{m, n} \sin[(2m+1)\frac{\pi}{2}X] \cos(n\pi Y), \qquad \dots (4)$$

where

$$F_{m,n} - \phi_{m,n}^{+}(1) \exp(\gamma Z) + \phi_{m,n}^{-}(1) \exp(-\gamma Z), \qquad \dots (5)$$

where I is the layer number and ϕ^+ and ϕ^- are constants that have to be determined in each layer of the sample using the boundary conditions.

The electric field $E_z = \nabla_z \phi$ is:

$$E_{z}(X, Y, Z) = \sum_{m} \sum_{n} H_{m,n} \sin[(2m+1)\frac{\pi}{2}X] \cos(n\pi Y), \qquad \dots (6)$$

where

$$H_{m,n} = \frac{\gamma}{\delta_x} \left[\phi_{m,n}^+(1) \exp(\gamma Z) - \phi_{m,n}^-(1) \exp(-\gamma Z) \right], \qquad \dots (7)$$

The imposed field at the top layer $E_i(X,Y,Z=0)$ can be expressed in terms of Fourier series as follows:

$$E_{i}(X, Y, Z=0) = D \sum_{m} A_{m} \sin \left[(2m+1) \frac{\pi}{2} X \right] + \sum_{m \ge 0} \sum_{n \ge 0} A_{m} B_{n} \sin \left[(2m+1) \frac{\pi}{2} X \right] \cos (n\pi Y) \dots (8)$$

where

$$A_{m} = \frac{4 \sin \left[(2m+1) \frac{\pi}{2} X_{0} \right] \sin \left[(2m+1) \frac{\pi}{2} C \right]}{(2m+1) \frac{\pi}{2}}, \dots (9a)$$
$$B_{n} = \frac{2 \sin (n\pi D)}{n\pi}, \dots (9b)$$

where $X_0 = x_0/\delta_x$, $C = c/\delta_x$, and $D = d/\delta_y$. For simplicity, it is assumed that the thickness of the third layer of the sample is very large compared with these of the first two layers resulting in $\phi^+(2)=0$. This leaves us with 5 unknowns (i.e. $\phi^+(0)$, $\phi^-(0)$, $\phi^+(1)$, $\phi^-(1)$, and $\phi^-(2)$) to be determined by the boundary conditions. The 5 boundary conditions are:

Jacob Street

- at z=0, the imposed field $E_i(X,Y,Z=0)$ is equal to $E_z(X,Y,Z=0)$.
- at $z=d_1$, the tangent field is continuous.
- at $z=d_2$, the tangent field is continuous.
- at $z=d_1$, the perpendicular current is continuous.
- at $z=d_2$, the perpendicular current is continuous.

Applying these boundary conditions lead to the following set of equations:

$$\frac{\gamma}{\delta_{x}} [\phi_{m,n}^{+}(0) - \phi_{m,n}^{-}(0)] = A_{m} B_{n}, \quad \dots \quad (10a)$$

$$\begin{bmatrix} \phi_{m,n}^{+}(0) \exp(\gamma T_{1}) + \phi_{m,n}^{-}(0) \exp(-\gamma T_{1}) \end{bmatrix} = \\ \begin{bmatrix} \phi_{m,n}^{+}(1) \exp(\gamma T_{1}) + \phi_{m,n}^{-}(1) \exp(-\gamma T_{1}) \end{bmatrix}, \dots (10b)$$

$$\begin{bmatrix} \phi_{m,n}^{*}(1) \exp(\gamma T_{2}) + \phi_{m,n}^{-}(1) \exp(-\gamma T_{2}) \end{bmatrix} = \begin{bmatrix} \phi_{m,n}^{-}(2) \exp(-\gamma T_{2}) \end{bmatrix}, \dots (10c)$$

$$\sigma_{0} [\phi_{m,n}^{+}(0) \exp(\gamma T_{1}) - \phi_{m,n}^{-}(0) \exp(-\gamma T_{1})] = \sigma_{1} [\phi_{m,n}^{+}(1) \exp(\gamma T_{1}) - \phi_{m,n}^{-}(1) \exp(-\gamma T_{1})], \dots (10d)$$

$$\sigma_{1} [\phi_{m,n}^{+}(1) \exp(\gamma T_{2}) - \phi_{m,n}^{-}(1) \exp(-\gamma T_{2})] = [-\sigma_{2} \phi_{m,n}^{-}(2) \exp(-\gamma T_{2})], \quad \dots (10e)$$

where $T_1 = t_1/\delta_x$ and $T_2 = t_2/\delta_x$. Solving the above 5 equations leads to:

$$\phi^+(0) = \phi^-(2) K^+ \exp(-2\gamma T_1), \dots (11a)$$

$$\phi^{-}(0) = \phi^{-}(2) K^{-}, \ldots (11b)$$

$$\phi^+(1) = \frac{1}{2}\phi^-(2) (1 - \frac{\sigma_2}{\sigma_1}) \exp(-2\gamma T_2), \dots (11C)$$

$$\phi^{-}(1) = \frac{1}{2}\phi^{-}(2)(1 + \frac{\sigma_{2}}{\sigma_{1}}), \dots (11d)$$

$$\phi^{-}(2) = \frac{(A_m B_n) \frac{\delta_x}{\gamma}}{K^* \exp(-2\gamma T_1) - K^-}, \quad \dots (11e)$$

where

$$K^{+} = \frac{1}{4} \left[\left(1 + \frac{\sigma_1}{\sigma_0} \right) \left(1 - \frac{\sigma_2}{\sigma_1} \right) \exp \left(2\gamma \left(T_1 - T_2 \right) \right) + \left(1 - \frac{\sigma_1}{\sigma_0} \right) \left(1 + \frac{\sigma_2}{\sigma_1} \right) \right], \quad \dots \quad (12a)$$

27

$$K^{-} = \frac{1}{4} \left[\left(1 - \frac{\sigma_1}{\sigma_0} \right) \left(1 - \frac{\sigma_2}{\sigma_1} \right) \exp \left(2\gamma \left(T_1 - T_2 \right) \right) + \left(1 + \frac{\sigma_1}{\sigma_0} \right) \left(1 + \frac{\sigma_2}{\sigma_1} \right) \right], \quad \dots \quad (12b)$$

The solution of Laplace's equation is now complete. The thickness correction factor is given by:

$$C.F. = \frac{cd}{\phi(-\delta_x, \delta_y, 0) - \phi(\delta_x, \delta_y, 0)}, \quad \dots \quad (13)$$

where 2cd is half the area of the contact that supplies current into the whole sample. Since the current density $\sigma E_y(X,0,Z)=0$, the total applied current splits in half between the upper (i.e. $y\geq 0$) and the lower (i.e. y<0) portions of the sample. Thus our rectangular sample can be considered as being composed of two square and separate samples.

This allows the calculation of current distribution in the three layers. Since the intermediate layer is highly resistive, the current I_1 will be very small and negligible compared to I_0 and I_2 . Therefore, the current ratio $\lambda = I_2/I_1$ can be calculated using this model.

BIBLIOGRAPHY

BIBLIOGRAPHY

(1) T.P. Chow and Ritu Tyagi, "Wide Bandgap Compound Semiconductors for superior High-Voltage Power Devices", in the 5th International Symposium on Power Semiconductor Devices and IC's, page 84, 1993.

(2) G. Muller and G. Krotz, "SiC as a new sensor material", in The 7th International Conference on Solid-State Sensors and Actuators, Yokohama, Japan, p. 948, 1993.

(3) E.O. Jhonson, RCA Rev. 26(163), 1965.

(4) R.W. Keyes, Proc. IEEE 60(225), 1972.

(5) J.A. Powell and L.G. Matus, "Recent Development in SiC (USA)", in Amorphous and Crystalline Silicon Carbide and Related Materials, Springer Proceedings in Physics Vol. 34, edited by G.L. Harris and C. Y.-W. Yang (Springer, Berlin, 1988), p. 2.

(6) Z. Li and R.C. Bradt, J. Amer. Cer. Soc., 70(445), 1987.

(7) R. Helbig, "Progress in New Materials for Power Electronics: SiC", in the 5th International Symposium on Power Semiconductor Devices and IC's, page 6, 1993.

(8) L.G. Matus and J.A. Powell, "Crystal Growth of SiC for Electronic Applications", Ceramic Transactions Volume 2, ed. by J.D. Cawley and C.E. Semler; Proceedings of the Silicon Carbide 1987 Symposium (The American Ceramic Society, Inc., 1989).

(9) R.F. Davis, G. Kelner, M. Shur, W. Palmour, and J.A. Edmond, "Thin film deposition and microelectronic and optoelectronic device fabrication and characterization in monocrystalline alpha and beta silicon carbide", Proceedings of the IEEE, 79(677), 1991.

(10) R.F. Davis and J.T. Glass, in Advances in Solid-State Chemistry, 2(1), (JAI Press Ltd., 1991).

(11) J.A. Powell, P.G. Neudeck, L.G. Matus, and J.B. Petit, "Progress in silicon carbide semiconductor Technology", Mat. Res. Soc. Symp. Proc. 242(495), 1992.

(12) M. Balooch, R.J. Tench, W.J. Sielhaus, M.J. Allen, A.L. Connor, and D.R. Olander, "Deposition of SiC films by pulsed excimer laser ablation", Appl. Phys. Lett. 57 (1540), 1990.

(13) R.J. Tench, M. Balooch, A.L. Connor, L. Bernardez, B. Olson, M.J. Allen, W.J. Siekhaus, and D.R. Olander, in Laser Ablation for Materials Synthesis, edited by D.C. Paine and J.C. Bravman, Mater. Res. Soc. Symp. Proc. Vol. 191 (Materials Research Society, Pittsburgh, PA, 1990), p. 61.

(14) L. Rimai, R. Ager, E.M. Logothesis, W.H. Weber, and J. Hangas, "Preparation of oriented silicon carbide films by laser ablation of ceramic silicon carbide targets", Appl. Phys. Lett. 59 (2266), 1991.

(15) L. Rimai, R. Ager, E.M. Logothesis, W.H. Weber, and J. Hangas, "Characteriztion of Silicon Carbide Thin Films Deposited By Laser Ablation on [001] and [111] Silicon Wafers", in Wide Band Gap Semiconductors, edited by T.D. Moustakas, J.I. Pankove, and Y. Hamakawa, Mater. Res. Soc. Symp. Proc. Vol. 242 (Materials Research Society, 1992), p.549.

(16) H. Matsunami, "Silicon Carbide Films", 1985.

(17) W.F. Knippenberg, "Growth Phenomena In Silicon Carbide", Philips Res. Repts, 18(161), 1963.

(18) R.C. Marshall, J.W. Faust, Jr., and C.E. Ryan, Eds., Silicon Carbide, Proc. Int. Conf., 3rd, 1973, University of South Carolina Press, Columbia, South Cardina, 1974.

(19) Yu.M. Tairov and V.F. Tsvetkov, "Investigation of growth progress of ingots of silicon carbide single crystals", J. Cryst. growth, 43(209), 1978.

(20) Yu.M. Tairov and V.F. Tsvetkov, "General principles of growing large-size single crystals of various silicon carbide polytypes", J. Cryst. growth, 52(146), 1981.

(21) G. Ziegler, P. Lanig, D. Theis, and C. Weyrich, "Single Crystal Growth of SiC Substrates Material for blue light emitting diodes", IEEE Trans. Electron Devices, ED-30(277), 1983.

(22) C.H. Carter, Jr., L. Tang, and R.F. Davis, "Growth of single crystal boules of $\alpha(6H)$ -SiC", presented at the Fourth National Review Meeting on the Growth and Characterization of SiC, Raleigh, NC, 1987.

(23) R.A. Stein, P. Lanig, and S. Leibenzeder, "Influence of surface energy on the growth of 6H- and 4H-SiC polytypes by sublimation", Mat. Sci. Engin., B11(69), 1992.

(24) V. Shields, M. Spencer, and K. Wongchotigul, "A Process for the Growth of Monocrystalline Beta-SiC Substrates", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(25) Jin-Wei Yang, Shigehiro Nishino, Mehran Mehregany, and Pirouz Pirouz, "Crystal Growth of Cubic SiC by the Sublimation Technique", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(26) S.R. Nutt, D.J. Smith, H.J. Kim, and R.F. Davis: Appl. Phys. Lett., 50(203), 1987.

(27) P. Pirouz, C.M. Chorey, and J.A. Powell: Appl. Phys. Lett., 50(221), 1987.

(28) J. Ryu, H.J. Kim, and R.F. Davis, Appl. Phys. Lett., 47(850), 1985.

(29) B. Segall, S.A. Alterovitz, E.J. Haugland, and L.G. Matus, "Compensation in epitaxial cubic SiC films", Appl. Phys. Lett., 49(584), 1987.

(30) M. Yamanaka, H. Daimon, E. Sakuma, S. Misawa, and S. Yoshida, "Temperature dependence of electrical prperties of n- and p-type 3C-SiC ", J. Appl. Phys., 61(599), 1987.

(31) J.D. Parsons, in Proc. Mats. Res. Soc. Symp., 97(271), 1987.

(32) S. Nishino, Y. Hazuki, H. Matsunami and T. Tanaka, "Chemical vapor deposition of single crystalline β -SiC films on silicon substrates with sputtered SiC intermediate layer", J. Electrochem. Soc., 127(2674), 1980.

(33) S. Nishino, J.A. Powell, and H.A. Will, "Production of large-area single-crystal wafers of cubic SiC for semiconductor devices", Appl. Phys. Lett., 42(460), 1983.

(34) G.L. Harris and C. Y-W Yang, Eds., Amorphous and Crystalline Silicon Carbide, Springer Proc. Physics, vol. 34. NY: Springer Verlag, 1988.

(35) T. Aselage, E. Emin, and C. Woods, Eds., "Novel refractory semiconductors", in Mater. Res. Soc. Symp. Proc. vol. 97. Pittsburgh, PA: Materials Research Society, 1987.

(36) R.F. Freer, Ed., The Physics and Chemistry of Carbides, Nitrides, and Borides, NATO ASI Series E: Applied Sciences, vol. 185. Dordrecht, The Netherlands: Kluwer Academic, 1990.

(37) J.T. Glass, R.F. Messier and N. Fujimori, Eds., Diamond, Boron Nitride, Silicon Carbide, and Related Wide Bandgap Semiconductors, Mater. Res. Soc. Symp. Proc., vol. 162. Pittsburgh, PA: Materials Research Society, 1990.

(38) I. Golecki, F. Reidinger and J. Marti, Appl. Phys. Lett., 60(1703), 1992.

(39) T. Fuyuki, M. Nakayama, T. Yoshinobu, H. Shiomi, and H. Matsunami, "Atomic layer epitaxy of cubic SiC by gas source MBE using surface superstructure", J. Cryst. Growth, 95(461), 1989.

(40) T. Sugii, T. Aoyama, and T. Ito, "Low-temperature growth of β -SiC on Si by gassource MBE", J. Electrochem. Soc., 137(989), 1990.

(41) H. Nakamatsu and S. Kawai, "Epitaxy of SiC films on sapphire by laser CVD", in Novel Refractory Semiconductors, vol. 97, Mater. Res. Soc. Symp. Proc., T. Aselage, E. Emin, and C. Woods, Eds. Pittsburgh, PA: Materials Research Society, 1987, pp.189-194.

(42) H. Nakamatsu, Ki. Hirata, and S. Kawai, "Synthesis of epitaxial silicon carbide films by laser CVD", in Laser Particle-beam Chemical Processing for Microelectronics, vol. 101, Mater. Res. Soc. Symp. Proc., D.J. Ehrlich and G.S. Higashi, Eds. Pittsburgh, PA: Materials Research Society, 1988, pp. 397-402.

(43) A. Chayahara, A. Masuda, T. Imura and Y. Osaka, "Formation of polycrystalline SiC in ECR Plasma", Japan. J. Appl. Phys., 25(L564),1986.

(44) K. Kamimura, Y. Nishibe, and Y. Onuma, "SiC/Si HBT Using Polycrystalline SiC Layers Prepared by Electron Beam Evaporation", in Amorphous and Crystalline Silicon Carbide II Recent Development, Springer Proceedings in Physics Vol. 43, edited by M.M. Rahman, C. Y.-W. Yang, and G.L. Harris (Springer, Berlin, 1989), p. 207.

(45) Y. Onuma, S. Miyashita, Y. Nishibe, K. Kamimura, and K. Tezuka, "Thin Film Transistors Using Polycrystalline SiC", in Amorphous and Crystalline Silicon Carbide II Recent Development, Springer Proceedings in Physics Vol. 43, edited by M.M. Rahman, C. Y.-W. Yang, and G.L. Harris (Springer, Berlin, 1989), p. 212.

(46) E.A. Fagen, in Silicon Carbide 1973, edited by R.C. Marshall, J.W. Faust, Jr., and C.E. Ryan (University of South Carolina Press, Columbia, SC, 1973), p. 542.

(47) H.S. Kong, J.T. Glass, and R.F. Davis, "Epitaxial growth of beta-SiC thin films on 6H alpha-SiC substrates via chemical vapor deposition", Appl. Phys. Lett., 49(1074), 1986.

(48) H.S. Kong, J.T. Glass, and R.F. Davis, "Growth rate, surface morphology and defect microstructures of β -SiC films grown on 6H-SiC substrates via chemical vapor deposition", J. Mater. Res., 4(204), 1989.

(49) H.S. Kong, B.L. Jiang, J.T. Glass, G.A. Rozgonyi and K.L. Moore, "An examination of double positioning boundaries and interface misfit in beta-SiC films on alpha-SiC substrates", J. Appl. Phys., 63(2645), 1988.

(50) J.A. Powell, D.J. Larkin, L.G. Matus, W.J. Choyke, J.L. Bradshaw, L. Henderson, M. Yoganathan, J. Yan, and P. Pirouz, "Growth of improved quality 3C-SiC films on 6H-SiC substrates", Appl. Phys. Lett., 56(1353), 1990.

(51) H.S. Kong, J.T. Glass, and R.F. Davis, "Chemical vapor deposition and characterization of 6H-SiC thin films on off-axis 6H-SiC substrates", J. Appl. Phys., 64(2672), 1988.

(52) Shibahara, N. Kuroda, S. Nishino, and H. Matsunami, "Fabrication of p-n junction diodes using homoepitaxially grown 6H-SiC at low temperature by chemical vapor deposition", Japan. J. Appl. Phys., 26(L1815), 1987.

(53) N. Kuroda, K. Shibahara, W. Yoo, S. Nishino, and H. Matsunami, "Growth of SiC films on off-axis $\alpha(6H)$ -SiC", Extended abstract of the 19th Conf. Solid State Devices and Materials, Tokyo, Japan, p. 227, 1989.

(54) J.A. Powell, D.J. Larkin, L.G. Matus, W.J. Choyke, J.L. Bradshaw, L. Henderson, M. Yoganathan, J. Yan, and P. Pirouz, "Growth of high quality 6H-SiC epitaxial films on vicinal (0001) 6H-SiC wafers", Appl. Phys. Lett., 56(1442), 1990.

(55) S. Karmann, W. Suttrop, A. Schöner, M. Schadt, C. Habersroh, F. Engelbrecht, R.A. Stein, and S. Leibenzeder, "Chemical vapor deposition and characterization of undoped and nitrogen-doped single crystalline 6H-SiC", J. Appl. Phys., 72(5437), 1992.

(56) W.E. Carlos, W.J. Moore, P.G. Siebenmann, J.A. Freitas, Jr., R. Kaplan, S.G. Bishop, P.E.R. Nordquist, Jr., M. Kong, and R.F. Davis, "Residual Donors in β -SiC Films", Novel Refractory Semiconductors, (Pittsburgh:Mat. Res. Soc.) Symp. Proc., edited by David Emin, T.L. Aselage, and Charles Wood, Vol. 97(253), 1987.

(57) A. Suzuki, A. Uemoto, M. Shigeta, K. Furukawa, and S. Nakajima, "Temperature Dependence of Electrical Properties of Non-doped and Nitrogen-doped beta-SiC Single Crystals Grown by Chemical Vapor Deposition", Appl. Phys. Lett. 49(450), 1986.

(58) C. Jacob, S. Nishino, M. Mehregany and P. Pirouz, "Effects of annealing and metal work function on contacts to 3C-SiC, in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(59) S.Y. Wu and R.B. Campbell, "Au-SiC Shottky Barrier Diodes", Solid-State Electronics, 17 (683), 1974.

(60) S. Yoshida, K. Sasaki, E. Sakuma, S. Misawa, and S. Gonda, "Schottky barrier diodes on 3C-SiC", Appl. Phys. Lett., 46 (766), 1985.

(61) K.M. Geib, C. Wilson, R.G. Long, and C.W. Wilmsen, "Reaction between SiC and W, Mo, and Ta at elevated Temperatures", J. Appl. Phys., 68 (2796), 1990.

(62) V.M. Bermudez and R. Kaplan, "Investigation of the structure and stability of the Pt/SiC(001) interface", J. Mater. Res., 5 (2882), 1990.

(63) J.A. Edmond, J. Ryu, J.T. Glass, and R.F. Davis, "Electrical Contacts to Beta Silicon Carbide Thin Films", J. Electrochem. Soc., 135 (359), 1988.

(64) J.S. Shor, R.A. Weber, L.G. Provost, D. Goldstein and A.D. Kurtz, "High Temperature Ohmic Contacts for n-type β -SiC Sensors", Mat. Res. Soc. Symp. Proc., 22 (573), 1992.

(65) A.J. Steckl, J.N. Su, P.H. Yih, C. Yuan, and J.P. Li, "Ohmic and Rectifying Contacts to SiC Using All-Ni Technology", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(66) Ho Jin Cho, Cheol Sung Hwang, Wook Bang, and Hyeong Joon Kim, "Effect of Reaction Products in Monocrystalline β -SiC/metal Contact on Contact Resistivity, in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(67) J.B. Petit, P.G. Neudeck, C.S. Salupo, D.J. Larkin, and J.A. Powell, "Electrical Characteristics and High Temperature Stability of Contacts to N- and P-Type 6H-SiC", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(68) J.Crofton, J.R. Williams, M.J. Bozack, and P.A. Barnes, "A High Temperature Ohmic Contact to n-type 6H-SiC", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(69) P.A. Ivanov, V.N. Panteleev, T.P. Samsonova, A.V. Suvorov, and V.E. Chelnokov, "Refractory Metal Silicides/n-6H-Silicon Carbide Ohmic Contacts", in Proceedings of International Conference on Silicon Carbide and Related Materials, Washington, Nov. 1993.

(70) J.W. Faust, Jr., Y. Tung and H.M. Liaw, "A Study of Etch Pits on Pure Polytypes of SiC", in Silicon Carbide 1973, edited by R.C. Marshall, J.W. Faust, Jr., and C.E. Ryan, (University of South Carolina Press, Columbia, SC, 1973), p. 215.

(71) M. Yoshikawa, G. Katagiri, H. Ishida and A. Ishitani, "Resonant Raman Scattering of Diamond-like Amorphous Carbon Films", Appl. Phys. Lett., 52(19), 1988.

(72) Z.C. Feng, A.J. Mascarenhas, W.J. Choyke, and J.A. Powell, J. Appl. Phys., 64(3176), 1988.

(73) F. Tuinstra and J.L. Koenig, J. Chem. Phys., 53(1126), 1970.

(74) D.S. Knight and W.B. White, J. Mater. Res., 4(385), 1989.

(75) W.J. Choyke and Lyle Patrick, "Review of Optical Work in SiC since 1968", in Silicon Carbide 1973, edited by R.C. Marshall, J.W. Faust, Jr., and C.E. Ryan, (University of South Carolina Press, Columbia, SC, 1973), p. 261.

(76) S. Furukawa, "Present and Future Applications of Amorphous Silicon Carbide", Springer Proceedings in Physics, 34(58), 1989.

(77) J.S. Shor, D. Goldstein, and A.D. Kurtz, "Evaluation of β -SiC for Sensors", IEEE, (912), 1991.

(78) Y. Kuwano and S. Tsuda, "Amorphous Silicon Solar Cells Using a-SiC Materials", Springer Proceedings in Physics, 34(167), 1989.

(79) C.-J. Chu, G.D. Soraru, F. Babonneau, and J.D. Mackenzie, "Preparation and Characterization of Amorphous SiC Film by a Liquid Route", Springer Proceedings in Physics, 43(66), 1989.

(80) Y. Onuma, F. Nagaune, and K. Kamimura, "Preparation and properties of polycrystalline Silicon carbide films produced by plasma enhanced chemical vapor deposition, and their applications", Springer Proceedings in Physics, 34 (142), 989.

(81) K. Kamimura, Y. Nishibe, and Y. Onuma, "SiC/Si HBT Using Polycrystalline SiC Layers Prepared by Electron Beam Evaporation", Springer Proceedings in Physics, 43 (207), 1989.

(82) Y. Onuma, K. Kamimura, Y. Nagura, K. Koike, and S. Yonekubo, "Polycrystalline Silicon-Silicon Carbide Thin Films Produced by Plasma Enhanced CVD", Amorphous and Crystalline Silicon Carbide III, ed. by G.L. Harris, M.G. Spencer, And C.Y.-W. Yang; Springer Proceedings in Physics 56 (Springer-Verlag, Berlin, Heidelberg (1990) p.69.

(83) S. Hasegawa, N. Furuta, T. Takeshita, T. Inokuma, and Y. Kurata, "Phosphorus and nitrogen doping into polycrystalline SiC films prepared by plasma-enhanced chemical vapor deposition at 700 C", J. Appl. Phys. 72(4), 1992.

(84) W.E. Nelson, F.A. Halden and A. Rosengreen, "Growth properties of β -SiC Single Crystals", J. Appl. Phys. 37 (333), 1966.

(85) D.K. Ferry, "High-field transport in wide-band-gap semiconductors", Phys. Rev. B12 (2361), 1975.

(86) R. Kaplan, R.J. Wagner, H.J. Kim, and R.F. Davis, Solid State Commun. 55(67), 1985.

(87) B. Molnar and G. Kelner, "Some observations on the electrical characterization of the heteroepitaxially grown cubic SiC", Mat. Res. Soc. Symp. Proc. Vol. 162 (481), 1990.

(88) T. Tachibana, H.S. Kong, Y.C. Wang, and R.F. Davis, "Hall Measurements as a Function of Temperature on monocrystalline SiC thin films", J. Appl. Phys. 67(10), pp. 6375-6381, 1990.

(89) K. Wasa, T. Tohda, Y. Kasahara, and S. Hayakawa, "Highly reliable temperature sensor using rf-sputtered SiC thin film", Rev. Sci. Instrum., 50(1084), 1979.

(90) T. Nagi and M. Itoh, "SiC Thin-Film Thermistors", IEEE Trans. Indust. Appl., 26(1139), 1990.

(91) T. Nagi, K. Yamamoto, and I. Kobayashi, "Rapid Response SiC thin-film thermistor", Rev. Sci. Instrum., 55(1163), 1984.

(92) T. Nagi, K. Yamamoto, and I. Kobayashi, "SiC thin-film thermistor", J. Phys. E: Sci. Instrum., 15(520), 1982.

(93) See, for example, the collection of papers in D.C. paine and J.C. Bravman, Eds., Laser Ablation for Materials Synthesis, Mater. Res. Soc. Symposium Proc., vol. 191. Pittsburgh, PA: Materials Research Society, 1990, p.61.

(94) J.P. Gavigan, "Laser ablation deposition of metallic thin films", in Science and Technology of Nanostructured Magnetic Materials, Proceedings of a NATO Advanced Study Institute, G.C. Hadjipanayis and G.A. Prinz, Eds. NY: Plenum, p. 81-9, 1991.

(95) Y. Rajakarunanayake, Y. Luo, A. Aydinli, N. Lavalle and A. Compaan, Mat. Res. Soc. Symp. Proc. 268, 1992.

(96) J.T. Cheung and H. Sankur, Crit. Rev. Solid State Mater. Sci., 15(63), 1988.

(97) R.K. Singh and J. Narayan, "Pulsed-laser evaporation technique for deposition of thin films: Physics and theoretical model", Phys. Rev., B41(8843), 1990.

(98) Y. Rajakarunanayake, Y. Luo, A. Compaan, and M.A. Tamor, "Time-resolved lightemission spectroscopy and ion current measurements from pulsed-laser-evaporated cadmium plumes", in Laser Ablation in Materials Processing: Fundamentals and Applications, Mater. Res. Soc. Symposium Proc., D.C. paine and J.C. Bravman, Eds., Pittsburgh, PA: Materials Research Society, vol. 285(93), 1990.

(99) O. Auciello, J. Emerick, J. Duarte, and A. Illingworth, "New rotating target holder for laser ablation and ion beam sputter deposition of multicomponent and multilayered thin films", J. Vac. Sc. Tech., A11(267), 1993.

(100) K.A. Snail and C.M. Marks, Appl. Phys. Lett. 60(3135), 1992.

(101) L.J. van der Pauw, Philips Res. Repts., 13(1), 1961.

(102) R.D. Barnard, Thermoelectricity in Metals and Alloys, John Wiley & Sons, pp. 37-39, 1972.

(103) N. Abu-Ageel, M. Aslam, R. Ager and L. Rimai, "Electrical characterization of polycrystalline SiC thin films deposited on fused silica substrates by laser ablation", in Silicon Carbide and Related Materials, Institute of Physics Conference Series, vol. 137, M.G. Spencer, R.P. Devaty, J.A. Edmond, M. Asif Khan, R. Kaplan and M. Rahman, Eds. Washington, DC, 1993, pp.137-140.

(104) L.G. Matus and J.A. Powell, "Growth of β -SiC Heteroepitaxial Films on Vicinal (001) Si substrates", in Amorphous and Crystalline Silicon Carbide and Related Materials, Springer Proc. Physics, G.L. Harris and C. Y.-W. Yang, Eds. Springer Berlin, 1988, pp. 40-44.

(105) J.A. Powell, D.J. Larkin, L.G. Matus, W.J. Choyke, J.L. Bradshaw, L. Henderson, M. Yoganathan, J. Yang, and P. Pirouz, "Growth of high quality 6H-SiC epitaxial films on vicinal (0001) 6H-SiC wafers", Appl. Phys. Lett., vol. 56, pp.1442-1444, 1990.

(106) L. Rimai, R. Ager, J. Hangas, E.M. Logothetis, N. Abu-Ageel, and M. Aslam, "Pulsed laser deposition of SiC films on fused silica and sapphire substrates", J. Appl. Phys., vol. 73, pp. 8242-8249, 1993.

(107) W. Shockley, Electrons and Holes in Semiconductors, Princeton: Van Nostrand, pp. 258-64, 1950.

(108) J.S. Blakemore, Semiconductor Statistics, New York: Pergamon, pp. 120-30, 1962.

(109) M. Bhatnagar and B.J. Baliga, "Comparison of 6H-SiC, 3C-SiC, and Si for Power Devices", IEEE Transactions on Electron Devices, vol. 40, pp. 645-655, 1993.

(110) B.J. Baliga, "Power Semiconductor Devices Figure of Merit for High-Frequency Applications", IEEE Electron Device Letters, vol. 10, pp. 455-457, 1989.

(111) R.J. Trew, J.B. Yan and P.M. Mock, "The Potential of Diamond and SiC Electronic Devices for Microwave and Millimeter-Wave Power Applications", Proceedings of the IEEE, vol. 79, pp. 598-620, 1991.

(112) I. Nashiyama, H. Okumura, E. Sakuma, S. Misawa, K. Endo and S. Yoshida, "Residual Carriers and ESR Centers in Epitaxially Grown 3C-SiC", in Amorphous and Crystalline SiC III, G.L. Harris, M.G. Spencer and C. Y.-W. Yang, Eds. Springer Berlin, 1992, pp. 149-154.

(113) W.J. Moore, "Transport Measurements and Shallow Donors in Cubic SiC", in Amorphous and Crystalline Silicon Carbide III, G.L. Harris, M.G. Spencer and C. Y.-W. Yang, Eds. Springer, Berlin, 1990, pp. 155-160.

(114) J.A. Freitas, W.E. Carlos, and S.G. Bishop, "Spectroscopic Studies of Donors in 3C-SiC Films", in Amorphous and Crystalline SiC III, G.L. Harris, M.G. Spencer and C. Y.-W. Yang, Eds. Springer, Berlin, 1992, pp. 135-142.

(115) H. Böttger and V.V. Bryskin, Hopping Conduction in Solids, Verlag Berlin, pp. 11-17, 1985.

(116) R.A. Smith, Semiconductors, Cambridge: University Press, pp. 100-108 and pp. 145-153, 1968.

(117) W. Götz, A. Schöner, G. Pensl, W. Suttrop, W.J. Choyke, R. Stein and S. Leibenzeder, "Nitrogen donors in 4H-silicon carbide", J. Appl. Phys., vol. 73, pp. 3332-3338, 1993.

(118) W. Suttrop, G. Pensl, W.J. Choyke, R. Stein and S. Leibenzeder, "Hall effect and infrared absorption measurements on nitrogen donors in 6H-silicon carbide", J. Appl. Phys., vol. 72, pp. 3708-3713, 1992.

(119) N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press: Oxford, 1971.

(120) A. Masood, "Technology and electronic properties of diamond film microsensors for thermal signals", Ph.D. Dissertation, Michigan State University, 1992.

(121) V.A. Johnson and K. Lark-Horovitz, "Theory of Thermoelectric Power in Semiconductors with Applications to Germanium", Physical Review, Vol. 92, No. 2, pp.226-232, 1953.

(122) S.M. Sze, Physics of Semiconductor Devices, Wiley-Interscience Publication, pp. 16-18 and pp. 41-42, 1981.

(123) V.A. Sandborn, Resistance Temperature Transducers, Metrology Press, pp. 1-37, 1972.

(124) P.A. Kinzie, Thermocouple Temperature Measurement, Wiley-Interscience Publication, pp. 20-21, 1973.

(125) J. Tauc, Photo and Thermoelectric Effects in Semiconductors, Pergamon Press, pp. 164-170, 1962.

(126) H. Werheit, "Boron-rich solids: a chance for high-efficiency high-temperature thermoelectric energy conversion", Materials Science and Engineering B, Vol. 29, pp. 228-232, 1995.

(127) R.R. Heikes and R.W. Ure, Jr., Thermoelectricity: Science and Engineering, Interscience Publishers, pp. 339-341, 1961.

(128) D.S. Campbell, M. Gundappa, and T.E. Diller, "Design and Calibration of a Local Heat-Flux Measurement System for Unsteady Flows", ASME Journal of Heat Transfer, Vol. 111, pp. 552-557, 1989.

(129) D.E. Beasley and R.A. Figliola, "A Generalized Analysis of a Local Heat Flux Probe ", J. Phys. E.: Sci. Instrum., Vol. 21, pp. 316-321, 1988.

(130) T.E. Diller, and D.P. Telionis, "Time-Resolved Heat Transfer and Skin Friction Measurements in Unsteady Flow", Advances in Fluid Mechanics Measurements, Lecture Notes in Engineering, M. Gad-el-Hak, ed., Springer-Verlag, Berlin, 1989.

(131) B. Molnar and G. Kelner, "Diamond, Boron Nitride, Silicon Carbide and Related Wide Bandgap Semiconductors", Mat. Res. Soc. Symp. Proc., Vol. 162, p. 481, J.T. Glass, R.F. Messier, and N. Fujimori, Eds. Pittsburgh, PA: Materials Research Society, 1990.

(132) D.E. Bahniuk, "The changing face of temperature measurement, Machine Design, pp. 111-114, 1989; W.J. Tompkins and J.G. Webster, "Interfacing Sensors to to the IBM PC", Prentice Hall, Englewood Cliffs, NJ, 1988.

(133) C.E. Woodhouse, "High precision readout of cryogenic temperature sensors in the space shuttle environment", IEEE Trans. Instrum. Meas., IM-39(1), pp. 279-284, 1990.

(134) S.A. Obukhov, B.S. Neganov, Y.F. Kiselov, A.N. Chernikov, V.S. Vekshina, N.I. Pepkik and A.N. Popkov, "Low temperature resistance of p-InSb(Mn)", Cryogenic (UK), Vol. 31(10), pp. 874-877, 1991.

(135) J.M. Hager, S. Onishi, L.W. Langley, and T.E. Diller, "Heat Flux Microsensors", in Heat Transfer Measurements, Analysis and Flow Visualization, Ed. R.K. Shah, ASME, 1989.

(136) J.M. Hager, S. Simmons, D. Smith, S. Onishi, L.W. Langley, and T.E. Diller, "Experimental Performance of a Heat Flux Microsensor", ASME Journal of Engineering for Gas Turbines and Power, Vol. 113, pp. 246-250, 1991.

(137) L. Gurevich, J. Phys., Moscow 9, p. 477, 1945; 10, p.67, p.174, 1946.

(138) D.T. Morelli, J.P. Heremans, C.P. Beetz, Woo Sik Yoo and H. Matsunami, "Phonon-electron scattering in single crystal silicon carbide", Appl. Phys. Lett., Vol. 63, pp. 3143-3145, 1993.

(139) W.J. Schaffer, G.H. Negley, K.G. Irvine and J.W. Palmour, "Conductivity Anisotropy in epitaxial 6H and 4H-SiC", Cree Research, Inc.

(140) A.F. Gibson, "Progress in Semiconductors", John Wiley & Sons, Vol. 1, pp.75-80, 1956.

(141) A.F. Ioffe, Physics of Semiconductors, New York: Academic Press Inc., pp.300-310.

(142) T.H. Geballe and G.W. Hull, "Seebeck Effect in Silicon," Physical Review, vol. 98, pp940-947, 1955.

(143) G.S. Yang, "Technology of CVD Diamond Thermistor and Thin Film Heater," Ph.D. Dissertation, Michigan State University, 1996.

(144) L. Rimai, R. Ager, W.H. Weber, J. Hangas, A. Samman, and W. Zhu, "Deposition of epitaxially oriented films of cubic silicon carbide on silicon by laser ablation: Microstructure of the silicon-silicon carbide interface," J. Appl. Phys., vol. 77, pp. 6601-6608, 1995.

(145) D.R. Hamilton, W.J. Choyke, and L. Patrick, Phys. Rev. Vol. 131, 127, 1963.

(146) A.R. Verma and P. Krishna, Polymorphism and polytypism in Crystals, New York: Wiley, 1966.

