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TITANIUM DIOXIDE NANOPARTICLE ARRAYS FOR PHOTOCATALYSIS

By

Heather Anne Bullen

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ABSTRACT

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Recent scientific interest in TiO_2 photocatalysis has been motivated by observations of size-dependent properties in TiO_2 nanoparticles. As such, correlating the surface morphology with particle size-dependent photoreactivity is important to understanding the photocatalytic behavior of TiO_2 nanomaterials. Currently, particles produced by solution phase methodologies are not amenable to surface characterization. A novel nanosphere lithography (NSL) approach to create supported TiO_2 nanoparticles of varied size and shape is presented in this dissertation. These TiO_2 nanoparticles were systematically characterized as a function of size (386-36 nm) using both microscopic and spectroscopic analytical techniques.

Two distinct TiO_2 nanoparticle arrays were produced by NSL from monolayer and bilayer masks of hexagonally close-packed polystyrene spheres. In addition, a third particle array, derived from cubic close-packed spheres, was observed. The TiO_2 nanoparticle diameter and height were varied independently by simply changing the mask sphere size or deposition time, respectively. Atomic force microscopy (AFM) analysis showed that the morphology of the nanoparticles changed as function of particle diameter, converting from a triangular (386 nm) to a circular profile (36 nm). X-ray photoelectron analysis indicated that the surface composition of Ti^{3+} states increased with

particle size. It was speculated that the morphological changes observed for the smaller nanoparticles were correlated with an increase in Ti-O surface coordination.

Synthesis of suitable conductive substrates other than glass (ones that could epitaxially stabilize a desired crystallinity of TiO_2 nanoparticles) was also investigated. RuO_2 single crystals with 2 mm dimensions were produced using a chemical vapor transport technique. CrO_2 thin films on $\text{TiO}_2(110)$ rutile single crystals were grown using a CVD technique. These films were highly (110) textured, continuous, and exhibited similar ferromagnetic and metallic behavior to bulk CrO_2 powder.

To my Family

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Chapter 1

Introduction

This dissertation presents research on the synthesis and characterization of titanium dioxide, TiO_2 , nanoparticle arrays. These arrays were produced using a nanosphere lithography (NSL) technique and their composition, morphology and reactivity were analyzed using a variety of surface sensitive techniques including atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) with complementary analytical techniques such as powder X-ray diffraction and UV-Vis spectroscopy.

This chapter aims to provide readers with the context of the present work. It begins with an overview of TiO_2 and the scientific significance of this material as a photocatalyst and a nanomaterial. Next, the basic mechanisms of semiconductor photocatalysis are described, followed by a discussion of the role of crystalline form and surface defects in TiO_2 photocatalysis and current synthetic methods used to grow TiO_2 nanoparticles. Finally, the motivation and objectives of the present work are then explained and an outline of this dissertation is presented.

1.1 Overview of the Scientific Interest in Titanium Dioxide

Transition metal oxides exhibit a wide range of physical, chemical and structural properties. One of the most widely studied metal oxides is the wide band gap semiconducting oxide, titanium dioxide (TiO_2). Titanium dioxide first attracted significant attention when, in 1972, Fujishima and Honda discovered that TiO_2 can act as

a catalyst for the photocleavage of water, producing H_2 and O_2 .¹ In the presence of a TiO_2 electrode, they observed that water was dissociated using photons with $\lambda \leq 410$ nm, whereas direct photodissociation of water requires photons with $\lambda \leq 185$ nm. This discovery sparked interest in the photocatalytic activity of TiO_2 and other metal oxide semiconductors as a possible approach to inexpensively convert solar radiation to chemical energy.^{2,3} Subsequent research efforts have focused on understanding the fundamental processes that drive these photoelectrochemical cells and in their application to energy storage applications.⁴⁻⁶

More recently, significant attention has also been placed on utilizing TiO_2 in environmental remediation applications, since it has been discovered that it possesses the ability to oxidatively decompose many organic molecules present as pollutants in the environment including aromatic, halogenated organic, and commercial dye molecules.⁷ The central mechanism involves the photoinduced generation of charge carriers at the surface of a semiconductor followed by interfacial charge transfer reactions with adsorbed molecules. The mechanistic aspects of these reactions have been reviewed^{7,8} but in many cases, the identities of intermediates have not been firmly established. However, it is clear that numerous hazardous organic contaminants can be fully mineralized to CO_2 by TiO_2 photocatalysis. Some examples include pesticides,⁹ herbicides,¹⁰ and explosives.¹¹

This phenomenon has resulted in the development of several commercial applications for TiO_2 . Compared with traditional advanced oxidation processes, the technology of TiO_2 photocatalysis has advantages such as ease of set up, operations at ambient temperatures, no post processes, low consumption of energy, and minimal costs.

For example, pilot programs in water treatment plants have incorporated photochemical reactors with TiO_2 fixed onto solid supports. A fixed bed allows continuous use of the photocatalyst and eliminates post-filtration processes that would be needed if slurries of the material were used. At this time, however, the efficiencies of these reactors are limited due to the decreased surface/volume ratio of the immobilized TiO_2 . As a result, attempts have focused on supporting TiO_2 onto more porous substrates such as layered clays,¹² inorganic fibers,¹³ and zeolites¹⁴ where larger surface areas can be exposed. Photocatalytic oxidation has also been applied to removing and decomposing pollutants in indoor air using reactor traps and in the near future may be readily integrated into new and existing ventilation systems.^{15,16} In addition to organic pollutants, it has recently been discovered that TiO_2 can degrade bacteria such as *Escherichia Coli* and fungal spores such as *Aspergillus Niger*.¹⁷ Commercial TiO_2 coated ceramic tiles, (Hydrotect® Tiles, patented by Toto Kiki (HK) Ltd., Wanchai, Hong Kong), are considered to be very effective against organic and inorganic materials, as well as bacteria, and may have applications in such areas as hospitals, care facilities, bathrooms, and schools.¹⁸ Other companies such as PPG in Pittsburgh, PA, have patented thin, transparent films of TiO_2 on windows (SunClean™) as "self-cleaning" surfaces.¹⁹ Self-cleaning surfaces such as SunClean™ and Hydrotect® not only combine the photocatalytic properties of TiO_2 to degrade contaminants, but are also "super-hydrophilic" so the contaminants can easily be swept away with a stream of water.

Although TiO_2 can oxidize a wide variety of pollutants, the photocatalytic activity of TiO_2 in many redox reactions is limited by the relatively large band gap ($E_g = 3.0\text{-}3.2$ eV) of the material, which limits absorption to the UV region of the solar spectrum,

below about 350 nm. This limitation has led to the development of chemically modified TiO₂ surfaces with better spectral absorption accomplished by dye-sensitization and doping.^{20,21} Recently, nitrogen doped TiO₂ films have broadened TiO₂'s absorption range into the visible region, up to 520 nm.²² Alternative semiconducting oxide materials with smaller band gaps, such as MoS₂²³ or composite semiconductors such as ZnO/ZnS²⁴ and CdS/PbS,²⁵ have also been investigated. However, despite a wide range of materials with suitable band gaps, titanium dioxide remains a primary candidate as a photocatalyst due to its thermodynamic stability, high abundance, low cost, and non-toxicity.

Current scientific interest in TiO₂ photocatalysts has been motivated by observations that aqueous solutions of colloidal TiO₂ nanoparticles exhibit significantly enhanced chemical and photochemical reactivity due to so-called quantum size effects (QSE).^{26,27} The chemical and electronic properties of semiconductor nanoparticles are distinct from either extended solids or single molecules and thus represent an exciting new class of materials.²⁸ It is known that the properties of such nanoparticles vary strongly as a function of particle size (as well as shape) and consequently have “tunable” optical, electronic, and chemical properties.²⁸⁻³⁰ In most cases, the TiO₂ nanoparticle surfaces and their role in chemical and photochemical reactivity are still poorly understood.

1.2 Fundamental Mechanisms of Semiconductor Photocatalysis

Band Gap Excitation and Charge Transfer. The central mechanism of photocatalytic activity in semiconductors relies on absorption of a photon of energy greater than or equal to the semiconductor band gap energy, E_g . Since solar radiation is a

natural and abundant energy source, most photocatalytic strategies have been directed toward exploiting this energy by choosing materials with band gaps within the range of terrestrial sunlight, approximately 4.1 to < 0.5 eV (see Figure 1.1). Many semiconductors have band gap energies within this desired range, and so are potential materials for promoting or photocatalyzing a wide variety of chemical reactions.³¹

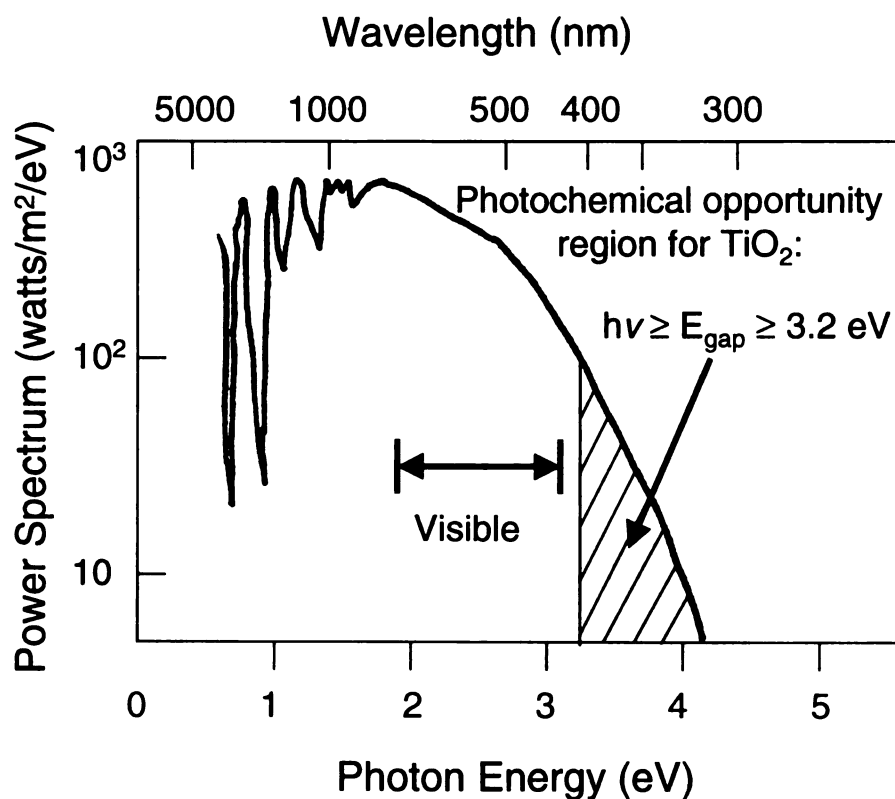


Figure 1.1 Solar spectrum at sea level with the sun at zenith. Photochemical opportunity region for TiO₂ within this spectrum is also shown (Adapted from Linsebigler et al.⁸).

When a semiconductor absorbs a photon of energy $\geq E_g$, excitation creates an electron (e^-) in the conduction band (CB) and leaves a hole (h^+) in the valence band (VB).³² In TiO_2 , the CB is composed of empty Ti 3d states and the VB is composed of filled O 2p states. The e^-/h^+ pair may spontaneously recombine with thermal or luminescent energy release, or may migrate toward the surface and react with adsorbed acceptor or donor species in reduction or oxidation reactions, respectively, as shown in Figure 1.2.

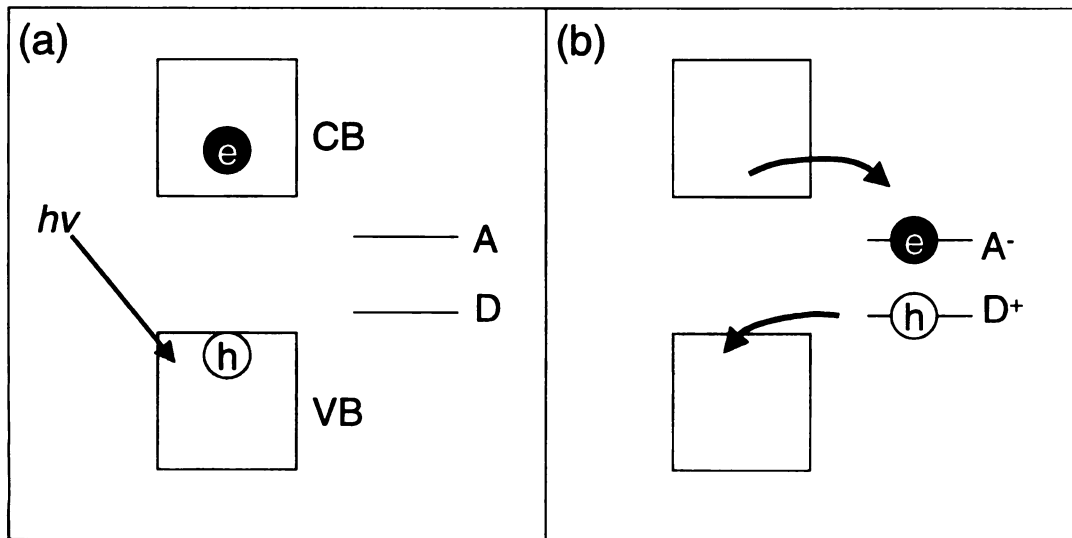


Figure 1.2 (a) Initial excitation across the band gap of semiconductor and creation of e^-/h^+ pair followed by (b) charge transfer to molecules adsorbed on the surface (A= acceptor and D= donor species on surface).

In order for redox reactions to occur, the energy of the adsorbate orbitals acting as electron acceptors or those acting as electron donors must lie within the band gap region of the photocatalyst as shown in Figure 1.3. Hence, the position of these adsorbate energy levels relative to those of the semiconductor surface is crucial. In the absence of redox active surface species, spontaneous e^-/h^+ recombination occurs within a few ns.³³

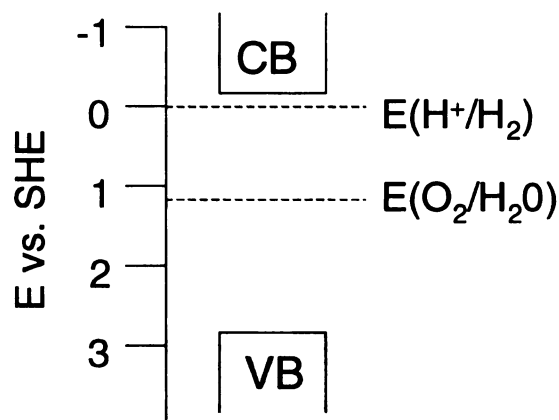


Figure 1.3 Approximate band edge positions for rutile TiO_2 at $\text{pH}= 1$.⁴

It should be noted that for TiO_2 , the oxidation of many organic molecules is not believed to be due to direct charge transfer of a hole to the organic substrate. Instead, the photocatalytic oxidation of many organic molecules is thought to be mediated by electron transfer from coadsorbed species on the surface,⁷ such as surface hydroxyl groups $\text{Ti}^{4+}\text{-OH}$,^{34,35} which form surface radicals that can oxidize the adsorbed molecule *directly* (as shown in equation 1.1).



Electron/hole Recombination. The reactivity of a photocatalyst is dependent on the rate of e^-/h^+ recombination in the bulk or at the surface. In order to be an efficient photocatalyst, the photogenerated holes and electrons must have a long lifetime since recombination is in direct competition with surface charge transfer to adsorbed species. Therefore, the recombination of the photogenerated e^-/h^+ pair must be minimized. Surface and bulk defects can generate electronic states that serve as charge carrier traps. The presence of these charge carrier trapping sites, such as Ti^{3+} or surface $TiOH$ sites on TiO_2 , can extend the effective lifetime of the photoexcited e^-/h^+ pair, increasing the probability of an electron transfer process to an adsorbed molecule.

Band Bending and the Schottky Barrier. When a semiconductor is in contact with another phase, such as a liquid or gas, there is a redistribution of charge within the semiconductor. As mobile charge carriers are transferred between the semiconductor and contact phase, or carriers are trapped at intrinsic or adsorbate-induced surface states, a space charge layer develops and there is no longer a uniform distribution of charge within the semiconductor. The electronic band potentials of the semiconductor are distorted depending upon whether there is an accumulation or depletion of charge in the near-surface region. As a consequence, bands may bend upward (n-type semiconductors) or downward (p-type semiconductors) close to the surface. For example, naturally occurring oxygen surface vacancies on TiO_2 create five-coordinate Ti^{3+} sites. The Ti^{3+} sites serve as strong electron traps, causing the surface region to become negatively charged with respect to the bulk of the semiconductor. To compensate for this effect, a positive space charge layer develops within the semiconductor causing a shift in the

electrostatic potential and the upward bending of bands. TiO_2 is therefore, considered an n-type semiconductor.

Following band gap excitation, photogenerated electrons move away from the surface while the holes move towards the surface due to the potential gradient that has formed from band bending (Figure 1.4). This band bending phenomenon assists in separating the e^-/h^+ pairs and in reducing recombination rates.

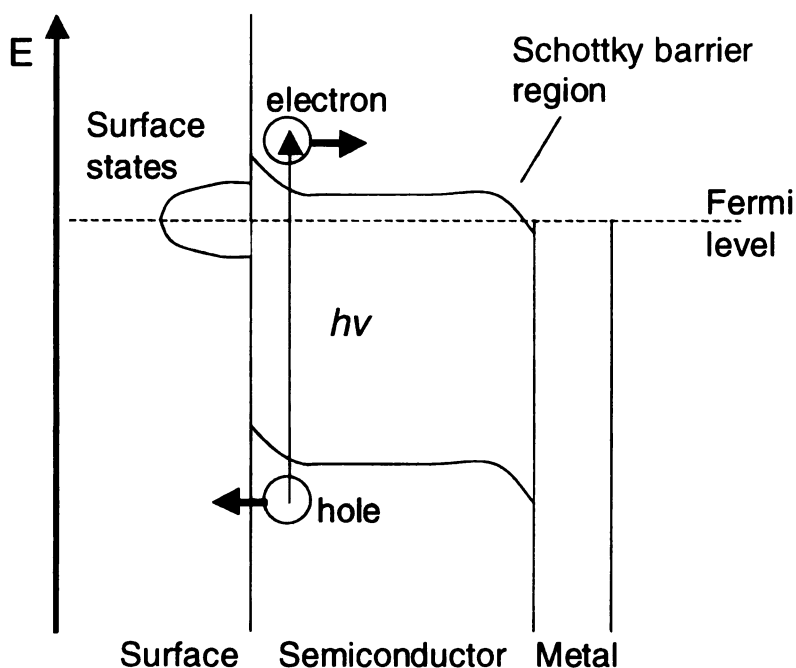


Figure 1.4 Diagram showing the surface band bending and Schottky barrier that serve to separate h^+ and e^- following band-gap excitation in a n-type semiconductor.

The potential gradient can be further enhanced by doping the surface with a metal.³⁶⁻⁴⁰ The metal dopant creates a favorable potential gradient (Schottky barrier)⁴¹ that acts as a sink for photogenerated electrons (as shown in Figure 1.4). The metal

surface then becomes the site of reduction reactions. Based on this phenomenon, discrete electrochemical cells incorporating small metal islands deposited onto TiO₂ nanoparticles have been prepared.⁴² For example, Dawson et al. determined that the photocatalytic oxidation of thiocyanate ions was increased by 40% using gold-capped TiO₂ nanoparticles.³⁸ With the addition of Lanthanide metals: Eu³⁺, La³⁺, Nd³⁺ and Pr³⁺ to TiO₂, Wang et al. found significant enhancement in the photocatalytic degradation of rhodamine B.³⁷ The amount of metal required to produce an effective Schottky barrier can correspond to less than a few percent of the surface covered.

Quantum Size Effects (QSE). Photocatalytic activity is also affected by particle size. When the physical dimensions of a semiconductor particle fall within the range of 5-20 nm, the diameter of the particle becomes comparable to the wavelength of the charge carriers (e^-/h^+) and quantum size effects (QSE) occur.^{30,43} The electronic structure of the semiconductor can no longer be described as an extended solid, with overlapping wavefunctions from each atom giving rise to continuous and delocalized electronic valence and conduction bands. Instead, the charge carriers become localized in the effective potential well of the nanoparticle and discrete quantized energy states are produced (Figure 1.5) that give rise to the strongly size-dependent optical and electronic phenomena.

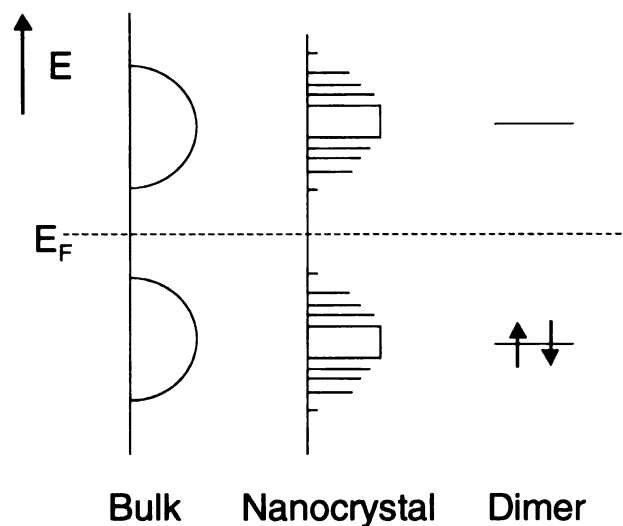


Figure 1.5 Density of states for semiconductor as a function of particle size.

Absorption intensities are perturbed and the effective band gap of a semiconductor particle is thought to increase as the particle size decreases, corresponding to a blue-shift of the absorption band.^{28,29} These phenomena can influence the photocatalytic properties of small semiconductor particles. For example, in the decomposition of 1-butene by SnO_2 , 5 nm particles were photoactive whereas 22 nm particles were not.⁴⁴ Similarly, Gao and Zhang discovered that 7.2 nm rutile TiO_2 particles had a much higher photocatalytic activity in the oxidation of phenol compared to 18.5 and 40.8 nm particles.⁴⁵

In addition to changes in the electronic structure of the material, other phenomena can occur as particle dimensions are reduced. Smaller particles present more surface adsorption/reaction sites per unit volume and are therefore expected to show increased

catalytic activity. Additionally, the formation of unique electronic surface states or reactive defects may become favored. The high curvature of the particle surface creates a large number of low coordination surface atoms of unique local geometry and bonding, which may also lead to substantial surface relaxation, reconstruction or faceting (Figure 1.6).

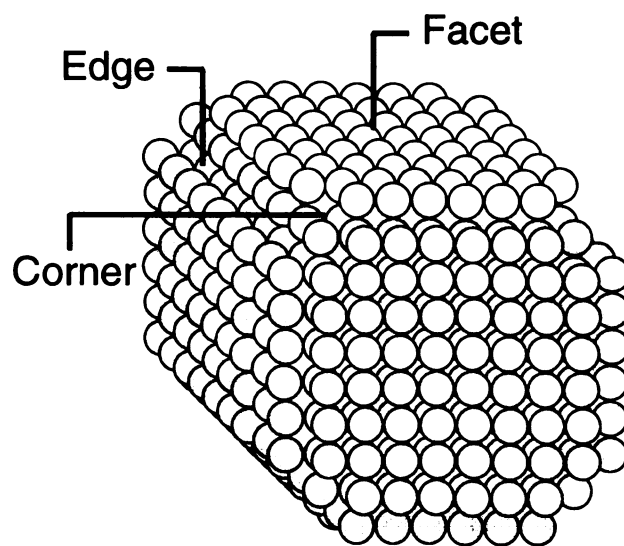


Figure 1.6 Simple faceted cubo-octahedral 3nm particle composed of 892 total atoms with 366 surface atoms.

In TiO_2 single crystals, these low coordination sites have been shown to markedly influence the adsorption and reactivity of small molecules.^{46,47} As the volume of the semiconductor becomes very small, the band-bending phenomenon that spatially separates the e^- and h^+ is reduced. Band bending typically operates on the 0.5 to 5 nm distance scale and becomes weak as particle diameters approach these dimensions.⁴ A small particle is almost completely depleted of charge carriers so its Fermi potential is

located approximately in the middle of the band gap. This implies that there is an optimum size semiconductor nanoparticle for surface photoreactivity, which is dependent upon the material.

1.3 TiO₂ Photocatalysis: Effect of Crystalline Form and the Surface

Titanium dioxide exists as three natural crystalline forms: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic), with rutile being thermodynamically the most stable.^{32,48,49} Anatase is meta-stable at low temperature and can be transformed irreversibly to rutile at elevated temperatures ranging from 400 to 1200 °C. The rarest form, brookite, is an intermediate phase between anatase and rutile.⁵⁰⁻⁵² The crystal structures of anatase and rutile differ by the assembly of their TiO₆ octahedra chains, as shown in Figure 1.7. The TiO₆ octahedra in the anatase form are significantly more distorted and are connected in zigzag chains, compared to straight chains in the rutile form. This distorted atomic arrangement in anatase leads to a less thermodynamically favored polymorph relative to rutile.^{48,53}

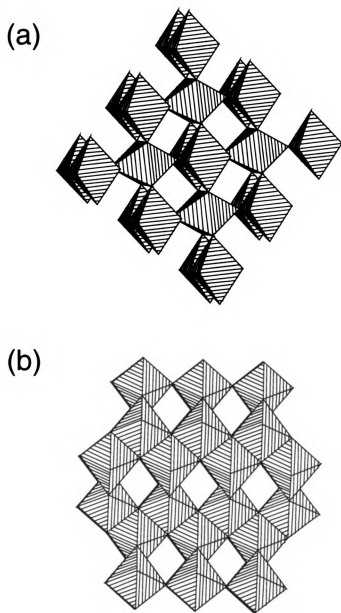


Figure 1.7 Polyhedral model of (a) rutile and (b) anatase structures.

Photocatalytic studies have focused on the most common and easy to synthesize forms of TiO_2 : rutile and anatase. Bulk powder, single crystal and thin film studies of anatase and rutile have helped to elucidate the photocatalytic mechanisms of TiO_2 as well as the application of this semiconductor to technologies of interest.^{7,8} Anatase appears to be slightly more photoactive than rutile TiO_2 , but reasons still remain inconclusive. The electronic density of states (Figure 1.8) shows that the band gaps of these materials are slightly different: rutile ($E_g = 3.0 \text{ eV}$) and anatase ($E_g = 3.2 \text{ eV}$). On this basis, anatase should be less photoactive. It is currently thought that increased photoactivity in anatase is due to its larger charge carrier diffusion rates⁵ and lower recombination rates compared to rutile.^{54,55} It should also be noted however, that the photoreactivity for anatase and rutile is highly variable, depending on the exact surface preparation methods.

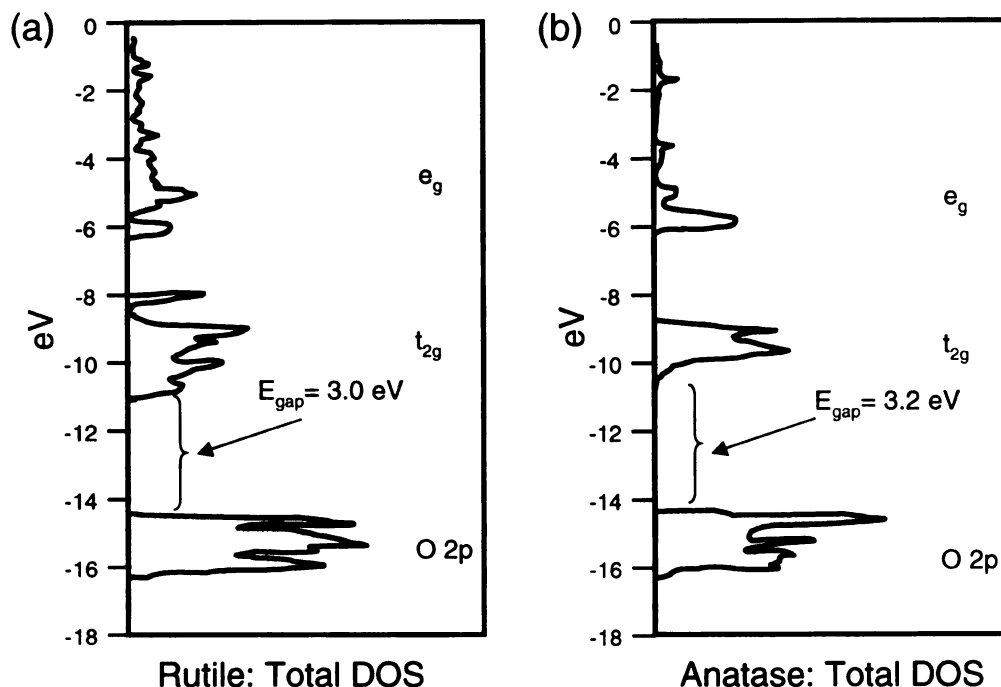


Figure 1.8 Calculated electronic density of states for (a) rutile and (b) anatase polymorphs of TiO₂. The shaded regions represent occupied states in O 2p. The unoccupied states t_{2g} and e_g make up the d band of the Ti atom (Adapted from Burdett et al.⁴⁸).

Complementary single crystal studies have assisted in understanding the photocatalysis of TiO₂ and the role of the surface. In many cases, the rutile TiO₂(110) surface is seen as the model surface for studies of TiO₂, as this is the thermodynamically most stable. Such single crystal studies in ultrahigh vacuum (UHV) have complemented ambient powder and film studies and have contributed to the development of a fundamental understanding of the role of the surface in the overall photocatalytic activity of TiO₂. These studies have determined the influence of parameters such as surface geometric structure, defect nature and concentration, and the identity of some reactive

intermediates.^{8,56,57} Unfortunately, single crystal studies of anatase are rare^{58,59} due to the difficulty of preparation, but bulk measurements of dispersed particles have been performed.⁶⁰

Single crystal studies on rutile $\text{TiO}_2(110)$ have shown that the surface chemistry of TiO_2 is significantly influenced by the concentration of oxygen defects. A stoichiometric rutile $\text{TiO}_2(110)$ surface is quite unreactive since a fully oxidized surface contains no occupied surface states in the band gap.⁶¹ However, defects increase the reactivity of the surface, particularly oxygen defects that produce low coordination Ti^{3+} sites. As mentioned earlier, these Ti^{3+} atoms create surface trap states in the band gap of TiO_2 , and ultimately lead to enhanced chemical reactivity.⁶²⁻⁶⁶ Similar oxygen defects are also expected to be present on anatase surfaces.

Several different types of O atom vacancies have been directly observed by scanning probe microscopies on TiO_2 single crystals,^{57,67-69} some of which are shown schematically in Figure 1.9. Depending on the concentration of oxygen defects, various reconstructions of the TiO_2 surface can occur. Commonly observed is a (1×2) reconstruction, where the periodicity of the bridging oxygen rows shown in the (1×1) stoichiometric surface, Figure 1.9, is doubled.⁷⁰ More complicated longer period $(1 \times n)$ reconstructions have also been observed.⁷¹

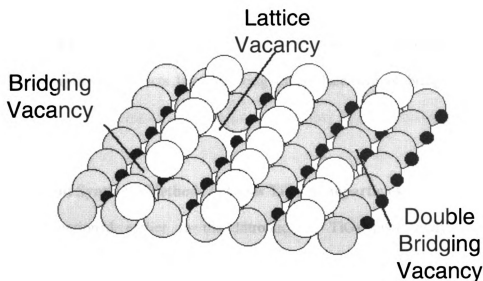


Figure 1.9 Oxygen atom vacancies (defect sites) on (1×1) stoichiometric surface of rutile $\text{TiO}_2(110)$, $\text{Ti} = \bullet$, $\text{O} = \circ$.

Chemisorption studies using various probe molecules (such as H_2 , CO , O_2 , S , and SO_2) indicate that adsorption on TiO_2 surfaces is dependent on oxygen defect sites on the surface.^{47,65,72-75} This dependence can influence the nature of the photocatalytic reactions on the surface that can take place. For example, Yates and co-workers have determined that molecularly adsorbed oxygen, which adsorbs preferentially at defect sites, is essential for photooxidation of methyl chloride.⁷⁶ In their study, they discovered that substrate-mediated excitation of adsorbed oxygen generates an ionic species, probably O_2^{2-} , that oxidizes coadsorbed CH_3Cl directly. They speculate that at the gas-solid interface, adsorbed oxygen may play a more important role in the oxidation of certain organic molecules, such as CH_3Cl , than photocatalytically generated $\cdot\text{OH}$ radicals. Defect concentration and adsorbed oxygen has been shown to play a similar role in the

photocatalytic dehydrogenation of 2-propanol.⁷⁷ High defect concentrations may also be detrimental in some cases. For example, Hebenstreit et al. have shown recently that adsorption of catalytic poisons, such as sulfur, is favored at undercoordinated Ti atoms, with the adsorption at defects later evolving to displacement of bridging oxygens by sulfur.^{74,75}

1.4 Current Synthetic Methods to Grow TiO₂ Nanoparticles

As mentioned earlier in the Introduction, TiO₂ photocatalytic activity is significantly influenced by particle size. Almost all of the studies of particle size-reactivity relationships for TiO₂ have been performed using solutions of colloidal nanoparticles. The most common methods used to prepare TiO₂ nanoparticles are sol-gel processes. The sol-gel method is based on the hydrolysis of metal alkoxide, Ti(OR)₄,^{27,36,78-83} or titanium tetrachloride, TiCl₄,^{45,84-86} followed by a calcination process. The temperature of hydrolysis can be used to control particle size. For example, Martini has shown that hydrolysis of tetraisopropoxide, Ti(OCH(CH₃)₂)₄, at 1 °C produces ~2 nm size anatase particles and at 20 °C ~20 to 30 nm size particles are synthesized.⁸³ The calcination process is used to control crystallinity and phase of the particles. Unfortunately, most sol-gel approaches have only focused on creating anatase nanoparticles, with little success in growing nanosized rutile particles.

The difficulty in making TiO₂ nanoparticles via hydrolysis is inherent in the calcination process. During calcinations, anatase crystallization occurs within the colloid composition. If the calcination temperature of TiO₂ colloids is not high enough, incomplete crystallization will occur and some organic molecules will remain in the

product. With an increase in temperature, the particles undergo a phase transformation from anatase to rutile, which begins with nucleation of rutile on the anatase particle surface. This process results in low surface area, large rutile particles that are often aggregated.^{87,88} Recently, advances have been made to produce smaller rutile nanoparticles via hydrolysis. Using low temperatures and incorporating a rutile seed crystal, needle-shaped rutile TiO_2 with average crystal sizes of 50-70 by 5-12 nm and large specific surface areas has been produced.⁸⁸

Hydrothermal synthesis may provide an easier route to prepare ordered crystalline and phase-pure TiO_2 nanoparticles at low temperature ($< 250\text{ }^\circ\text{C}$). With this method, crystalline nanoparticles of TiO_2 can be formed with different morphologies by controlling the temperature, pH, and additives in a tightly closed vessel.^{89,90} For example, the rarest crystalline form of TiO_2 , brookite, has been precipitated from acidic solutions of TiCl_4 by carefully controlling the Ti:Cl ratio.⁸⁶ Phase transformations can be promoted by adding additives such as HCl and NaCl rather than temperature, and can also be used to confine sizes of particles.⁹⁰ Although the size of particles can be controlled, there are still similar problems to hydrolysis with this method including aggregation and impure phases.⁹¹ Alternative approaches, such as solvothermal synthesis in organic media instead of water, may be more effective in producing smaller nanoparticles with high crystallinity and large surface areas.⁹²⁻⁹⁴

1.5 Motivation and Objective of Present Work

Despite the ability to synthesize TiO_2 nanoparticles of various size and composition, little is known of the detailed composition or morphology of TiO_2

nanoparticulate surfaces. The particles produced by solution methodologies tend to agglomerate, are non-uniform in size and shape, and are generally not amenable to surface characterization by experimental techniques such as electron spectroscopy or scanning probe microscopy.

The surface is as important as particle size in understanding the dynamic and equilibrium properties of nanoparticles.⁹⁵ Investigation of oxide nanoparticles such as ZnO,⁹⁶ MgO,⁹⁷ and CaO,⁹⁸ have indicated that the increased reactivity of nanophase materials may be related to the increased surface area-to volume ratio and a large number of surface atoms in unique bonding environments. Single crystal studies have already revealed the influence oxygen defects have on reactivity. Therefore, correlating the surface morphology with particle size-dependent photoreactivity in TiO₂ nanomaterials is an important component to understanding their photocatalytic behavior.

To allow a detailed spectroscopic and microscopic examination of the surface properties of TiO₂ nanoparticle materials, we have turned to model systems of TiO₂ particles supported on solid planar substrates. These models can be studied using conventional UHV spectroscopic techniques. Although there are several different nanofabrication techniques, including standard photolithography⁹⁹ and electron beam lithography,¹⁰⁰ these approaches are often complex, expensive and are limited to the minimum size of features that they can produce. This dissertation presents an approach to producing ordered arrays of TiO₂ nanoparticles using a nanosphere lithography (NSL) technique that utilizes polystyrene nanospheres as a removable deposition mask. This technique has been developed and applied successfully by Van Duyne et al.¹⁰¹⁻¹⁰⁴ to create various metallic nanoparticle arrays but has not been extensively applied to make

metal oxide nanoparticles. To our knowledge, there is only one previous reference to producing metal oxides using a nanosphere template method. In that work, the production of Y_2O_3 particles on top of ZnS particles was mentioned briefly.¹⁰⁵

In the nanosphere lithography method, an aqueous solution of polystyrene microspheres (~50-500 nm in diameter) is drop-coated onto a suitable substrate and the solvent is allowed to evaporate under controlled conditions. The nanospheres order spontaneously into a hexagonal close-packed array on the surface due to electrostatic interactions between the spheres. Depending upon the initial sphere concentration, different periodic particle array (PPA) masks can be produced: a close-packed single layer periodic particle array (SL- PPA) or a double layer periodic particle array (DL- PPA) from a monolayer or bilayer of spheres, respectively.¹⁰² The desired material of interest is then evaporated through the nanosphere mask, coating the exposed surface between the spheres. The microsphere mask is subsequently removed by organic solvents such as ethanol or methylene chloride. These solvents dissolve the polystyrene spheres, leaving the material deposited through the mask on the substrate (Figure 1.10). Complete mask removal becomes difficult if the height of the islands exceeds the radius of the microspheres used to make the mask.

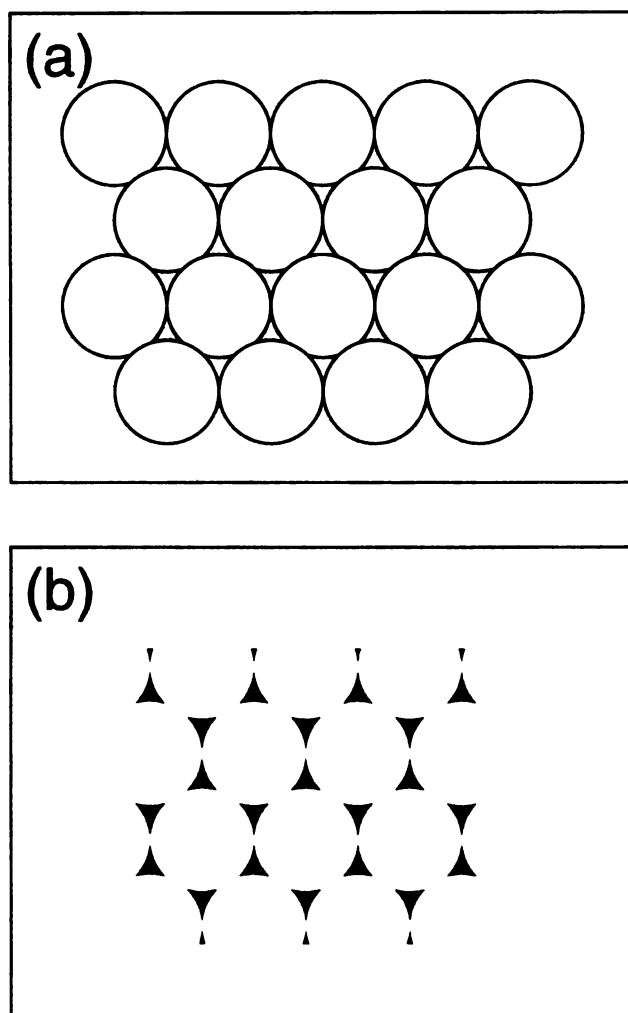


Figure 1.10 (a) A close-packed array of polystyrene microspheres and (b) array of nanoparticles produced by evaporation through mask and subsequent mask removal.

The diameter of the nanoparticle islands is approximately 25% of the diameter of the polystyrene microspheres. Therefore, by changing the size of the microspheres, various diameter nanoparticles can be made using this technique. Polystyrene spheres with diameters down to 20 nm are commercially available, allowing nanoparticles on the order of 3-5 nm minimum diameter (i.e. quantum size particles) to be generated. Changing the incidence angle of the evaporative source with respect to the substrate normal can alter the shape of the supported nanoparticles somewhat,¹⁰⁴ but to date, nanosphere lithography has been limited to triangular and circular particle shapes. Unfortunately, the particle arrays contain up to 1% point and line defects due to polydispersity in the spheres used to form the mask. These disadvantages may be overcome with continued development. In general, however, the NSL methodology is simple, intrinsically parallel, relatively inexpensive, and highly precise. It has the ability to produce particles with uniform size and shape that is comparable or better than other nanofabrication approaches.¹⁰⁴

In this dissertation the study on using a NSL approach to directly grow monodisperse, controlled sizes of supported TiO₂ nanoparticles is presented. These arrays should mimic some of the properties of colloidal nanoparticles, but offer specific experimental advantages and the potential for simple control of crystallography and Schottky barrier creation.

1.6 Outline of the Dissertation

In Chapter 2, the primary analytical characterization techniques employed in this work will be described to provide a foundation for understanding the experimental

results. The operating principles of the primary characterization techniques used in this work: atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) will be presented.

Chapter 3 details the initial work on implementing and improving the nanosphere lithography technique to prepare TiO_2 nanoparticle arrays.^{106,107} The goal of this work was two fold. The first was to develop methods to improve the formation and degree of order within the polystyrene monolayers and bilayers used as removable masks. The second aspect of this study was to prepare two types of TiO_2 nanoparticle arrays: single layer-periodic particle arrays (SL-PPA) and double layer-periodic particle arrays (DL-PPA). These arrays were characterized using AFM, XPS, and UV-absorption and provided a solid foundation for later work presented in Chapter 4.

Chapter 4 reports a more detailed characterization of the TiO_2 nanoparticle arrays produced via the NSL technique. The size and shape tunability and defect characterization is presented.

Chapter 5 describes the preparation of a suitable substrate that could be used to control the crystallinity of TiO_2 nanoparticle arrays. The goal of this work was to produce metallic oxide substrates with similar lattice parameters and symmetry to rutile that would provide epitaxial control of TiO_2 nanoparticles and in addition offer experimental advantages due to their conductivity. The synthesis and characterization of ruthenium dioxide, RuO_2 , and chromium dioxide, CrO_2 , supports are presented here. Suitable substrates of CrO_2 were produced by epitaxially growing thin films on rutile $\text{TiO}_2(110)$ single crystal supports.¹⁰⁸ RuO_2 single crystals with dimensions of $2.0 \text{ mm} \times 0.14 \text{ mm} \times 0.14 \text{ mm}$ have also been grown.

Finally, Chapter 6 concludes this dissertation with a summary of the results and directions of future work.

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Chapter 2

Analytical Techniques

Various analytical techniques have been utilized in the work presented in this thesis to ascertain the composition, morphology, and activity of TiO₂ nanoparticle arrays and to characterize the potential substrates suitable for epitaxial control of the TiO₂ nanoparticles. The primary characterization techniques used in this work were atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). AFM was used to provide a surface topology of the TiO₂ nanoparticle arrays and the substrate supports. XPS provided the quantitative chemical composition of the TiO₂ nanoparticle arrays and substrate surface. In addition to AFM and XPS, supporting information was obtained by bulk characterization methods such as X-ray diffraction, UV-Vis spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), contact angle, and magnetic measurements. These methods were complimentary to XPS and AFM measurements and assisted in determining some of the macroscopic properties of these materials.

In this chapter, the operational principles of AFM and XPS will be presented briefly. Issues important to good AFM performance, including calibration and tip selection, will be discussed. Details regarding XPS calibration, analysis of metal oxides, and angle resolved XP spectroscopy will also be reviewed. Readers who are interested in more details of the supporting techniques used in this work should refer to the following references.¹⁻⁷

2.1 Atomic Force Microscopy (AFM)

Tip-Surface Force Interaction. Atomic force microscopy (AFM) relies on measuring forces between a sharp tip (<10 nm diameter) and a surface at very short distances (0.2-10 nm tip-surface separation). There are three operational modes: contact, non-contact, and intermittent contact, as shown in Figure 2.1. Contact AFM is the most common method of operation and is based on electron-electron repulsion with a <0.5 nm tip-surface separation. Non-contact AFM is based on van der Waals attraction with a 1-10 nm tip-surface separation. Intermittent contact AFM (tapping mode AFM), probably the second most common method of operation, measures the force of interaction between the tip and sample by oscillating between the contact and non-contact regions, with tip displacements of 0.5-2 nm.

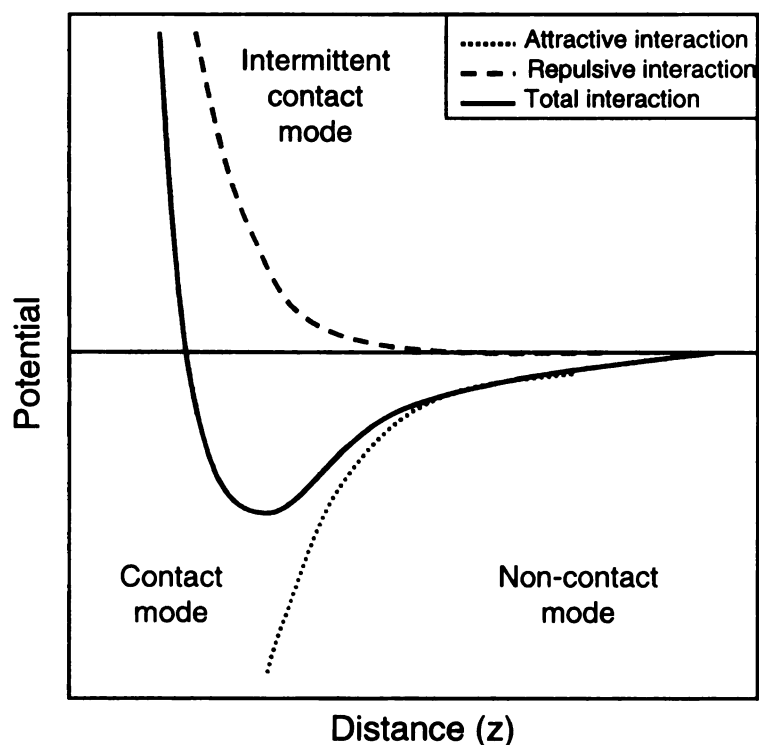


Figure 2.1 Short range force interactions between an AFM probe and a sample, which is the sum of the potentials from an attractive van der Waals interaction and a hard wall repulsive interaction between two points (Adapted from Celotta et al.⁸).

Basic Operating Principles. In AFM, the probe tip is mounted on a cantilever as shown in Figure 2.2. Topographic images are obtained by detecting changes in the cantilever's position as the tip interacts with the surface. In contact mode AFM, this is done with an optical lever by monitoring the deflection of a laser reflected from the back of the cantilever onto a position-sensitive photodiode as shown in Figure 2.3. A four-segment diode can quantify the vertical and/or lateral motion by summing the ratio of signals in each quadrant. The data is acquired by measuring the cantilever deflection signal as the tip is scanned at a constant height or by adjusting the height of the sample using a feedback system to maintain a constant cantilever deflection signal.

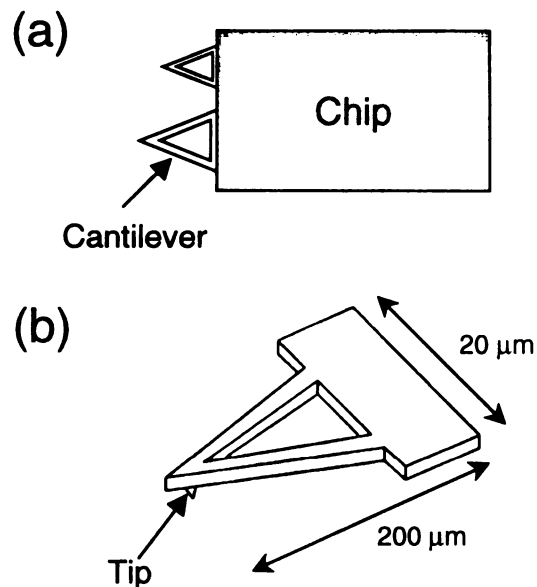


Figure 2.2 (a) Diagram of a standard AFM probe, which includes a chip typically made of silicon that holds a cantilever and (b) representation of a standard cantilever with tip, which is commonly made of Si_3N_4 or Si.

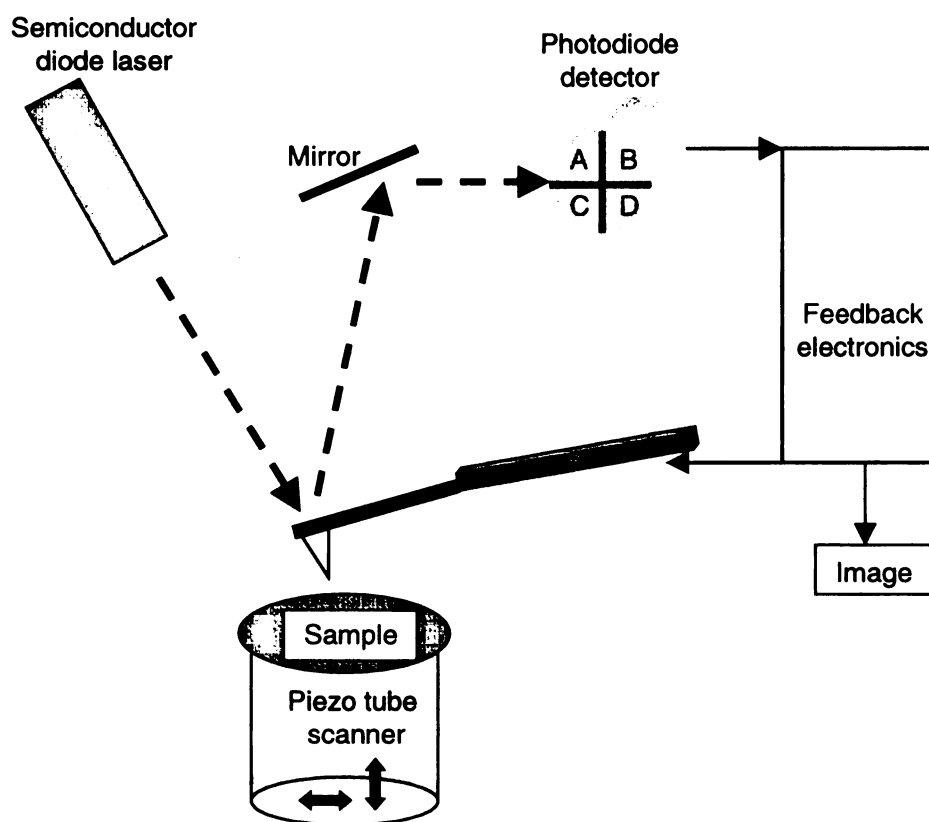


Figure 2.3 Operating principles of AFM. The sample is mounted on a piezoelectric scanner. The cantilever and tip are positioned near the surface via a motorized device and the sample is then scanned against the tip. The cantilever deflection is detected with a photodiode incorporated into a feedback system that controls tip oscillation and position (Adapted from Bonnell⁹).

In contact mode AFM, the cantilever is bent away from the surface, with a total force on the sample of approximately 10^{-6} - 10^{-8} N. This interaction can be described in terms of Hooke's Law to describe a coiled spring, where k equals the spring constant of the cantilever and x equals the distance between the surface and the cantilever:

$$F(x) = -k \cdot x \quad (2.1)$$

In non-contact mode AFM, there is a very small attractive force between the tip and the surface of $\sim 10^{-12}$ N. This mode is best for soft or elastic surfaces. Such small forces are difficult to measure using direct beam-bounce methods. Instead an AC driven oscillating cantilever is often used, which oscillates at a resonant frequency typically around of 100-1000 Hz. This resonant frequency is given by the equation shown below, where k equals the spring constant of the cantilever, and m equals the effective mass of the cantilever.

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (2.2)$$

The resonant frequency of the oscillating cantilever shifts with a change in external force. In non-contact mode, an electronic feedback system adjusts the tip-surface distance to keep the resonant frequency constant, i.e. constant force. Intermittent contact (tapping mode) also uses a vibrating cantilever, but the tip "taps" into contact mode during every vibration. This approach is useful for soft surfaces, is less prone to external vibration/noise than non-contact mode, and is also less destructive than contact mode AFM.

Tip Parameters and Resolution. The resolution of an AFM image is determined by various parameters associated with the tip including the tip shape, sidewall angle, and radius of curvature, as shown in Figure 2.4. Three basic geometries of tips are available commercially: pyramidal, tetrahedral, and conical. Most contact mode AFM

measurements use standard pyramidal, and in some cases tetrahedral, shaped tips. For non-contact and tapping mode AFM however, conical high aspect-ratio tips are used.

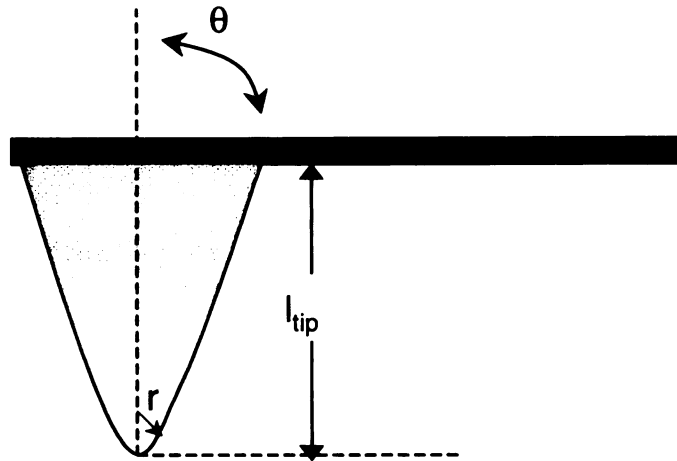


Figure 2.4 The AFM tip showing: tip length, l_{tip} , radius of curvature, r , and sidewall angles, θ (Adapted from Bonnell⁹).

For AFM analysis, the sidewall angle and length of a tip influence its ability to accurately image steep slopes and to measure the depths of trenches and pits on the surface. As long as the tip is much sharper (large aspect ratio) than the feature being imaged, the true edge profile of the feature is represented. However, when the feature is sharper than the tip the image will be dominated by the shape of the tip, as shown in Figure 2.5. Similarly, for depressions in the surface, the cross section (determined by the geometry and sidewall angles) of the tip must be less than the pit. If it is greater than the pit, the depression depth will be underestimated. Tip broadening can also occur if the radius of curvature of the tip is comparable to, or greater than, the size of the feature being imaged.

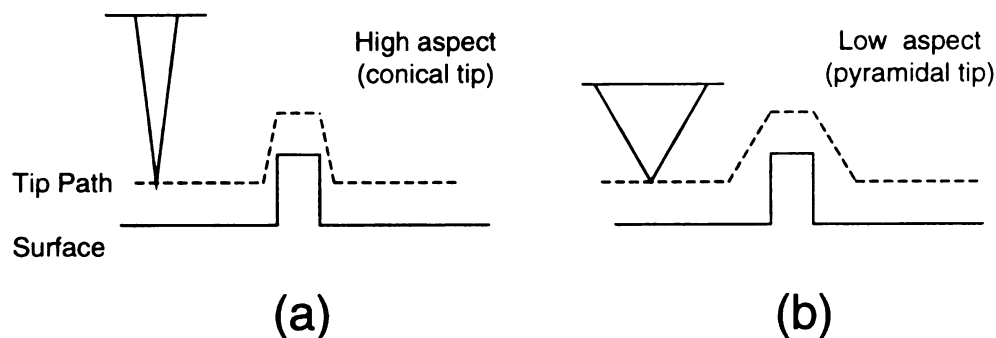


Figure 2.5 Diagram depicting how the aspect ratio of a tip can affect resolution in AFM for (a) conical tips and (b) pyramidal tips.

It should be noted that standard Si_3N_4 pyramidal tips are suitable for imaging a variety of surfaces as long as deep narrow features are not present. They are exceptionally wear resistant and they have been used for imaging atomic scale contrasts in contact mode.¹⁰ Generally with commercially available tips, spatial resolution using AFM is limited by the tip radius. In most cases, typical lateral AFM resolution is 5 nm and height resolution is 0.1 nm. Tips can be sharpened by etching or ion beam milling to reduce the sidewall angles and radii of curvature. For example, etched Si probes have radius of curvature down to ~5 nm and can be ion etched to sidewall angles approaching 0° . Further enhancement of tips may improve resolution in AFM, but these tips are not as robust and significantly more expensive than standard AFM probes.

Typically, only AFM operating in the non-contact regime with specially designed sharp tips in ultrahigh vacuum has demonstrated the ability to obtain atomic resolution.^{11,12} It should also be noted that in AFM, true atomic resolution is generally not achieved. Instead of individual atom interaction of forces between the tip and surface, several atoms on the tip interact simultaneously with several atoms on the

sample. The periodicity of an atomic lattice is reproduced, but features such as vacancies and depression are often not clearly defined, as shown in Figure 2.6. Recent force interaction simulations, however, show that atomic defects may be imaged in non-contact modes but not in contact mode AFM.¹³ Despite the issues of true atomic imaging, AFM is promising for imaging atomic scale features and eliminates the requirement of a conductive surface as in scanning tunneling microscopy (STM). In addition to topography resolution with AFM based on tip-surface force interactions, specially coated AFM tips can be used to probe other features such as the magnetic structure¹⁴ and chemical and molecular interactions.¹⁵

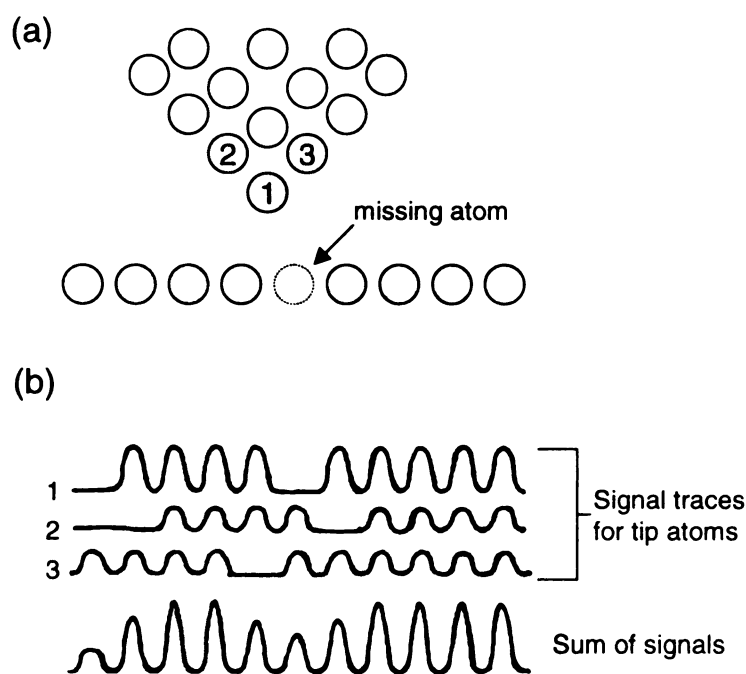


Figure 2.6 (a) Interatomic interaction of AFM tip with a surface. (b) AFM scan of periodic lattice showing the sum signal trace from contributions of three atoms on the tip. Note that the atomic vacancy is not resolved in the sum signal trace (Adapted from Howland et al.¹⁶).

AFM Calibration. To ensure that the scales of features in an AFM image are accurate, the AFM must be calibrated in both the lateral and height dimensions. This is typically done using special fabricated grids of known dimensions. In addition to x-y and z calibration, the quality of the tip can also be monitored during this procedure. For example, it can indicate if an AFM probe is blunt, as shown in Figure 2.7 (a). A blunt tip will influence the resolution of an image and may introduce tip-artifact features. Typical AFM lateral calibration images using suitable tips yielded an x-y interspacing between square grids of $1.02 \pm 0.02 \mu\text{m}$, for a $1 \times 1 \mu\text{m}$ gold scribed grid, as shown in Figure 2.7 (b). The height was calibrated using a $10 \mu\text{m}$ pitch, 200 nm deep platinum coated silicon sample, as shown in Figure 2.8. The depth of these depressions was determined with new calibrated sharp tips to be $204 \pm 0.02 \text{ nm}$, which is good agreement with the known dimensions of the sample.

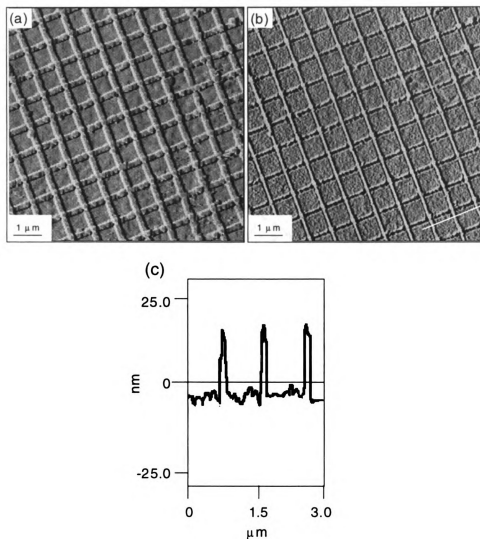


Figure 2.7 AFM calibration of the x-y direction using a $1 \times 1 \mu\text{m}$ gold scribed grid: (a) AFM image ($100 \mu\text{m}^2$ area) of grid using a blunt probe, (b) typical AFM image ($100 \mu\text{m}^2$ area) using a sharp standard Si_3N_4 probe, and (c) cross-sectional line scan of image b showing periodicity is consistent with grid dimensions.

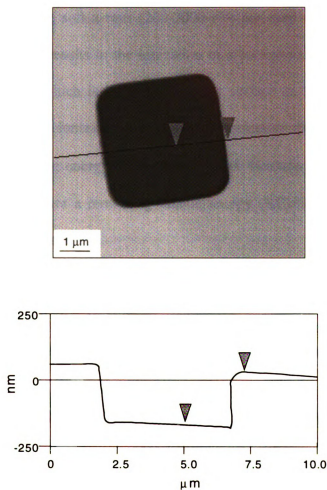


Figure 2.8 AFM calibration ($100\ \mu\text{m}^2$ area) of the z direction using a $10\ \mu\text{m}$ pitch, 200 nm deep platinum coated silicon grid and a standard Si_3N_4 probe. The line scan shows that the depth of the depression is consistent with grid dimensions.

2.2 X-ray Photoelectron Spectroscopy (XPS)

Basic Operating Principles. XPS is a surface technique that allows for quantification of chemical composition based on the photoelectric effect. In this technique, monochromatic soft x-rays (200-2000 eV) are used to irradiate the surface. Absorption of the x-rays results in the ionization of a core shell. In response, the atom creates a photoelectron which is transported to the surface and escapes to vacuum as shown in Figure 2.9. The ionization potential a photoelectron must overcome to escape into vacuum is the binding energy (BE) plus the work function of a material (ϕ). The emitted photoelectrons have a remaining kinetic energy (KE), which can be measured using an electron energy analyzer.

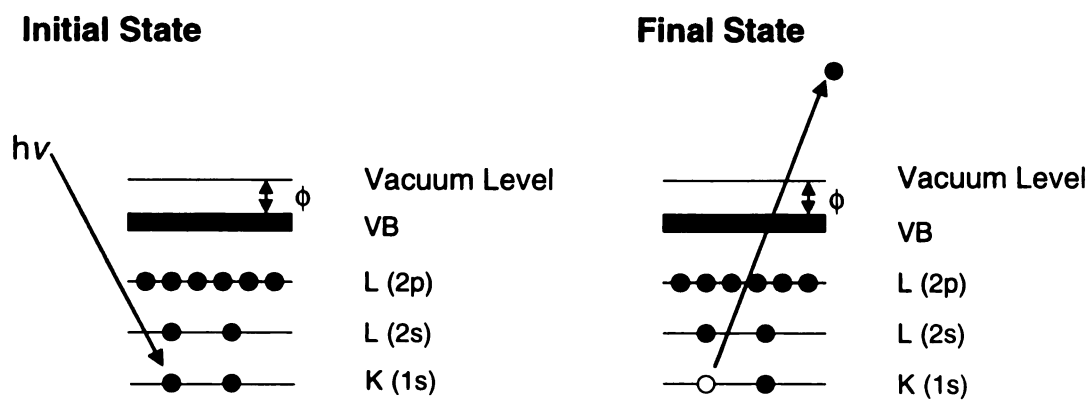


Figure 2.9 Diagram showing the basic process in X-ray photoelectron spectroscopy. Absorption of X-ray photons leads to emission of a core level electron.

From the kinetic energy, individual elements can be fingerprinted, based on their binding energy.

$$KE = h\nu - BE - \phi \quad (2.3)$$

Binding energies (BE) are characteristic to each atomic core level of an element, giving rise to a distinguishing set of peaks for a specific element in an XPS spectrum. The exact binding energy of an element depends on its oxidation state and environment. Therefore, changes in the chemical state of an element give rise to small, but observable shifts in the peak positions of a spectrum, which allows for chemical sensitivity. In addition, quantification can be determined from the intensity of the peaks using atomic sensitivity factors that correct for the photoemission cross-sections for a given element as well as several instrumental parameters.

Analysis of Metal Oxides. The XPS signatures of materials and their sub-oxides are well known. Based on chemically shifted photoemission peaks, XPS can be used to quantitatively determine the presence and proportions of each oxidation state for concentrations exceeding 1-2%. In addition, the photoemission peak envelope for spin-orbit split metal oxides usually contains a wealth of information about the electronic structure of the material. The presence or absence of satellite peaks, together with shifted metal peaks can indicate whether the solid is conducting or insulating, the degree of ionicity, and the formal oxidation state(s) of the metal atoms. Information about the electronic properties of the surface can also be obtained by examining the valance region of the XPS spectrum. Insulating or semiconducting materials are indicated by an absence of states at the Fermi level. The density of states at the Fermi level in a metallic material provides a crude indication of the electrical conductivity.

Calibration. To detect reproducible small BE shifts for sub-oxides in a material, the spectrometer should be consistently calibrated at both the high BE and low BE regions. Doing so can reduce error in the mid range to 0.035 eV.¹⁷ The calibration is usually done using the Au 4f_{7/2} and Cu 2p_{3/2} photoemission peaks and typical calibration spectra for these regions can be found in Appendix A. Table 2.1 shows the calibrated BEs of these photoemission regions, which are in good agreement with reference values and are repeatable to ± 0.04 eV.¹⁸

Table 2.1 XPS calibrated binding energies for the Al K α and Mg K α anodes.

	Al K α	Mg K α
Au 4f _{7/2}	84.0 eV	84.0 eV
Cu 2p _{3/2}	932.4 eV	932.4 eV

For insulating materials (such as TiO₂), surface charging can be a significant problem, shifting peaks to higher BE. Therefore, even with spectrometer calibration, the BE of peaks may need to be referenced to a known and reliable peak. This is commonly done using the BE of adventitious carbon at 285.0 eV.

Angle-resolved XPS. X-ray photons create photoelectrons at all accessible depths in a material, but the short mean free path of the electron allows only electrons produced at or near the surface to escape and be detected. The sampling depth (d) of XPS is described below, where I is the measured intensity of photoelectrons, I_0 is the theoretical maximum intensity, λ is the inelastic mean free path (IMFP) of an electron and θ is the angle electrons escape from the surface relative to the surface plane:

$$I = I_0 \exp(-d/\lambda \sin \theta) \quad (2.4)$$

Assuming a take-off angle (θ) that is 90° to the surface plane, this equation shows that approximately 95% of the photoelectron signal detected comes from within 3λ of the surface.

Angle-resolved XPS can be used to analyze the composition of the surface as a function of depth. The degree of surface sensitivity is varied, by collecting photoelectrons emitted at different take-off angles as shown in Figure 2.10.

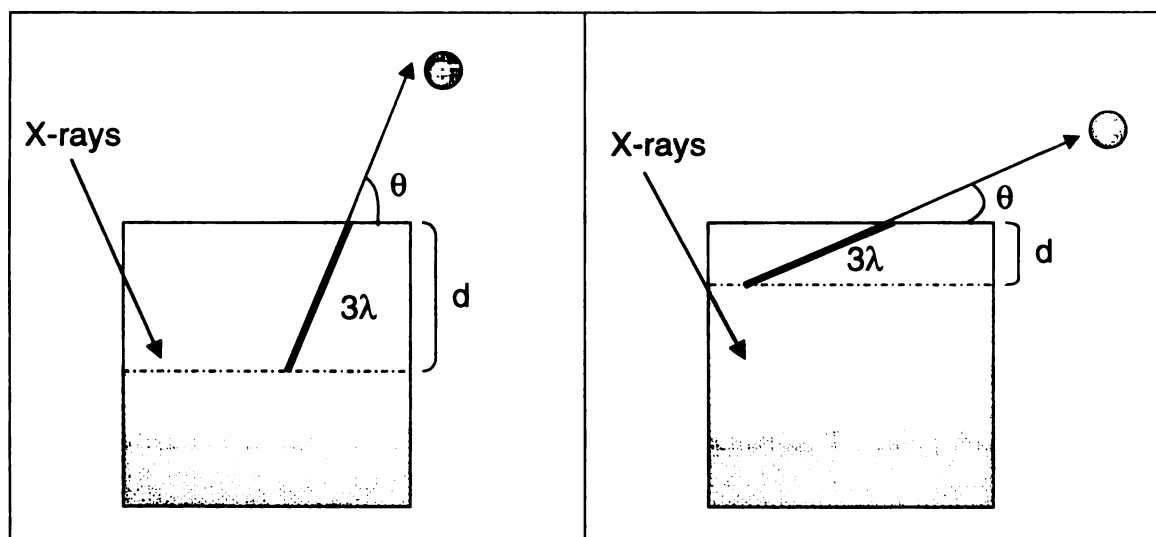


Figure 2.10 XPS surface sensitivity enhancement by variation of the electron "take-off" angle measured. The image shows how the sampling depth (d) of 3λ varies with take-off angle.

For further information regarding the basic principles of XPS and angle-resolved XPS refer to the following textbooks.^{17,19}

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Chapter 3

Nanosphere Lithography (NSL) Technique to Prepare TiO₂ Nanoparticle Arrays

Abstract

A nanosphere lithography technique has been used to synthesize periodic nanoparticle arrays of TiO₂ on glass substrates. Both monolayer and bilayer evaporation masks were generated from hexagonally close-packed polystyrene nanospheres, each one producing a different array of TiO₂ nanoparticles. Atomic force microscopy (AFM) showed that the masks typically consisted of ordered 10–100 μm^2 domains. X-ray photoelectron spectroscopy confirmed that the surface composition of the particles corresponded to TiO₂ with minor amounts of a Ti³⁺ species, presumably associated with edges, corners and oxygen vacancy defects. Analysis of the AFM images indicated that the nanoparticles were circular in shape with array dimensions approximately consistent with simple geometric considerations for the 420 nm diameter polystyrene nanospheres used as masks in this work. The monolayer and bilayer masks yielded TiO₂ particle diameters of 169 ± 12 nm and 140 ± 13 nm, respectively. The absorption edge of the nanoparticle arrays were blue-shifted from single-crystal rutile.

3.1 Introduction

There is a need to understand the chemical properties of nanostructured materials on a fundamental atomic level. In catalysis and surface science, lithography patterned surfaces have been proposed as model nanostructures.¹ Such an approach would also be beneficial to understanding the size-dependent photocatalytic activity observed for TiO₂ nanoparticles.^{2,3} Standard lithography techniques, using photon or electron beams, produce nanostructures, but they are limited by factors such as high cost and low sample throughput.^{4,5} An alternative method, nanosphere lithography (NSL),⁶⁻⁹ is a general, inexpensive, and flexible process to produce nanostructures (refer to Section 1.5). In addition, unlike solution phase synthesis of nanoparticles or self-assembled nanostructured materials, the arrays produced by NSL are near identical in size and shape. Nanosphere lithography should be applicable to growing many oxide nanoparticles, including TiO₂, on a variety of substrates including single-crystals, introducing the potential for controlling nanoparticle crystallography through epitaxy.

This chapter reports the preparation and characterization of TiO₂ nanoparticle arrays using nanosphere lithography. We present our assessment of how this method can be applied to grow TiO₂ nanoparticles. The emphasis of this work was focused on mask formation and included evaluating substrate preparation, controlling the evaporation rate of the polystyrene sphere solution, and developing approaches to determine mask quality. Both monolayer and bilayer 2D crystalline polystyrene sphere masks were produced on glass and TiO₂(110) single crystal substrates. Masks on glass substrates were used to make two different nanostructured patterns: single layer periodic particle arrays (SL-PPA) and double layer periodic particle array (DL-PPA). Atomic force microscopy and

X-ray photoelectron microscopy were used to evaluate the quality of the masks and arrays produced. The absorption edge of the TiO₂ nanoparticle arrays was also examined.

3.2 Experimental

Substrate Preparation. Glass substrates (10 × 10 × 1 mm) were cleaned by immersion in piranha solution (3:1 concentrated H₂SO₄:30% H₂O₂ – *caution, strong oxidizer*) at room temperature for 15 minutes, followed by rinsing with copious quantities of deionized water and sonication for 30 minutes in 5:1:1 H₂O:NH₄OH:30% H₂O₂ solution. Following sonication, the substrates were rinsed with more deionized water, and stored in water for up to 24 hours until used. Rutile TiO₂(110) single crystal substrates (10 × 10 × 1 mm, 99.99% purity, Superconductive Components, Inc., Columbus, OH) were either heated to 500 °C in air for 1 hour or irradiated with ultraviolet radiation from a Hg Arc Lamp (Oriel 6286) operating at 350 W for 2 hours. The lamp was equipped with a condenser lens and a visible/infrared filter (~ 1M NiSO₄ solution) that primarily transmitted wavelengths in the range between 225 and 350 nm.

Contact Angle Measurements. Advancing contact angles of water were measured in air with an AST model VCA-2500XE goniometer, using the sessile drop technique in which a drop (~2 μL) was formed on the end of a hydrophobic, blunt-ended needle. The sample was raised until the drop touched the surface, and then the needle was removed and the contact angles were measured.

Nanoparticle Array Preparation. Masks were created using the technique of nanosphere lithography.⁶⁻⁹ Solutions of surface-modified polystyrene nanospheres

derivatized with carboxylate (Bangs Laboratories, Inc., Fishers, IN) were diluted to a working concentration (see Appendix B) and used without further treatment. A 10 μL volume of the solution was drop-coated onto the prepared substrate to form the nanosphere mask. The mask-covered glass substrates were then placed in a vacuum chamber and evacuated to 2×10^{-8} Torr. A custom-built evaporation source containing a resistively heated Ti ribbon filament effusively coated the room temperature substrate. No attempt was made collimate the Ti beam. Titanium dioxide was deposited by back-filling the chamber with O_2 to approximately 10^{-6} - 10^{-5} Torr during evaporation. Subsequent removal of the polystyrene masks was accomplished by sonication in 100% ethanol or CH_2Cl_2 for 3-4 minutes.

AFM Analysis. Images were taken using a Digital Instruments Nanoscope III AFM operating in contact mode in air using a standard silicon nitride probe with a spring constant of approximately 0.06 N/m. Micrographs were collected at several different positions on the surface in both height and deflection modes to ensure that the images obtained were representative. The AFM images presented in this chapter represent raw, unfiltered data. Cross-sectional image analysis and root-mean square (RMS) roughness analysis was performed using Nanoscope software. Further image analysis of the packing order within the masks was performed using SCION Imaging¹⁰ and Image J Software.¹¹

XPS Analyses. A Perkin-Elmer Φ 5100 series XP spectrometer (base pressure 2.0×10^{-10} Torr) equipped with an unmonochromatized Al $\text{K}\alpha$ ($h\nu = 1486.6$ eV) source operating at 300 W was used to acquire XP spectra. All spectra were collected using a hemispherical mirror analyzer operating at a pass energy of 44.7 eV, and acquired at

normal takeoff angle (90° from the surface plane). After a Shirley-type background subtraction, the spectra were fit using simple Gaussian-Lorentzian peak shapes. The observed BE's were referenced to the adventitious C 1s photoemission line at 285.0 eV and compared to reference XP spectra of a $\text{TiO}_2(110)$ single crystal ($10 \times 10 \times 1$ mm, 99.99% purity, Superconductive Components, Inc., Columbus, OH) measured in our spectrometer.

UV-Visible Spectra. An ATI Unicam UV2 instrument was used to determine the absorption edge of the nanoparticle arrays. A rutile $\text{TiO}_2(110)$ single crystal (99.99% purity, Superconductive Components, Inc., Columbus, OH) was also measured as a reference.

3.3 Results and Discussion

3.3.1 Mask Preparation

Substrate Preparation. In order to create TiO_2 nanoparticle arrays of uniform size and shape, the polystyrene sphere masks used in NSL must contain large defect-free domains. It was found that to achieve successful self-assembly of a close packed layer of polystyrene spheres, several factors had to be controlled. First, an aqueous suspension of polystyrene spheres must be able to freely diffuse in solution across a substrate. Therefore, to promote surface diffusion, the substrate must be hydrophilic. In the previous NSL studies, glass substrates have been used since they are easiest to prepare and work with.⁷⁻⁹ In our work, self assembly of polystyrene spheres was also investigated on rutile single crystals, to determine if alternative supports to glass could be used.

Cleaning glass substrates with the procedure described in the experimental section of this chapter functionalizes the glass surfaces with hydroxyl groups, making them hydrophilic with average contact angles of $6 \pm 2^\circ$ for a pure water droplet (Table 3.1). A clean defect free $\text{TiO}_2(110)$ surface is naturally hydrophobic with contact angles of $\sim 84^\circ$. However, by treating the surface with UV irradiation or heating in air, the $\text{TiO}_2(110)$ surface could be transformed to a hydrophilic one (Figure 3.1). It is believed that irradiation of the TiO_2 surface allows for photon-stimulated desorption of surface oxygen atoms, creating oxygen defects that act as sites for dissociative water adsorption.¹²⁻¹⁴ Heating the TiO_2 single crystal creates similar defects at the surface, producing surface Ti^{4+} -OH groups that decrease the hydrophobicity of TiO_2 .^{15,16} The advancing water contact angles for the treated TiO_2 surfaces are shown in Table 3.1 and are in agreement with previous studies.^{13,14,17}

Table 3.1 Advancing contact angles for glass and TiO_2 substrates.

	Cleaned Glass Slides	Untreated $\text{TiO}_2(110)$ Single Crystal	UV Treated $\text{TiO}_2(110)$ Single Crystal	Heated (500°C) $\text{TiO}_2(110)$ Single Crystal
Water Contact Angles	$6 \pm 2^\circ$	$84 \pm 3^\circ$	$10 \pm 3^\circ$	$8 \pm 3^\circ$

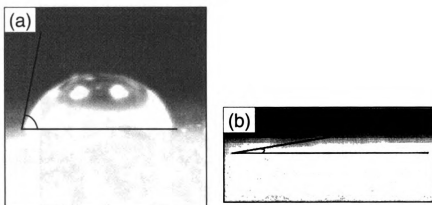


Figure 3.1 Average advancing water contact angles for rutile $\text{TiO}_2(110)$ single crystal: (a) clean, untreated surface and (b) UV treated surface.

In addition to achieving wetting by an aqueous drop of polystyrene spheres, the density of OH^- groups produced from hydrophilic substrates also allows for lateral migration of the polystyrene spheres along the surface. The mobility of negatively charged spheres (surface-modified with carboxyl in our case) is promoted by the electrostatic repulsion between the sphere and the negatively charged surface. With a sufficient surface density of hydroxyl groups, migration of the spheres and self-assembly can occur.

Evaporation Rate. The second key factor in controlling the quality of the polystyrene sphere mask is the rate of solvent evaporation compared with the rate of surface diffusion and packing. If the evaporation rate of the solvent is too high, disordered layers do not have a chance to anneal sufficiently and masks containing agglomerates, poor packing order, uncovered regions and multiple layers are produced. An example is shown in Figure 3.2.

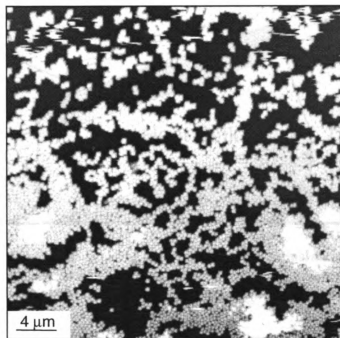


Figure 3.2 AFM 1600 μm^2 area image (height mode) showing poor packing of 420 nm polystyrene spheres on glass when evaporation rate is uncontrolled. Images were similar for TiO_2 when evaporation is not controlled.

To improve 2-D crystallization, a Plexiglass chamber was designed as shown in Figure 3.3. This chamber incorporated similar strategies to Michelletto et al.,¹⁸ Rakers et al.,¹⁹ and Burmeister et al.²⁰ The chamber contained a Peltier cell (Tellurex Corp., Traverse City, MI) tilted to $\sim 10^\circ$ from the horizontal plane. This arrangement minimized any thermal gradients on the surface and allowed 2-D crystallization to commence at the uppermost edge of the drop where the solution film was thinnest. Saturated K_2SO_4 salt solution placed inside the chamber maintained a relative humidity inside the chamber of $\sim 97\%$, further reducing the rate of evaporation.

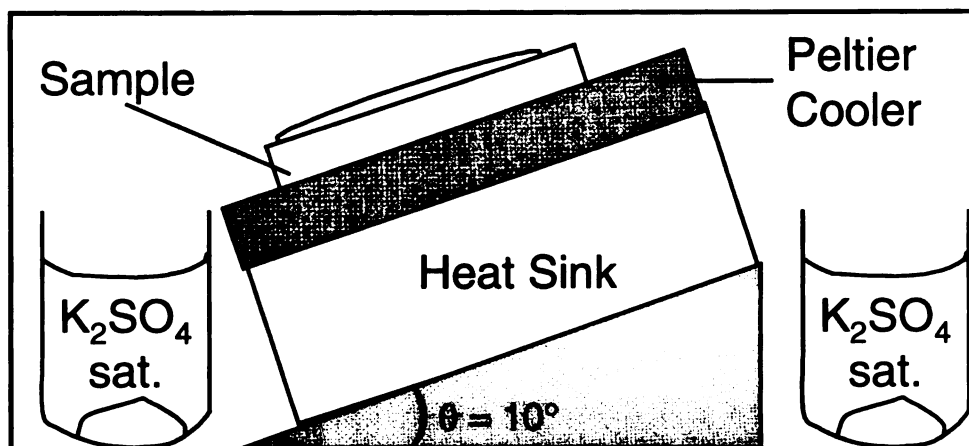


Figure 3.3 Schematic drawing of experimental preparation chamber used for nanosphere lithography masks. A Plexiglass box encases a sample placed on a tilted Peltier cooler. The relative humidity is fixed using saturated salt solutions.

Using this experimental preparation chamber, ordered polystyrene masks have been produced on glass and TiO₂(110) substrates. Typical domain sizes were on the order of 10-100 μm^2 as shown in the AFM image in Figure 3.4 for a mask made from 420 nm diameter nanospheres. The masks consist of a monolayer of spheres forming an ordered close-packed hexagonal array on the surface.

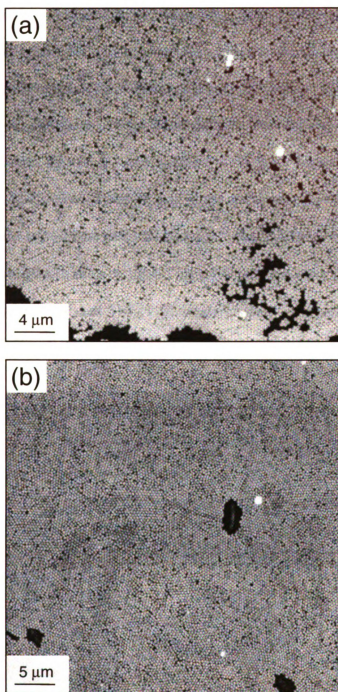


Figure 3.4 AFM image (height mode) of 420 nm polystyrene spheres in a close packed array under controlled conditions: (a) 1600 μm^2 area on $\text{TiO}_2(110)$ single crystal and (b) 2500 μm^2 on glass.

Mask Quality. An optical microscope assisted in initially determining the condition of the films, as ordered layers of spheres exhibited different uniform colors. It has been suggested that these colors are due to interference of light at plane parallel films.²¹ AFM measurements provided images of the masks of different thickness (monolayer, bilayer, multilayer). Monolayer images were typical to the ones seen in Figure 3.4. It should be noted that variations in "height" between the nanospheres, visible as spheres of different shades of gray in the monolayer masks, are due largely to polydispersity in the nanosphere diameter and not to the roughness of the substrate. The substrate has typical RMS values of 1.0 nm for a 100 μm^2 area on a freshly cleaned glass substrate and a freshly polished $\text{TiO}_2(110)$ single crystal. A typical AFM image of a glass substrate is shown in Figure 3.5.

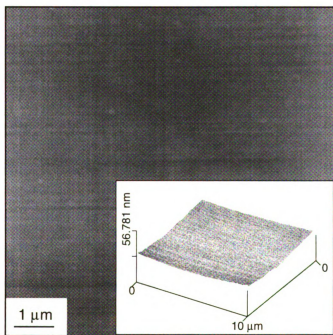


Figure 3.5 AFM 100 μm^2 area image (height mode) of a freshly cleaned glass substrate. Inset shows 3D surface plot of image.

Figure 3.6 shows a representative bilayer mask. Order in a double layer mask was generally more difficult to control than in a monolayer, as multilayers tended to form at high polystyrene sphere concentrations. However, from Figure 3.6 it is evident that the bottom layer at the uppermost portion of the image has large ordered hexagonal domains. The inset in Figure 3.6 shows a higher magnification area ($100\ \mu\text{m}^2$) of the edge of a double layer mask. Disorder is evident at the overlap between the two layers. It should be noted that images of the edge of the bilayer system, showing a monolayer of nanospheres underneath, were relatively rare: most of the surface contained simple close-packed mask features.

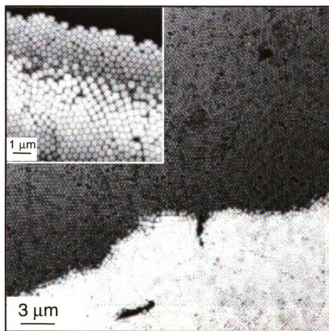


Figure 3.6 AFM $900\ \mu\text{m}^2$ area image (height mode) of a double layer mask made of 420 nm polystyrene spheres. Inset, $100\ \mu\text{m}^2$ area, shows edge of double layer.

A deviation from hexagonal packing was observed occasionally in the bilayer and multilayer masks. In some instances, cubic "square" packing was favored as shown below in Figure 3.7. This type packing may be due to spheres that are confined in a narrow region between two different ordered hexagonal close-packed regions of spheres within the mask.²² It also should also be noted that the hexagonal packing is an equilibrium structure, and other structures such as square packing may be found in some regions of the mask. Square packing was not observed in the monolayer masks in this work, and was found only in bilayer or multilayer masks.

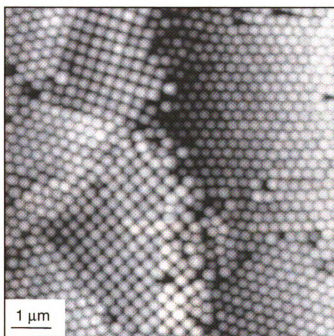


Figure 3.7 AFM $100\ \mu\text{m}^2$ area image (height mode) of a multilayer mask made of 330 nm polystyrene spheres. Square packing is evident in the mask in the center of this image, located between two hexagonal close-packed regions.

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Although, AFM provides visual evidence of the quality of the masks, this method does not provide quantitative information. Additional analyses were completed to assess the mask quality. These included autocovariance analyses as well as particle counting.

Figure 3.8 shows a $100\ \mu\text{m}^2$ AFM image of a 420 nm polystyrene monolayer mask on a glass substrate.

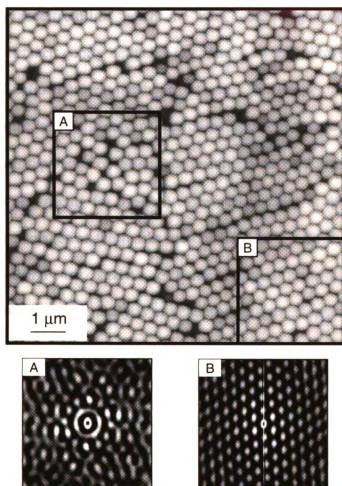


Figure 3.8 AFM $100\ \mu\text{m}^2$ area image (height mode) of 2D hexagonal close-packed mask made of 420 nm polystyrene spheres on a glass substrate. Insets show autocovariance analyses of AFM image: Inset (A) is autocovariance of disordered region within mask; Inset (B) is an autocovariance of an ordered region within the mask.

The insets in Figure 3.8 represent autocovariance analyses of parts of the AFM image. These are the correlation products of the image data as they are shifted relative to one another and can indicate the degree of order within various regions of the masks. Autocovariance images were used here to provide additional qualitative and some quantitative description of the quality of the masks produced. Less ordered polystyrene sphere regions produced autocovariance images that consisted of rings, as shown in inset A. The autocovariance from this part of the mask indicates general disorder, with the nearest neighbor distance poorly defined. In contrast, inset B shows an autocovariance image with a well-defined nearest neighbor distance. This image of a hexagonal pattern of dots, highlights the inherent hexagonal periodic features in the mask and indicates that the average size and separation of the surface features is 420 ± 7 nm, consistent with the expected interparticle spacing for a 6-fold close packed array of 420 nm nanospheres. The autocovariance images of the masks are comparable to a Fourier transform power spectrum and to other Fourier analyses of colloidal crystal growth.^{18,23} They are also consistent with autocovariance analysis of generated models of sphere packing as found in Appendix C.

Multiple AFM images of different areas of the masks, similar to those shown in Figure 3.8, indicate that the degree of 2-D crystallization of the spheres is approximately uniform across a 10×10 mm glass substrate. From these measurements we estimate that roughly 50% of the nanospheres deposited on the glass substrate were in ordered environments.

In addition to autocovariance evaluations, we have also tried to evaluate the quality of the masks through particle counting of the spheres found in a given AFM

image. An example is shown in Figure 3.9. There is some variability in this approach, as the threshold of the image has to be adjusted manually by the user. This threshold allows the program to be able to distinguish an object in the image as being counted as a sphere, and by varying it a different number of spheres may be calculated. The particle counting procedure as shown in Figure 3.9 succeeded in detecting point vacancies and counting spheres, except at the edges of the image where a complete sphere was not present. For Figure 3.9, it was found that there is an 11% difference in the number of particles counted using the Image J Software¹¹ and for theoretical $100\ \mu\text{m}^2$ area of hexagonal close-packed mask of 330 nm spheres.

In general, the masks prepared using the experimental methods described in this chapter are moderately well ordered. With continued optimization of the nanosphere deposition procedure we expect to be able to improve the order of the masks further. Although suitable masks have been prepared on TiO_2 single crystals as well as glass substrates, at this time they have not been used to create TiO_2 nanoparticle arrays. This is partially due to the high cost of $\text{TiO}_2(110)$ substrates. In addition, there are experimental difficulties associated with distinguishing the TiO_2 nanoparticles from the TiO_2 substrate with characterization measurements such as XPS. The characterization of the TiO_2 nanoparticle arrays on glass substrates will be described in Section 3.3.2.

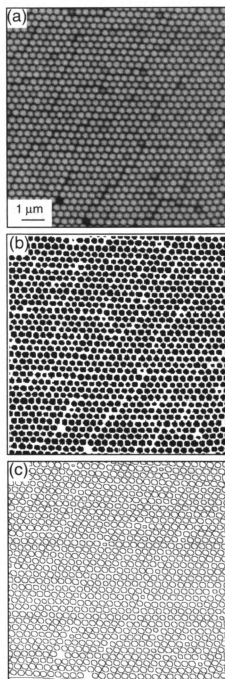


Figure 3.9 Particle counting of the spheres in a AFM $100\ \mu\text{m}^2$ area image (height mode) of 2D hexagonal close-packed monolayer mask made of 330 nm polystyrene spheres on a glass substrate: (a) AFM image, (b) threshold set to distinguish spheres, and (c) particle counting analysis of image b. The theoretical maximum number of spheres is 1169 particles and 1040 spheres were counted using the Image J Software.

3.3.2 TiO₂ Nanoparticle Arrays

XPS Analysis. Using close-packed 420 nm polystyrene nanospheres as masks, TiO₂ nanoparticle arrays have been fabricated using the approach described in the Experimental Section. The average composition of the particles was confirmed using XPS. Previous XPS studies have demonstrated that various Ti oxides can be distinguished based on their Ti 2p XPS spectrum.²⁴⁻²⁷ For example, the Ti 2p_{3/2} peak in TiO₂ is at approximately 459.0 eV, in Ti₂O₃ is at approximately 457.6 eV and in TiO is at approximately 455.3 eV. Metallic Ti exhibits a 2p_{3/2} peak at 453.8 eV. Figure 3.10 shows the Ti 2p spectrum of a nanoparticle array grown on glass after removal of the polystyrene mask. The shape, BE and spin-orbit splitting of the Ti 2p photoemission envelope are characteristic of TiO₂. Comparison with the spectrum of a TiO₂(110) single crystal, shown in Figure 3.10(a), with that of the TiO₂ nanoparticle array, shown in Figure 3.10(b), reveals some evidence for Ti³⁺ species as indicated by a slight low BE shoulder on the Ti 2p_{3/2} emission peak. Quantitating the concentration of Ti³⁺ on the surface is difficult due to the close proximity of the Ti⁴⁺ (TiO₂) and Ti³⁺ binding energies, but it is on the order of a few percent. The large surface area-to-volume ratio and high curvature of these particle surfaces suggest that these Ti³⁺ species may be associated with corner, edge, or terrace defect sites. It should be noted that the sampling depth of the XPS technique at these binding energies is about 6 nm, meaning that a substantial fraction of the interior of each nanoparticle is not probed. However, these data confirm that the surface of the nanoparticles is predominately composed of TiO₂.

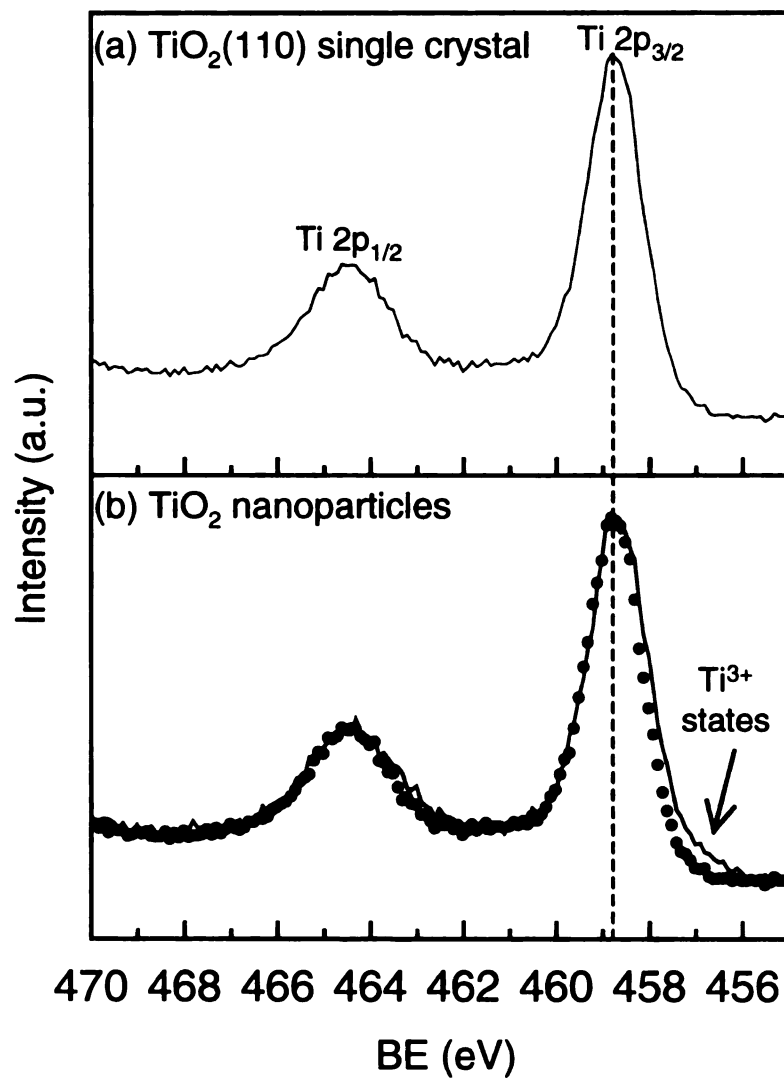


Figure 3.10 XPS comparison of Ti 2p region for rutile $\text{TiO}_2(110)$ single crystal and TiO_2 nanoparticle arrays on glass substrates. The dotted line in part (b) corresponds to the data in part (a) and highlights the presence of Ti^{3+} surface species on the nanoparticle.

AFM Analysis. Atomic force microscopy was used to characterize the distribution and shape of the nanoparticles produced by the nanosphere lithography method. The nanoparticle arrays and shapes were compared to geometric models (Figure 3.11) for a single layer periodic particle array (SL-PPA) and double layer periodic particle array (DL-PPA) produced from a monolayer and bilayer mask respectively.

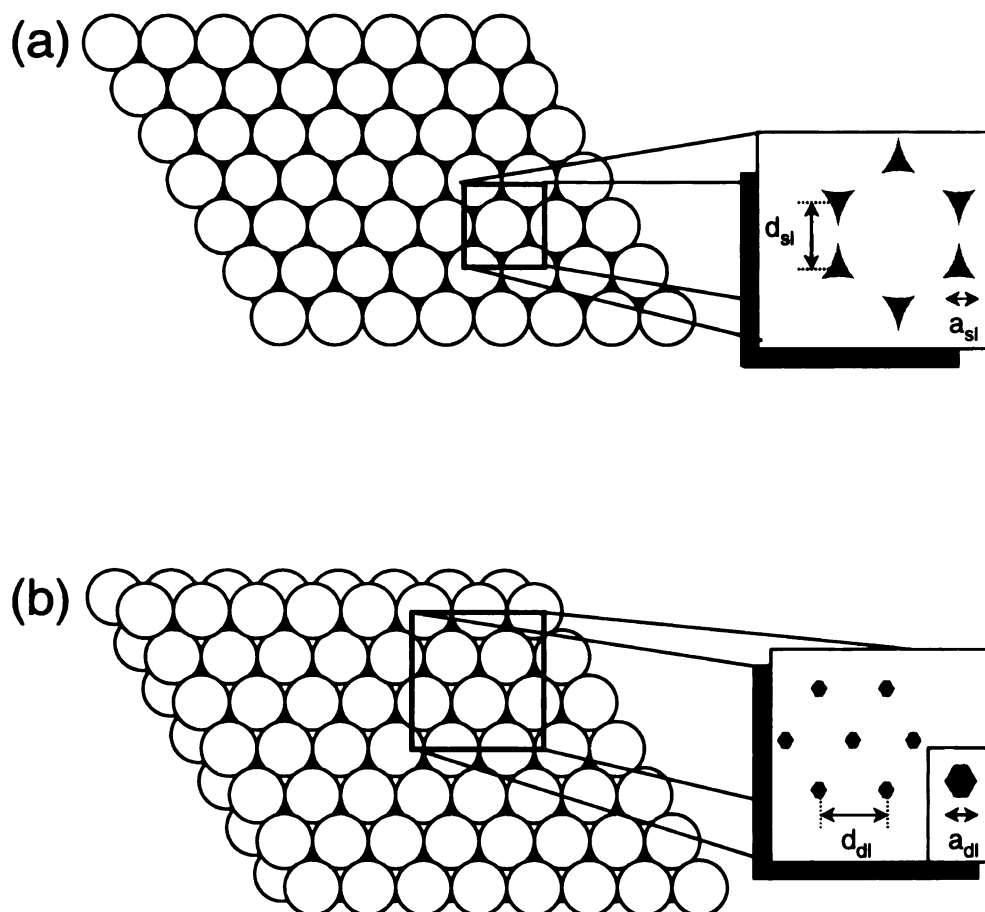


Figure 3.11 Projection of the holes created by (a) single layer mask and (b) a double layer mask. For the monolayer mask the predicted particle geometry in a single layer periodic particle array (SL-PPA) is described as follows: an equilateral triangle with an interparticle spacing of, $d_{sl} = 0.577D$, and an in-plane particle diameter of, $a_{sl} = 0.233D$, where D is the diameter of the sphere used to make the mask. For the bilayer mask the predicted particle geometry in a double layer periodic particle array (DL-PPA) is as follows: a regular hexagon with an interparticle spacing of, $d_{dl} = D$, and an in-plane particle diameter of, $a_{dl} = 0.155D$ (Adapted from Hulsteen et al.⁷).

Figure 3.12 shows an ordered array of TiO_2 particles on a glass substrate. The spatial arrangement of the particles is consistent with a single layer periodic particle array (SL-PPA) derived from a monolayer of 420 nm diameter spheres. The array shows hexagonal primitive surface unit cells, the "diameter", D , of which is 414 ± 8 nm and the interparticle distance, d_{sl} , is 248 ± 12 nm. These dimensions are consistent with geometric projection arguments using a monolayer 420 nm nanosphere mask. AFM cross sectional analysis indicates that the nanoparticles are approximately uniform in size with a height of 13 ± 2 nm and an apparent diameter, a_{sl} , measured at the base of the particle, of 169 ± 12 nm. The height can be varied by changing the deposition time.

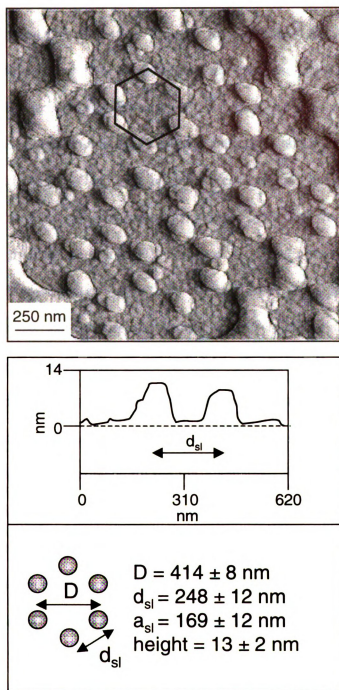


Figure 3.12 AFM 4 μm^2 area image (deflection mode) and cross sectional height analysis of TiO₂ nanoparticle array on a glass substrate. This particle array is typical of that made from a single layer mask made of 420 nm polystyrene spheres.

Although the interparticle spacing of the nanoparticle array in Figure 3.12 is in agreement with geometric projection arguments, the shape and size of the TiO_2 nanoparticles produced from the SL-PPA deviate from those expected. Geometric models for a SL-PPA indicate that the shape of the free space between three polystyrene spheres, arranged as in a close-packed monolayer and projected onto the surface beneath, is approximately triangular. The TiO_2 nanoparticles produced here are circular in the plane of the surface and not the triangular shape predicted from this model and predominately observed in the work by Van Duyne et al.⁶⁻⁹ Furthermore, the measured diameter of the nanoparticles is larger than expected from these geometric projection arguments. The largest diameter circle that could be projected through the free space of a hexagonally close-packed 420 nm sphere monolayer, is about 100 nm. The measured diameter of the circular TiO_2 nanoparticles in this work is about 170 nm. Clearly, AFM cross-sectional analysis indicates that material is apparently deposited in the areas of the substrate that should be "shadowed" by the mask spheres. Some possible explanations for the increased size and unexpected shape of the TiO_2 nanoparticles include divergence in the effusive Ti beam during evaporation, AFM tip convolution artifacts, or substantial particle reconstruction due to internal crystallographic or interface effects.

On the basis of the geometry of the evaporation chamber, we estimate that the divergence of the Ti beam has a half-angle of no more than 4° . This will increase the apparent particle diameter by up to 30 nm compared with that expected from simple geometric projection with no beam divergence. However, such a mechanism, while decreasing the overall resolution of the nanosphere lithographic technique, will tend to maintain the expected triangular shape. The magnitude of the particle broadening by

such beam divergence effects will decrease in importance as the diameter of the mask particle decreases.

It is well known that the shape of the tip apex has a significant influence on the apparent resolution of the AFM technique. As such, tip convolution artifacts may contribute to the observed size and edge profile of the nanoparticles depicted in our AFM images. Van Duyne et al^{6,7} found that differences between the theoretical and experimentally measured particle sizes could be partly explained by tip convolution effects. In our studies, the quoted nominal radius of curvature for the AFM tips was 20-60 nm. We estimate that, for a 13 nm thick TiO₂ island measured with a hemispherical tip, such tip convolution artifacts could increase the measured base diameter of the particle by approximately 37-75 nm. Therefore, while tip-particle convolution can account for the apparent increase in diameter, it is not expected to significantly alter the general shape of the particle, and moreover, very similar images were obtained using several different tips or by rotating the scan direction.

It seems likely that thermodynamic considerations leading to general reconstruction of the TiO₂ particle through bulk and/or interface effects, contribute to controlling the particle shape. Such reconstruction may be driven by faceting of the particle, diffusion of material across the surface (at a "wetting" interface), or by surface melting effects. We cannot ascertain at this time what contribution these factors play or provide direct evidence of such effects, but further experiments are underway.

From Figure 3.12 it is also evident that there is some disorder in the SL-PPA, with the presence of larger island-like features. This variability in the array is believed to be due to imperfections in the mask layer, primarily at domain boundaries, vacancies,

dislocations, and regions of general disorder. The disorder may be attributable to the nonuniformity in size of the polystyrene spheres. The supplier of the nanospheres reports coefficient of variation (CV) in the diameters of $<3\%$. Our autocovariance analysis, as in Figure 3.8, is in agreement with these measurements, yielding a $CV \approx 2\%$. There is also some structure evident within the regions between particles. This may be due to roughness of the substrate. However, despite the disorder between 2-D crystalline domains in the masks and substrate roughness, regions of ordered TiO_2 nanoparticles arrays can be deposited.

Using a double layer mask of 420 nm nanospheres, DL-PPAs of TiO_2 nanoparticles were grown on glass substrates. Figure 3.13 shows a $100\ \mu\text{m}^2$ image of the TiO_2 nanoparticle array created from such a bilayer mask. As with the SL-PPA, the structure and dimensions of the DL-PPA are consistent with geometric projection arguments. Instead of a hexagonal primitive surface unit cell for a SL-PPA, the array shown in Figure 3.13 consists of a parallelogram primitive cell with an interparticle spacing, d_{dl} , of 400 ± 10 nm. The in-plane shape of the nanoparticles deposited for a bilayer mask is as expected (approximately hexagonal or circular). However, as with the SL-PPA, the diameter of the nanoparticles is larger than predicted. Atomic force microscopy cross sectional analysis indicates that the nanoparticles produced are roughly uniform in size with a height of 18 ± 3 nm and a base diameter, a_{dl} , of 140 ± 13 nm, compared to a predicted diameter of approximately 65 nm. Similar factors, as with the SL-PPA, may play a role in determining the diameter of particles produced in DL-PPA. Although we cannot yet assess the contribution from each of these factors in the measured diameter, it is known that beam divergence effects would be less significant for

a DL-PPA than for a SL-PPA due to the increased thickness of the mask. As with the SL-PPA, disorder within the bilayer mask is likely the predominate source for inconsistencies in the distribution of particle arrays produced in the DL-PPA.

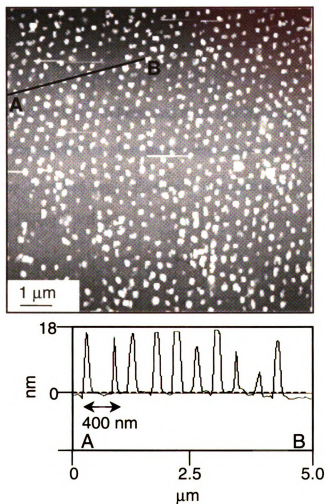


Figure 3.13 AFM $100\ \mu\text{m}^2$ area image (height mode) and cross sectional height analysis of TiO_2 nanoparticle array on a glass substrate. This particle array is typical of a double layer mask made of 420 nm polystyrene spheres.

Optical Absorption. Figure 3.14 shows the absorption edge of a typical TiO₂ nanoparticle SL-PPA array compared to the absorption edge of a bulk TiO₂(110) rutile single crystal. The apparent absorption edge for the TiO₂ nanoparticle array on glass is blue-shifted by ~1 eV compared with the single crystal. At this time, a correlation between optical absorption spectra and TiO₂ particle size has not been systematically studied by us; however, it has been suggested that the position of the absorption edge of TiO₂ nanoparticles may be influenced more by the structure of the particles rather than their size.²⁸ From Figure 3.14 is it evident that there is a significant tail on the absorption edge for the TiO₂ nanoparticles on glass that extends into the visible region (the arrays appear grayish blue to the naked eye). This tail is consistent with TiO₂ containing small particles or high defect levels.²⁹⁻³¹

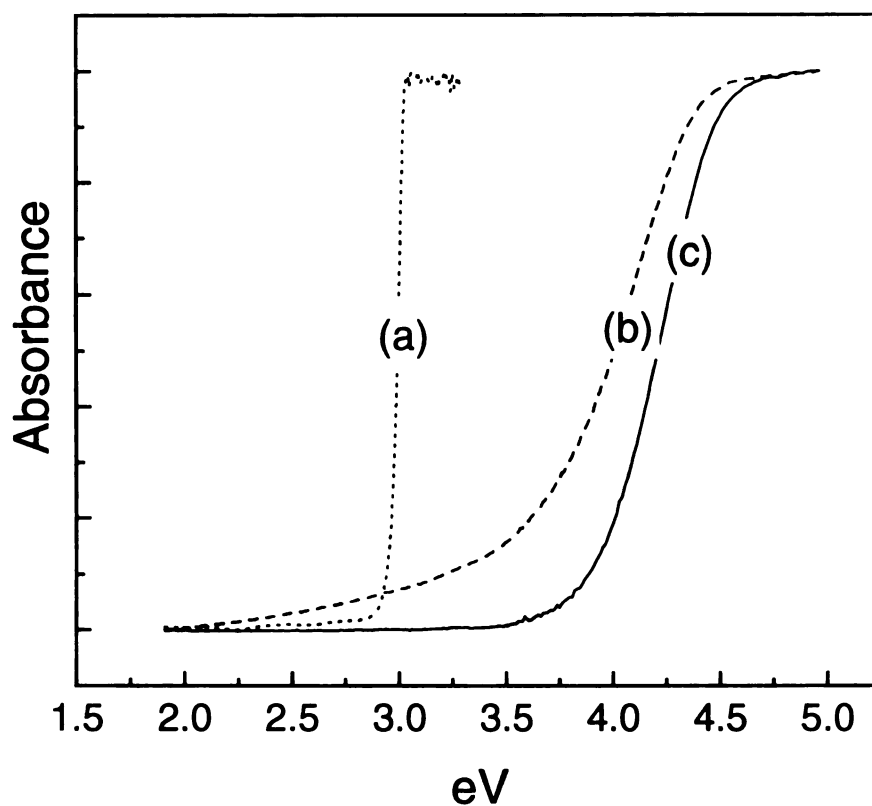


Figure 3.14 UV-Vis absorption spectra of (a) rutile $\text{TiO}_2(110)$ single crystal, (b) SL-PPA of ~ 170 nm diameter TiO_2 nanoparticles on glass substrate, and (c) bare glass substrate. Spectra have been normalized.

3.4 Conclusions

Titanium dioxide nanoparticle arrays on glass substrates have been successfully grown using a nanosphere lithography technique. The polystyrene nanosphere masks used to make the nanoparticle arrays exhibited hexagonal close-packed 2-D crystallization as indicated by AFM images, autocovariance and particle counting analysis. In addition these masks could be grown on TiO_2 single crystals as well as the

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glass substrates used in this work. Using monolayer and bilayer masks of 420 nm nominal diameter polystyrene spheres on glass, two different periodic particle arrays of TiO_2 were produced. XPS indicated the surface composition of the nanoparticles was generally consistent with TiO_2 although it provided evidence for the presence of Ti^{3+} species, probably associated with nanoparticle corners, edges, or defects. Atomic force microscopy measurements of the array parameters were found to be in good agreement with geometric considerations, although the particles produced were somewhat larger than expected and those produced from a monolayer mask were circular, not triangular as anticipated, in shape. Divergence in the Ti beam used to deposit the array and tip artifacts likely contribute to the increased apparent diameter; however, we believe that reconstruction of the particle, driven by interfacial energetic factors, may be responsible for determining the observed particle morphology. Although the individual nanoparticles produced in this study are probably too large to exhibit QSE for TiO_2 , they do have a different optical absorption spectrum compared with rutile single crystals.

The regularity of the nanoparticle structures produced, as well as the properties of smaller TiO_2 nanoparticle arrays will be discussed in more detail in Chapter 4.

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Chapter 4

Characterization of TiO₂ Nanoparticle Arrays

Abstract

Titanium dioxide nanoparticles produced using a nanosphere lithography technique were characterized in detail as a function of particle size. Atomic force microscopy (AFM) analysis indicated that the radius of curvature of the probe tip could significantly impact the measured in-plane shape and dimensions of the nanoparticles, but not the out-of-plane height. Using an etched Si probe of tip radius 5-10 nm, convolution was minimized and a linear relationship of between nanoparticle diameter and mask sphere diameter was found for particles in the 36-386 nm range. Furthermore, AFM analysis indicated that the height of the nanoparticles could be varied independently of particle diameter size. It was observed that the morphology of TiO₂ nanoparticles changed as a function of particle dimension, converting from a triangular (386 nm) to a circular profile (36 nm), with a hexagonal intermediate shape. An additional square TiO₂ particle shape was detected for mask areas that exhibited square packing. X-ray photoelectron spectroscopy confirmed the chemical composition of the nanoparticle surface corresponded to TiO₂ and showed an increase of Ti³⁺ defects with increasing nanoparticle diameter. It was speculated from that the morphological changes observed for the smallest nanoparticles were a result of an increased average Ti-O coordination within the nanoparticle. Raman spectra provided some evidence for a rutile crystallography for the nanoparticles.

4.1 Introduction

In Chapter 3, an investigation of the fabrication of ordered TiO₂ nanoparticles arrays using a nanosphere lithography (NSL) technique was reported. Monodisperse TiO₂ nanoparticles of uniform size and shape were produced.^{1,2} Unlike the triangular particles expected from geometric models³ and observed for Ag nanoparticle arrays using this technique,³⁻⁷ the TiO₂ nanoparticles were larger in diameter than predicted and exhibited a circular profile.

This chapter addresses the origin of the observed differences in diameter and shape of the TiO₂ nanoparticles produced using NSL. The versatility of NSL to create particles with different dimensions was evaluated, with the goal of achieving size and shape tunability. The morphology and composition of the TiO₂ nanoparticles were characterized in detail as a function of particle size using atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). To gain further understanding of factors governing the out-of-plane particle height and in-plane particle diameter, nanoparticles of various dimensions were analyzed and the effect of AFM tip radius on these dimensions was investigated. In addition, the crystallinity of the nanoparticles was examined using powder X-ray diffraction and Raman spectroscopy.

4.2 Experimental

Nanoparticle Array Preparation. Titanium dioxide nanoparticle arrays on glass substrates were created using the technique of nanosphere lithography as described in detail in the experimental section in Chapter 3.^{3,5-7} In brief, solutions of surface-carboxylate derivatized polystyrene nanospheres of 960 nm, 420 nm, 330 nm, (Bangs

Laboratories, Inc., Fishers, IN) 220 nm, and 100 nm (Interfacial Dynamics Corp., Portland, OR), were used to make masks of various dimensions. The coefficient of variance for the sphere diameter as quoted by the manufacturer was 960 nm: 2%, 420 nm: 3.5 %, 330 nm: 3 %, 220 nm: 4.6%, and 100 nm: 10%. In all cases, hexagonally close-packed monolayers and bilayers were produced after careful optimization of the evaporation conditions.

AFM Analysis. Images of the mask layers and nanoparticles were acquired using a Digital Instruments Nanoscope III AFM operating in contact mode in air using etched silicon probes with a spring constant of approximately 0.06 N/m and a radius of curvature, r , of 5-10 nm. Comparison measurements were made using a standard silicon nitride probe with a spring constant of approximately 0.06 N/m and radius of curvature of 20-60 nm. Micrographs were collected at several different positions on the surface in both height and deflection modes to ensure that the images obtained were representative. The AFM images presented in this chapter represent raw, unfiltered data. Cross-sectional image analysis and root-mean square (RMS) roughness analysis was performed using Nanoscope software. Reported nanoparticle dimensions are representative of >30 cross sections from multiple regions on a sample.

XPS Analyses. A Perkin-Elmer Φ 5100 series XP spectrometer (base pressure 2.0×10^{-10} Torr) equipped with an unmonochromatized Al $K\alpha$ ($h\nu = 1486.6$ eV) source operating at 300 W was used to acquire XP spectra. All spectra were collected using a hemispherical mirror analyzer operating at a pass energy of 44.7 eV, and acquired at normal takeoff angle (90° from the surface plane). After a Shirley-type background subtraction, the spectra were fit using simple Gaussian-Lorentzian peak shapes. The

observed BEs were referenced to the adventitious C 1s photoemission line at 285.0 eV BE and compared to reference XP spectra of a TiO₂(110) single crystal (10 × 10 × 1 mm, 99.99% purity, Superconductive Components, Inc., Columbus, OH) measured in our spectrometer.

Raman Spectroscopy. The TiO₂ nanoparticle arrays were analyzed with a Raman 2000 Chromex instrument equipped with a microprobe, CCD detection system, and using a diode-pumped solid state laser operating at 532 nm as an excitation source. The spectra were obtained at room temperature with a resolution of 1.0 cm⁻¹. Reference spectra were taken of powdered anatase (99.9% purity, Aldrich Chemical Company, Inc., Milwaukee, WI) and rutile (99.7% purity, Aldrich Chemical Company, Inc., Milwaukee, WI) polymorphs of TiO₂.

Powder X-ray Diffraction. Analyses of the TiO₂ nanoparticle arrays were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer operating at 50 kV/100 mA with a 1°/min scan rate, employing Ni-filtered Cu radiation in a Bragg-Brentano geometry.

4.3 Results and Discussion

AFM Analysis. Atomic force microscopy was used to analyze the distribution and shape of the TiO₂ nanoparticle arrays created from close-packed masks produced from various sizes of polystyrene spheres. As with our previous work on TiO₂ nanoparticle arrays,² it became evident that the in-plane diameter, a_{sl} , of the nanoparticles measured by AFM were larger than expected from geometric predictions.³ In Chapter 3 it was suggested that one of the possible explanations for the apparent increase in

diameter of the nanoparticle compared with expectations based on mask geometry was due to AFM tip convolution effects.⁸⁻¹⁰ This possibility was explored in detail in this chapter by comparing images and cross sectional analyses for various size nanoparticle arrays using standard Si₃N₄ probes with a quoted radius of curvature of $r = 20\text{-}60$ nm and etched Si probes with a significantly smaller radius of curvature of $r = 5\text{-}10$ nm.

Figure 4.1 provides clear evidence that a difference in the radius of curvature of the AFM tip can alter the apparent nanoparticle profile. The TiO₂ SL-PPA produced from a 330 nm polystyrene sphere mask looks markedly different when measured using the two different probes. In Figure 4.1(a), a typical AFM image using the etched Si probe shows triangular TiO₂ nanoparticles with an in-plane diameter of 122 ± 6 nm and a height of 8.1 ± 0.7 nm. However, in Figure 4.1(b), TiO₂ nanoparticles measured with the standard AFM Si₃N₄ probe exhibit elliptical shapes with an apparent diameter of 164 ± 4 nm and a height of 8.2 ± 0.3 nm. The observable difference in the in-plane shape and size of the nanoparticles, measured from the same SL-PPA, confirms that the Si₃N₄ probe with a larger radius of curvature generates feature broadening due to tip convolution. Although, the convolution distorts the lateral x-y dimensions of the nanoparticles, the vertical z dimension (height) is unaffected, as shown in Table 4.1. In addition, the measured interparticle distance, d_{sl} , (measured between the center of the nanoparticles as discussed in Chapter 3) and the “diameter”, D , of the hexagonal primitive surface unit cell are also similar for the two AFM probes, as shown in Table 4.1.

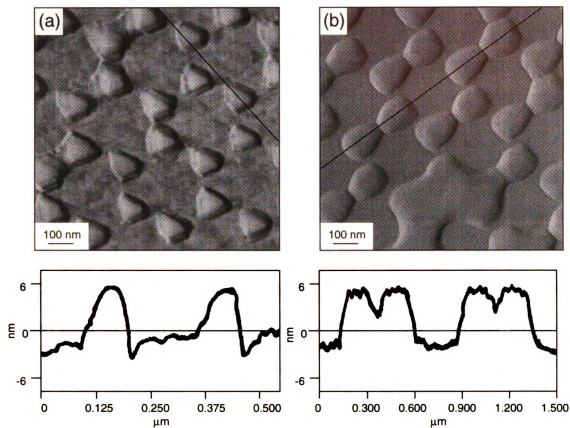


Figure 4.1 AFM $1\ \mu\text{m}^2$ area images (deflection mode) and cross sectional height analyses of TiO_2 nanoparticle array on a glass substrate produced from a 330 nm polystyrene sphere mask. AFM images were measured using (a) an etched Si probe ($r=5\text{-}10\ \text{nm}$) and (b) a standard Si_3N_4 probe ($r=20\text{-}60\ \text{nm}$).

Table 4.1 Structural parameters for TiO₂ nanoparticles produced from a monolayer mask of 330 nm polystyrene spheres; parameters measured using AFM probes with different radius of curvature, r . For a definition of the parameters d_{sl} , D , and a_{sl} see Figure 3.11.

	d_{sl}	D	a_{sl}	Height
Standard Si ₃ N ₄ Probe ($r = 20\text{-}60\text{ nm}$)	$192 \pm 9\text{ nm}$	$327 \pm 3\text{ nm}$	$164 \pm 4\text{ nm}$	$8.1 \pm 0.7\text{ nm}$
Etched Si Probe ($r = 5\text{-}10\text{ nm}$)	$194 \pm 8\text{ nm}$	$330 \pm 4\text{ nm}$	$122 \pm 6\text{ nm}$	$8.2 \pm 0.3\text{ nm}$

Another interesting feature present in the SL-PPA measured with the standard Si₃N₄ tip is that the space between nanoparticles is poorly imaged, as evident in the "bow tie" structures in Figure 4.1(b). These bow tie features, however, cannot be entirely associated with tip convolution effects as they are also occasionally observed in AFM images using the etched Si probe, as shown in the upper left portion of Figure 4.1(a). In general, the bow tie structures in Figure 4.1(a) remain predominately triangular and are smaller in overall lateral dimension compared to those in Figure 4.1(b).

Similar SL-PPAs to that in Figure 4.1(a) were observed for TiO₂ nanoparticles of considerably smaller dimensions, produced from polystyrene spheres of 220 nm and 100 nm diameters. Figure 4.2 shows AFM images (using etched Si probe) of a typical mask and nanoparticle array created from a 220 nm mask. On average, approximately 50% of a 100 mm² glass substrate consisted of 0.5 - 1 μm^2 ordered domains, as shown in Figure 4.2(a). TiO₂ "rows" or islands separate the ordered domains and are a result of dislocations and domain boundaries between ordered hexagonally close-packed regions of the polystyrene sphere masks. Cross sectional analysis of the TiO₂ SL-PPA shown in

Figure 4.2(b) indicates that the TiO_2 nanoparticles are uniform in size with a base diameter of 89 ± 4 nm and a height of 6.0 ± 0.7 nm. As with the 330 nm mask, some “bow tie” features are present within the SL-PPA produced from the 220 nm mask.

For the TiO_2 nanoparticles produced from 100 nm mask spheres, satisfactory AFM micrographs could only be obtained using the etched Si probe tips, an example of which is shown in Figure 4.3. The nanoparticle arrays were comprised of small $0.06 - 0.25 \mu\text{m}^2$ ordered domains. In addition, defects within the mask are also more evident than in masks made from larger spheres, presumably associated with the increased coefficient of variance for the smaller diameter spheres. However, statistical analysis of the cross sectional analysis of the TiO_2 nanoparticles shown in Figure 4.3(b) indicates that they are consistent in size with a diameter of 39 ± 10 nm and a height of 6.3 ± 0.4 nm. These particles are the smallest TiO_2 nanoparticles produced using NSL to date.

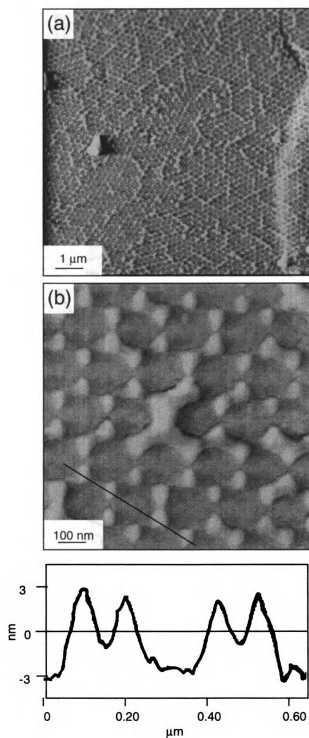


Figure 4.2 AFM images (deflection mode, etched Si probe) and cross sectional height analysis of TiO_2 nanoparticle array on a glass substrate produced from a 220 nm mask: (a) $100 \mu\text{m}^2$ (b) $1 \mu\text{m}^2$.

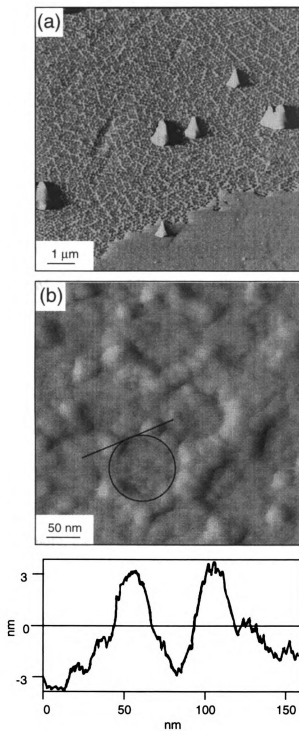


Figure 4.3 AFM images (deflection mode, etched Si probe) and cross sectional height analysis of TiO_2 nanoparticle array on a glass substrate produced from a 100 nm mask: (a) $100\ \mu\text{m}^2$ (b) $0.16\ \mu\text{m}^2$.

Figure 4.4 shows the relationship between the average TiO_2 nanoparticle diameter as a function of polystyrene sphere diameter. It includes the complete statistical analyses of the in-plane particle diameters for the different TiO_2 nanoparticle arrays produced in this work. The experimental diameters measured with the standard Si_3N_4 probe ($r = 20\text{--}60\text{ nm}$) and etched Si probe ($r = 5\text{--}10\text{ nm}$), are shown as square and round data points, respectively, with error bars representing 1 standard deviation in the data for >30 measurements. For comparison, predicted diameters based on geometric models of the masks³ are also presented as triangular data points. Evaluation of the diameters measured from the different AFM probes establishes that unlike for the smaller nanoparticles, the radius of curvature had a minimal affect on the measured in-plane diameter, a_{sl} , of the largest TiO_2 particles in this study (formed from a 960 nm diameter mask): the a_{sl} is effectively identical when measured with both probes. Equally, Figure 4.4 verifies that convolution effects become more pronounced as the dimensions of the nanoparticles decrease. The disparity between the measured a_{sl} for the two AFM probes, for example, increases from 30 nm to 56 nm for polystyrene sphere masks of 420 nm and 220 nm , respectively. Furthermore, the diameters of smallest nanoparticles were distorted to such an extent by tip convolution, that it was impossible to acquire any clear AFM measurements of them using the standard Si_3N_4 probe.

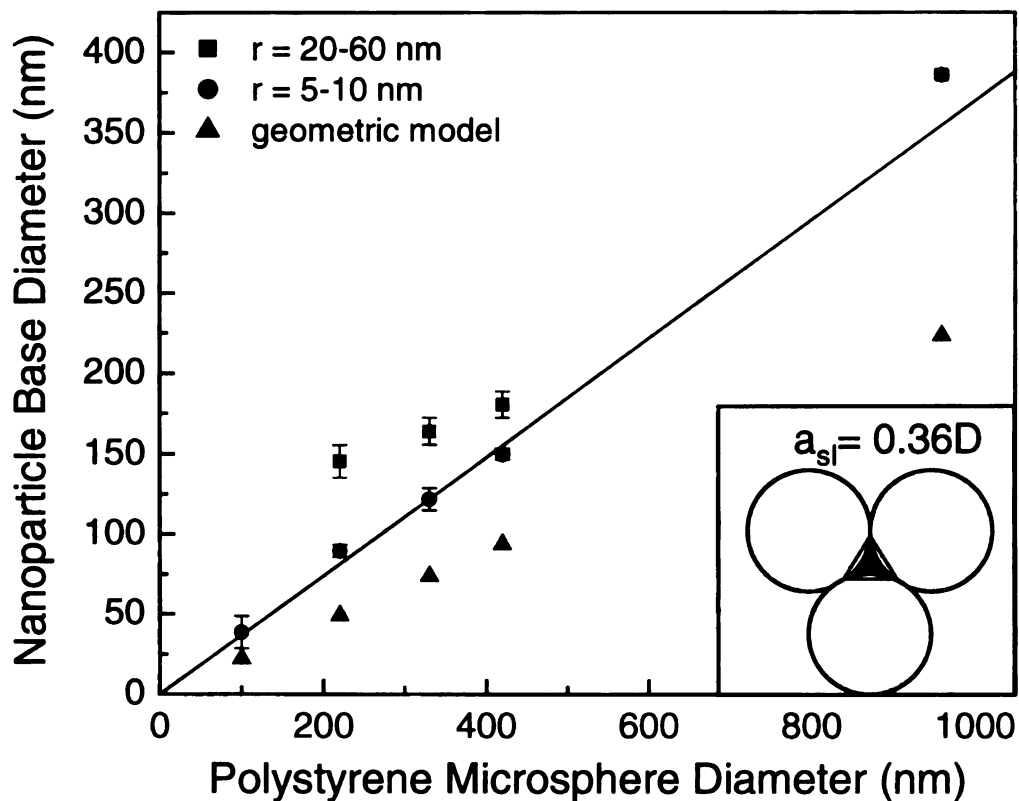


Figure 4.4 Plot of TiO_2 nanoparticle in-plane base diameter, a_{sl} , as a function of polystyrene microsphere diameter, D . Nanoparticle diameters were measured using both an etched Si probe (radius of curvature, $r = 5-10$ nm) and a standard Si_3N_4 probe (radius of curvature, $r = 20-60$ nm). For comparison, predicted diameters based on geometric models of the masks are also displayed. The correlation between a_{sl} and D for the etched Si probe data is shown in the inset with a graphic depiction of a TiO_2 nanoparticle overlaid on top of the spacing in between a hexagonally close packed array of spheres of a given D .

A linear correlation between measured a_{sl} and polystyrene sphere size, D , is absent from the experimental measurements using the standard Si_3N_4 probe. However, there is a direct relationship between a_{sl} and D in the experimental data acquired with the etched Si probe, as predicted from geometric modeling. The experimentally measured dependence of nanoparticle diameter on masks of a given D is given below:

$$a_{sl} = 0.36 D \quad (4.1)$$

The linearity of the data shown in Fig. 4.4 indicates that the radius of curvature of the etched Si AFM probes does not significantly influence the particle diameter by any notable amount, at least for TiO_2 nanoparticles greater than about 36 nm in diameter. Furthermore, it is clear that tip convolution effects were completely absent when analyzing the largest sized TiO_2 nanoparticles (~386 nm diameter).

Despite a linear correlation with polystyrene sphere diameter, D , the measured TiO_2 nanoparticle diameters are approximately 55% larger than those predicted from geometric models published by Van Duyne ($a_{sl} = 0.233D$), as shown Figure 4.4. The inset in Figure 4.4, however, demonstrates that although these nanoparticle dimensions of $0.36D$ are larger than predicted, they are not unreasonable when compared directly to geometric depictions of the void space between a hexagonal close-packed monolayer of spheres of diameter D . Additional factors, such as divergence of the effusive Ti beam during evaporation or interfacial effects between the nanoparticle and glass surface may be the cause for the increased particle dimensions. Calculations, estimating a Ti beam half angle divergence of 4° , indicate that only 30% of the observed increase in nanoparticle diameter can be accounted to beam divergence effects which scale as a function of particle size. This therefore, suggests that the interfacial interaction between

the glass surface and the TiO₂ nanoparticles might be the controlling factor of the projected TiO₂ particle size.

The geometric model largely determines the diameter of the nanoparticle based on the projected free space between a hexagonally close-packed monolayer of polystyrene spheres. According to the inset in Figure 4.4, in which a triangular particle with a perpendicular bisection, $a_s = 0.36D$, is projected over this open space, it appears as if material is deposited underneath the mask spheres. This might be a result of some degree of surface diffusion occurring during or following evaporation. Such diffusion may be expected for a “wetting” system such as a metal oxide deposited on a metal oxide substrate as is the case for TiO₂ on SiO₂. The fact that triangular particles of approximately the expected dimensions are deposited implies that diffusion cannot be very large. Facile surface diffusion would destroy the masking effect.

Surface diffusion might be expected to increase the diameter of the nanoparticle in proportion to the amount of material in each particle. This effect was tested by synthesizing TiO₂ nanoparticles on glass of varying volume from a mask of 330 nm polystyrene spheres. By varying the evaporation duration by a factor of about five, TiO₂ nanoparticles from ~5 to ~25 nm height were generated. The base diameters of these particles were measured by AFM and the results are shown in Figure 4.5. Clearly, the height of the nanoparticle can be varied independent from the diameter. Such an observation also supports the idea that surface diffusion does not appear to contribute to the measured diameter. Moreover, Figures 4.4 and 4.5 together demonstrate that the nanosphere lithography method is flexible and can be used to tune both the TiO₂ nanoparticle diameter and height.

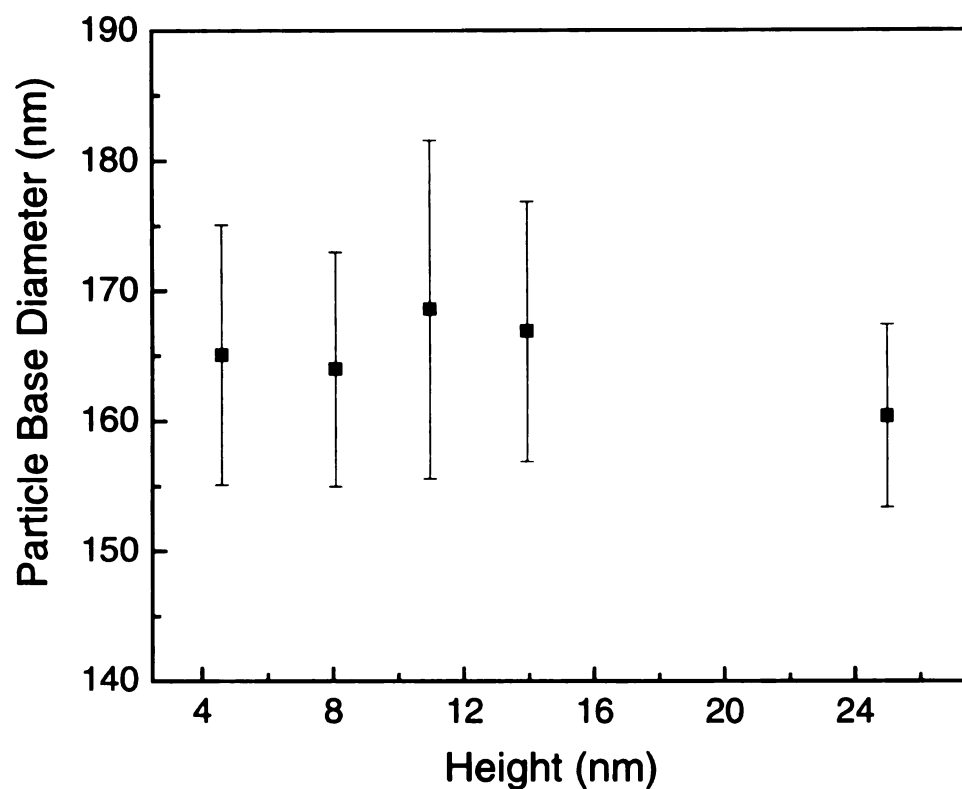


Figure 4.5 Plot of TiO₂ nanoparticle base diameter, a_{sl} , as a function of particle height. Data reported here are for TiO₂ arrays of various heights, produced from a 330 nm polystyrene microsphere mask and measured with a standard Si₃N₄ probe.

In order to learn more about the growth mechanism of the individual TiO_2 nanoparticles, relatively large particles were produced from a $D= 960$ nm mask. Figure 4.6(a) shows a typical ordered SL-PPA for a mask of 960 nm diameter spheres. The array was composed of the characteristic hexagonal primitive surface unit cell with $D= 960 \pm 5$ nm, and $d_{sl}= 550 \pm 4$ nm; dimensions that are consistent with the geometric models. AFM cross sectional analysis indicates that the nanoparticles are uniform in size with a base diameter, a_{sl} , of 386 ± 4 nm and a height of 13.5 ± 0.4 nm. A higher resolution image of the same SL-PPA is shown in Figure 4.6(b). Each triangular TiO_2 nanoparticle appears to display a series of steps and terraces. Although the resolution is not sufficient to determine anything about the crystallography of the TiO_2 nanoparticles, for example by showing atomic detail, it does establish a probable growth mechanism. Figure 4.6(b) points to a layer-by-layer growth of the TiO_2 nanoparticles deposited on glass substrates. Similar growth has been reported for TiO_2 films supported on SiO_2 ^{11,12} and $\text{Mo}(100)$ single crystal¹³ substrates. The layered growth within the nanoparticles, leads to an out-of-plane tetrahedral shape, with terraces that are approximately 80 nm wide. It should be noted that these are not atomic-level terraces, as the step height is ~ 3 -5 nm.

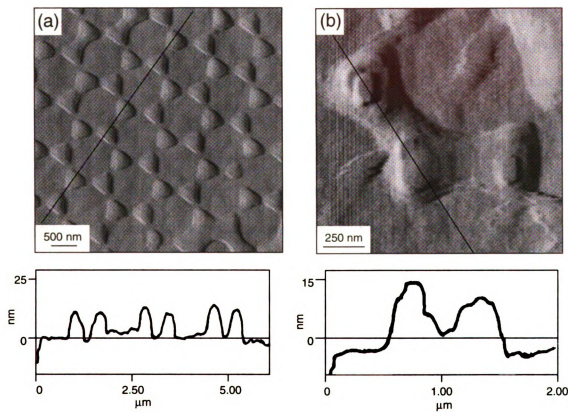


Figure 4.6 (a) AFM 25 μm^2 area image (deflection mode) and cross sectional height analysis of TiO_2 nanoparticle array on a glass substrate. This particle array is typical of that made from a single layer mask of 960 nm polystyrene spheres. (b) AFM 2.25 μm^2 area image (deflection mode) and cross sectional height analysis of TiO_2 nanoparticle array on a glass substrate produced from a 960 nm polystyrene sphere mask, which shows the speculated layer by layer growth of the TiO_2 nanoparticles.

Careful examination of the TiO_2 nanoparticle shape made from various diameter mask particles reveals that the TiO_2 nanoparticle morphology is size-dependent. This is illustrated in Figure 4.7. Large nanoparticles, ~ 386 nm in diameter, are approximately triangular in shape, whereas the smaller nanoparticles, ~ 89 nm in diameter, appear to have a circular profile. This conversion seems to be progressive with decreasing particle size and proceeds through a hexagonal intermediate. For example, hexagonal particles are visible in Figure 4.7(b) for 150 nm TiO_2 particles and for 122 nm TiO_2 nanoparticles as shown in Figure 4.7(c). As the particle size further decreases to 89 nm, as displayed in Figure 4.7(d), the nanoparticles apparently display a uniform circular shape. Van Duyne et al. reported a similar transition from a triangular to an elliptical shape for Ag nanoparticle sizes created from polystyrene sphere masks of $D < 500$ nm^{3,4} and attributed this change in shape profile to surface melting of the nanoparticles. The nanoparticle shape profiles here are likely a result of equilibrium structures. Such changes in particle morphology may result from the increasing contribution of surface energy to the total energy of the nanoparticle as size decreases. The drive towards surface energy minimization, achieved by both Ti coordination and structural constraints, will become more important as the fraction of surface atoms increase. Evidence for an increased average Ti coordination, manifest as a reduction in the number of five-coordinate Ti^{3+} species as the particle diameter decreases, will be discussed below.

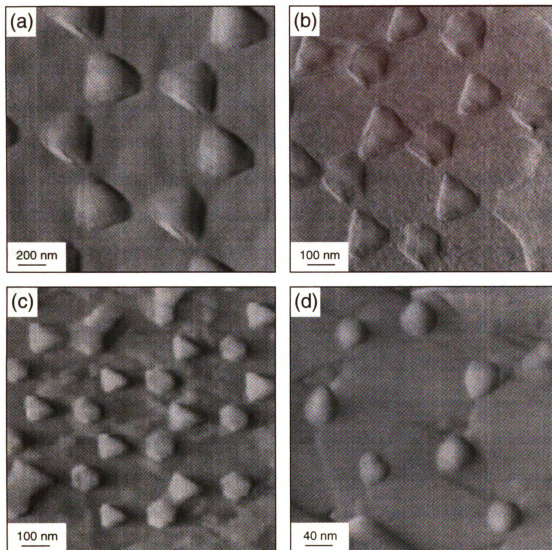


Figure 4.7 AFM images (deflection mode, etched Si probe) of TiO_2 nanoparticle arrays on glass substrates: (a) $4 \mu\text{m}^2$ area image, $D= 960 \text{ nm}$, $a_{\text{sl}}= 386 \text{ nm}$; (b) $1 \mu\text{m}^2$ area image, $D= 420 \text{ nm}$, $a_{\text{sl}}= 150 \text{ nm}$; (c) $1 \mu\text{m}^2$ area image, $D= 330 \text{ nm}$, $a_{\text{sl}}= 122 \text{ nm}$; (d) $0.16 \mu\text{m}^2$ area image, $D= 220 \text{ nm}$, $a_{\text{sl}}= 89 \text{ nm}$.

Unexpectedly, monolayer masks of 960 nm diameter polystyrene spheres contained regions of cubic "square" packing within the characteristic hexagonal close packing, as shown in Figure 4.8(a). Previously, square packing had only been found in multilayers of spheres, as discussed in Chapter 3. This cubic-packed structure is likely an equilibrium structure resulting from the confinement of domains composed of hexagonally close-packed spheres. Since the square packing for the 960 nm spheres is present within a monolayer mask, resulting TiO₂ single layer periodic particle arrays consist of both the typical nanoparticle geometry expected from NSL shown in Figure 4.6 and 4.7(a) as well as a geometry consistent with cubic packing, as found in Figure 4.8(b). Analysis of several 960 nm masks indicates that on average up to 10% of an ordered mask is composed of cubic-packed regions. The TiO₂ nanoparticles produced from these regions, Figure 4.8(b), are approximately square in shape with a diameter of 998 ± 4 nm and height of 12 ± 1 nm. The vertical dimensions of the square TiO₂ nanoparticles are equivalent to triangular TiO₂ nanoparticles made during the same evaporation. To the best of our knowledge, this is the first report of nanoparticles being produced from cubic-packed masks using the NSL technique. If this equilibrium structure within the mask can be generated at will, a new avenue for shape and size tunability may be possible.

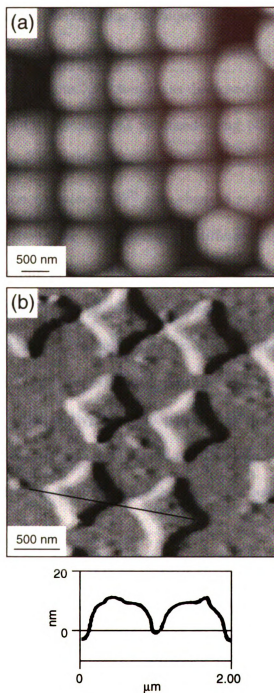


Figure 4.8 (a) AFM 25 μm^2 area image (height mode) of 960 nm polystyrene monolayer mask, with square packing evident in the upper right corner of the image. (b) AFM 9 μm^2 area image (deflection mode) and cross sectional height analysis of subsequent TiO_2 nanoparticle array on a glass substrate produced from a similar mask with square packing as shown in (a).

XPS Analysis. The composition of the TiO₂ nanoparticle arrays was evaluated with XPS. Since the sampling depth of the technique under the experimental conditions used is 6-8 nm, for particles of height less than 6-8 nm, effectively the entire particle composition is measured. Previous XPS studies, as discussed in Chapter 3, had verified that the composition of TiO₂ nanoparticles produced using NSL were consistent with TiO₂, and provided evidence for Ti³⁺ sites on the nanoparticle surface.^{1,2} XPS was used here to determine if the concentration of Ti³⁺ sites changed as a function of nanoparticle diameter. Figure 4.9(a) shows the XPS spectra for different sized TiO₂ nanoparticles overlaid on the XP spectrum of a rutile TiO₂(110) single crystal. The shape, BEs and spin-orbit splitting of the Ti 2p photoemission regions for the nanoparticles are characteristic of TiO₂^{14,15} as demonstrated by the close coincidence with the TiO₂ single crystal. The BEs for the Ti 2p_{3/2} peaks are at approximately 458.9 eV, with a spin-orbit splitting of 5.7 eV. Additionally, the nanoparticle spectra in Figure 4.9(a) are characterized by a low BE shoulder on both of the Ti 2p peaks. For the 2p_{3/2} peak, the additional structure is located at approximately 457.5 eV and consistent with Ti³⁺ states.^{14,16,17}

The simple overlay of the XP spectra suggests that the concentration of Ti³⁺ states is largest for the largest (~386 nm diameter) TiO₂ nanoparticles. Further evidence was obtained by calculating difference spectra (single-crystal minus nanoparticle PPA) for each nanoparticle spectrum shown in Figure 4.9(a), as presented in Figure 4.9(b). The difference spectra show that the nanoparticle spectra have increased intensity between ~458.3 and 454.9 eV, being maximum at ~457.6 eV, for all of the TiO₂ nanoparticles. The magnitude of the intensity gradually decreases as a function of particle size.

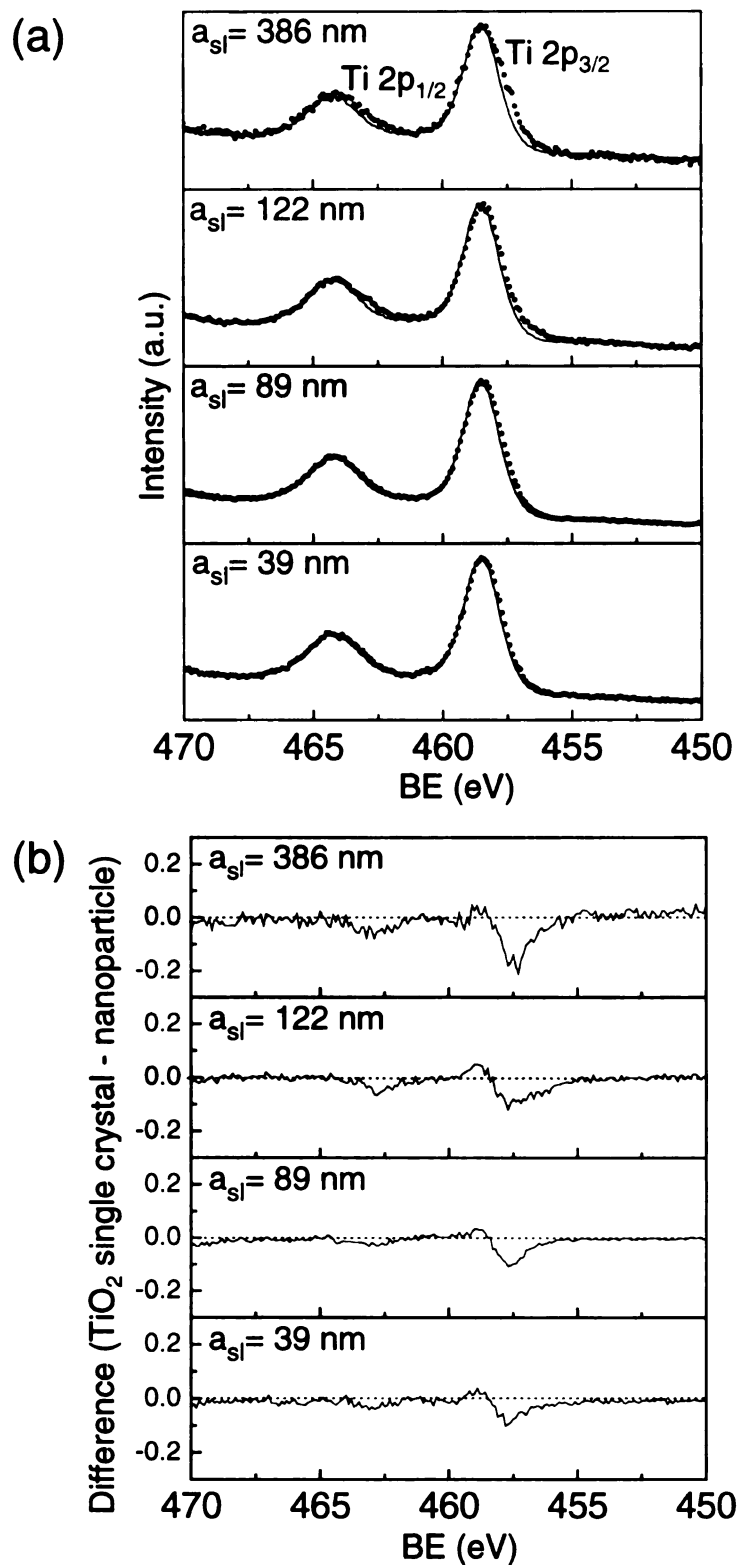


Figure 4.9 (a) XPS comparison of Ti 2p region for TiO_2 nanoparticle arrays on glass substrates and rutile $\text{TiO}_2(110)$ single crystal. The dotted line corresponds to the TiO_2 nanoparticle arrays. (b) Difference spectrum for TiO_2 single crystal minus nanoparticle data.

As a first approximation, the XPS difference data imply that the ratio of Ti^{4+} to Ti^{3+} species is largest for the smallest TiO_2 nanoparticles. Although the XPS technique is most sensitive to the near-surface region, as mentioned above, the technique effectively probes the entire particle in these cases and it is not possible to identify the location of the Ti^{3+} sites. However, it seems likely that they are associated with the surface of the particle since the deposition conditions (especially oxygen partial pressure and temperature) were identical for all nanoparticle syntheses. The observation of size-dependent morphology in these TiO_2 particles coupled with evidence for varying concentrations of Ti^{3+} suggests that these phenomena share a common origin. As such, it is speculated that the particle surface energy becomes more important with reduced diameter and the mechanism responsible for the gross reconstruction of the smallest particles is the oxidation of surface Ti^{3+} sites to Ti^{4+} . Reduced Ti^{3+} sites may be supported on larger TiO_2 particles because the large number of fully coordinated bulk Ti^{4+} atoms dominate the morphology of the particle. However, for smaller particles, the total energy contribution by the surface atoms may become dominant and drive reconstruction through oxidation.

Crystallinity Determination. Different analytical techniques were used to try and assess the crystallinity of the TiO_2 nanoparticles. Previous analysis of TiO_2 films grown on SiO_2 substrates has indicated that the resulting films can exhibit a variety of different phases, including mixtures of anatase and rutile^{18,19}, amorphous,¹¹ and primarily anatase with an amorphous thin layer (~1 nm) between the substrate and the film.²⁰ Although, rutile TiO_2 is the thermodynamically most stable oxide, the glass substrate does not offer any epitaxial control of the nanoparticles and so is not expected to favor any particular

phase over any other. In addition, substrate temperature, oxygen partial pressure and deposition rate can influence the crystallinity of the TiO_2 .

Initial analysis of the crystallinity of the TiO_2 nanoparticles produced here, was determined using powder XRD, as shown in Figure 4.10. Unfortunately, the glass or fused quartz substrates used were incompatible with the XRD analysis of the nanoparticles. Weak ordering within the substrates generated a broad feature in the 2θ region of $20\text{-}25^\circ$, which overlapped with the primary diffraction peaks for the different polymorphs of TiO_2 , as shown in Figure 4.10(a). Therefore, relevant information about the crystallinity of the TiO_2 nanoparticles on glass or quartz substrates cannot be determined: the background of the substrate buried any weak signal from the nanoparticles. To determine if a weak signal was present under this broad background peak, XRD of TiO_2 nanoparticle arrays on oxidized Si substrates was examined, as shown in Figure 4.10(b). Silicon has a narrow diffraction peak at 2θ of $\sim 33^\circ$ which is isolated from the primary diffraction peaks for anatase and rutile TiO_2 . Despite the use of a more appropriate substrate for evaluation of the nanoparticles, however, it is evident from Figure 4.10(b) that no other diffraction peaks are present. The lack of diffraction peaks is inconclusive; it may be due to a limited amount of sample, amorphous nanoparticles, small particles generating broad diffraction peaks or a combination of these factors.

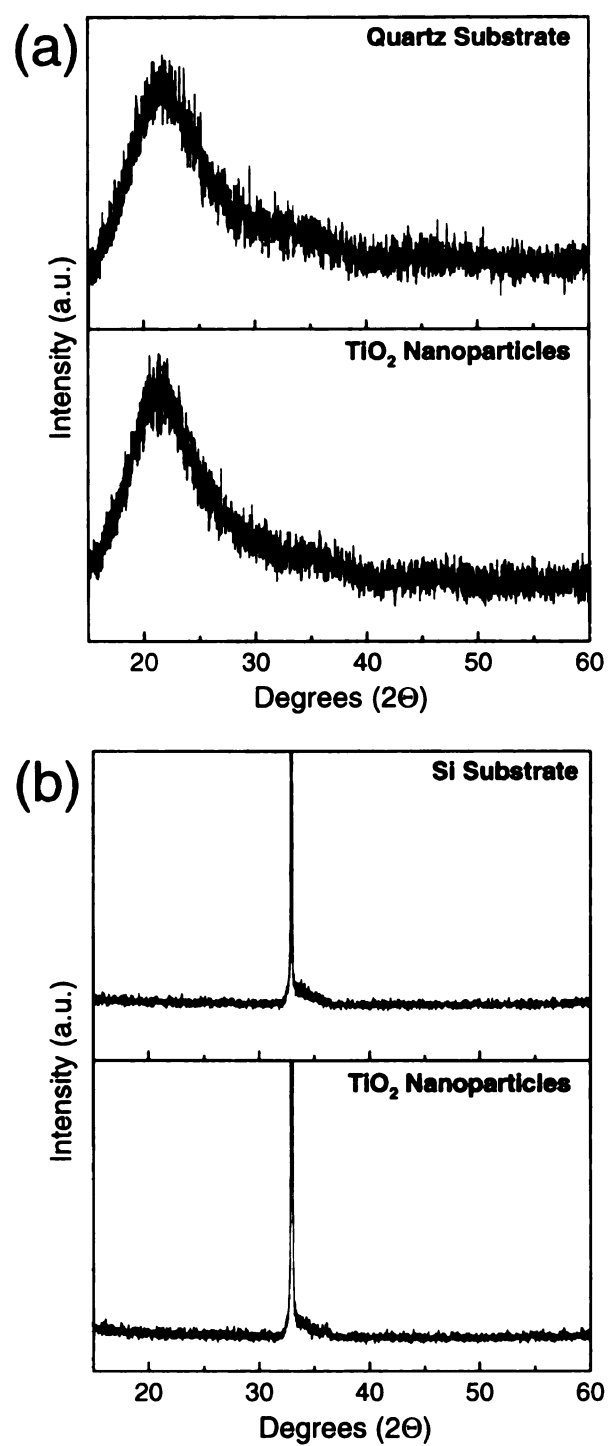


Figure 4.10 Powder XRD of TiO_2 nanoparticle arrays on (a) fused quartz and (b) Si substrates.

Several reports have shown that Raman spectroscopy is another useful technique to determine the crystallinity of TiO₂ films and powders.²¹⁻²⁵ Figure 4.11 verifies that anatase and rutile TiO₂ have distinct Raman active modes. The frequencies and symmetry assignments for the Raman active modes of anatase and rutile samples are given in Table 4.2 and are in agreement with reported values.^{26,27} It should be noted that the rutile sample measured appears to have an anatase impurity, as shown Figure 4.11. The broad band at 250 cm⁻¹ is a second order phonon feature that disappears at low temperatures.^{22,26}

Table 4.2 Raman frequency modes for anatase and rutile TiO₂.

	Raman Frequency (cm ⁻¹)	Mode
Anatase	637.3	E _g
	514.6	A _{1g} , B _{1g}
	396.8	B _{1g}
	194.7	E _g
	142.9	E _g
Rutile	609.5	A _{1g}
	447.1	E _g
	142.9	B _{1g}

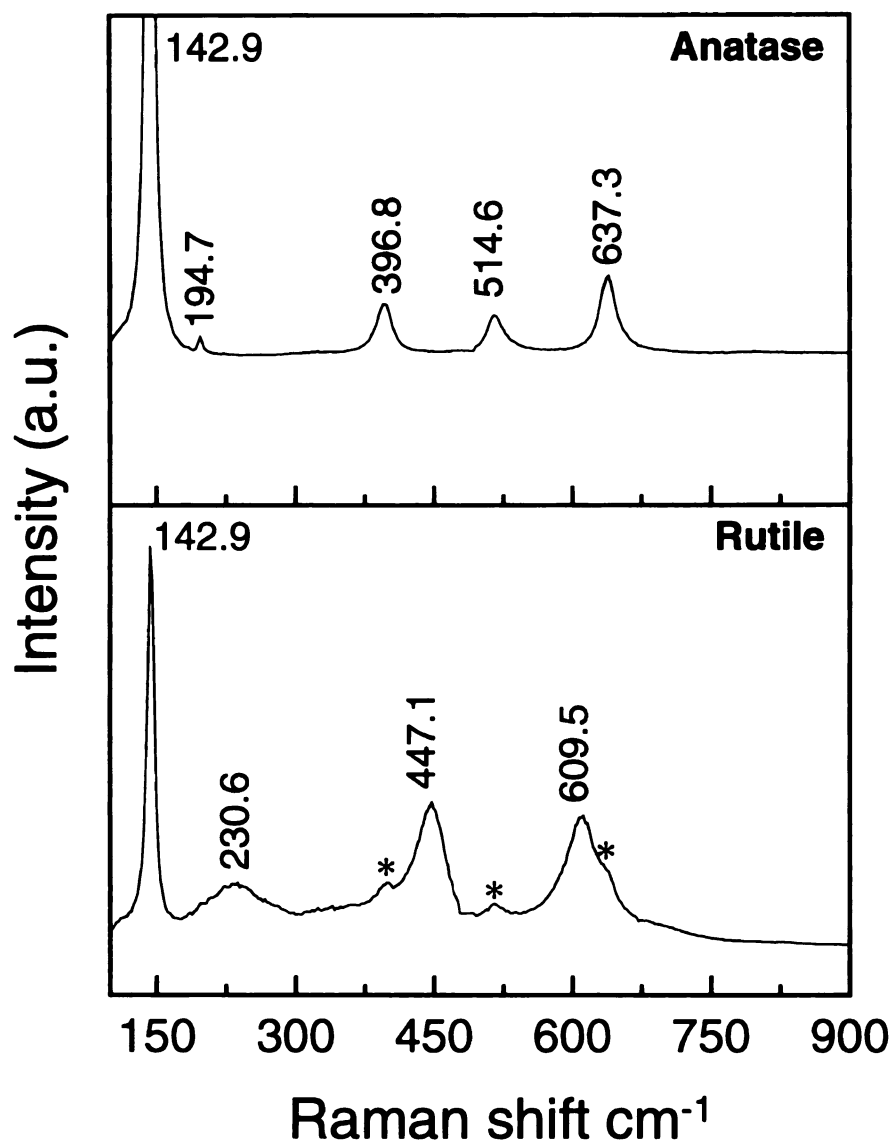


Figure 4.11 Raman spectra of anatase and rutile TiO₂ powders. The asterisks indicate the anatase impurity in the rutile sample.

A Raman spectrum of 122 nm TiO_2 nanoparticles on the oxidized silicon substrate is shown in Figure 4.12. As with the powder XRD, Si was a more suitable substrate than glass, as it has a relatively flat background in the frequency range of analysis. Comparison of the spectral features between the TiO_2 nanoparticle array and the Si substrate shows a weak features centered at $\sim 616.5 \text{ cm}^{-1}$ and $\sim 444.5 \text{ cm}^{-1}$. This suggests that the nanoparticles may adopt the rutile structure. However, the noise associated with this data, and the low signals obtained from the TiO_2 nanoparticles cannot allow for a direct confirmation of this assignment at this time.

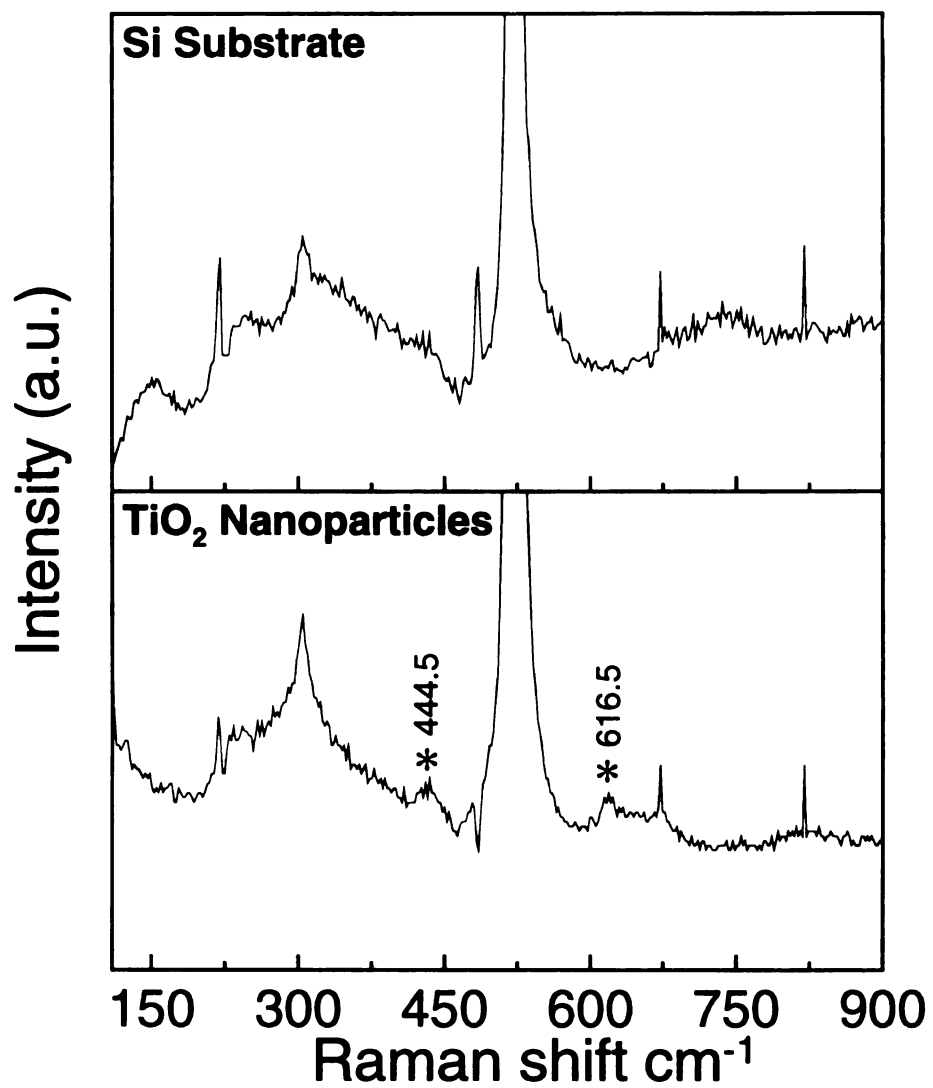


Figure 4.12 Raman spectra of bare Si substrate and TiO₂ nanoparticle array on a Si substrate.

4.3 Conclusions

The nanosphere lithography (NSL) technique has successfully produced TiO_2 nanoparticle arrays with a range of sizes on glass substrates. Furthermore, a new TiO_2 nanoparticle structure was observed, produced from square packed spheres. AFM analysis of the particles produced from hexagonal close-packed spheres indicates that tip radius can influence the measured in-plane dimensions of the nanoparticles, but will not affect the measured out-of-plane height. By using etched Si probes, tip convolution was minimized and a linear relationship between mask sphere diameter, D and nanoparticle in-plane diameter, a_{sl} , was observed for particles in the 36-386 nm range. Regardless, the size of the particles (described by $a_{sl} = 0.36D$) is still larger than predicted from geometric models. The particle height could be varied independently of particle diameter, by changing the deposition time. The profile of the TiO_2 nanoparticle shape seems to be dependent on interfacial energetic factors. The nanoparticles exhibit layer-by-layer growth, as indicated by AFM analysis of 386 nm particles, but appear to change their morphology as a function of decreasing particle size converting from triangular to circular with a hexagonal intermediate shape. X-ray photoelectron spectroscopy indicates that the ratio of $\text{Ti}^{4+}/\text{Ti}^{3+}$ states increases with a decrease in particle size. We speculate that the observed particle restructuring is due to an increased Ti-O coordination within the particle. At this time Raman spectroscopy provides slight evidence for rutile nanoparticles.

4.4 Literature Cited

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Chapter 5

Substrates for Epitaxial Control of TiO₂ Nanoparticle Arrays

Abstract

The synthesis of conductive metal oxide substrates that adopt the rutile crystal structure has been studied. Ruthenium dioxide single crystals have been grown using a chemical vapor transport method. The synthesis produced needle-like crystals with maximum sizes on the order of 2 mm $\times$ 0.14 mm $\times$ 0.14 mm. Chromium dioxide films on TiO₂(110) single crystals have been grown using chemical vapor deposition. The average growth rate was ~ 1.8 nm $\cdot$ min⁻¹. Powder x-ray diffraction indicated that the films were highly (110) textured. X-ray photoelectron spectroscopy showed that the CrO₂ films were continuous and no other chromium oxides were present. The CrO₂ films were composed of grains typically 200-300 nm in diameter and appeared consistent with the rutile crystal structure. Atomic force microscopy suggested that the films were relatively rough, with a root-mean-square roughness of ~ 114 nm for an 850 nm thick film. The resistivity at room temperature was found to be ~ 137 $\mu\Omega\cdot$ cm which decreased to ~ 16 $\mu\Omega\cdot$ cm at 5 K, consistent with metallic behavior. The films were ferromagnetic with a Curie temperature of 398 K.

5.1 Introduction

We have successfully prepared TiO_2 nanoparticles on glass substrates using a nanosphere lithography (NSL) technique as shown in Chapters 3 and 4.^{1,2} The amorphous glass surface offers no chance of epitaxially controlling or stabilizing the crystallinity of the nanoparticles that are deposited, possibly allowing for amorphous or mixed TiO_2 phases to be produced. Crystalline TiO_2 nanoparticles are desirable to ensure reproducible surface properties from particle-to particle and to allow detailed spectroscopic characterization of their surfaces. In addition, there is also some evidence that amorphous or mixed TiO_2 phases exhibit reduced photoactivity.³ At this time the crystallinity of these nanoparticles on glass is uncertain.

The synthesis of crystalline TiO_2 nanoparticle arrays may be epitaxially achieved by using a substrate that is crystallographically compatible with TiO_2 . In order to test whether this can be accomplished, the substrate must not only have similar lattice parameters and symmetry to TiO_2 , but it should be metallic enough to allow electron spectroscopy and scanning tunneling microscopy investigations. A metallic substrate is also desirable for photocatalytic systems to act as a counter electrode (site of reduction reactions) and to provide a suitable Schottky barrier⁴ to separate photogenerated electrons and holes as described in Section 1.2. Initially, we have chosen to work with substrates that have similar lattice parameters to the rutile polymorph of TiO_2 . Rutile has been selected due to the thermodynamic stability of this crystalline form and the detailed surface characterization that has already been done on rutile $\text{TiO}_2(110)$ single crystals. This can be used as a comparison when examining the crystalline TiO_2 nanoparticle arrays.

Studies of epitaxial control in metal oxides have primarily focused on growing thin films on metal single-crystal substrates such as Mo(100), Mo(110), Ta(110) and Re(0001).^{5,6} This approach has been successful for oxides adopting a simple cubic structure, such as MgO and NiO, but not for metal oxides with more complex crystal habit such as Al₂O₃ or TiO₂. Rutile TiO₂(001) films have been grown on Mo(100) substrates, but they were found to be thermodynamically unstable, reconstructing to form (110) microfacets.⁷ The instability of TiO₂ thin films grown on metal substrates, such as Mo, is due to the dissimilarity in crystal structure between the metal substrate and film. No elemental metal single crystal adopts the rutile crystal structure of TiO₂. Therefore, as an alternative approach, we have chosen to use metallic oxide materials as substrates instead.

Several conducting metal dioxides adopt a rutile or slightly distorted rutile structure, but of these, ruthenium dioxide ($a = 4.49$ Å, $c = 3.11$ Å) and chromium dioxide ($a = 4.41$ Å, $c = 2.91$ Å) most closely match the lattice parameters of rutile TiO₂ ($a = 4.59$ Å, $c = 2.96$ Å), shown in Figure 5.1.

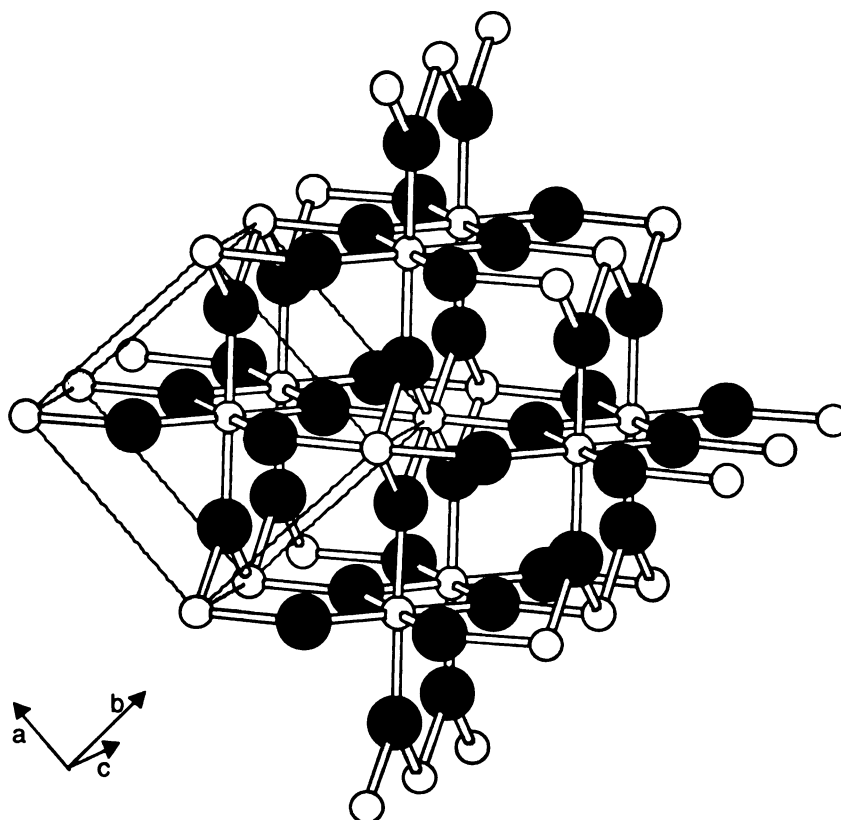


Figure 5.1 Idealized rutile crystal structure. The boxed region indicates a single unit cell composed of TiO_6 octahedra. (The oxygen atoms are the black circles, and titanium atoms are small gray circles.)

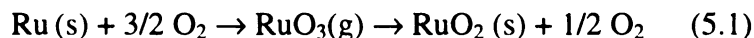
Ruthenium dioxide is a paramagnetic metallic blue-black solid that has been considered for many applications because of its low electrical resistivity, good thermal conductivity and high chemical and thermal stability.⁸ Chromium dioxide is a ferromagnetic metallic black solid that has attracted significant attention due to its commercial importance as a particulate recording medium for data storage applications.⁹ Both of these metal oxides are promising candidates for the formation of ordered epitaxial rutile TiO_2 nanoparticles. Unfortunately, unlike most metals, large single

crystal surfaces of both RuO₂ and CrO₂ are not commercially available. To address this problem, two different approaches are presented in this chapter.

5.1.1 Approach I: Synthesis of Large Single Crystals (RuO₂)

The primary method that has been used to try and grow large single crystals of RuO₂ is chemical vapor transport (CVT). In this method, material is volatilized at one temperature and then transported by a carrier to a region of a different temperature, where crystallization occurs. The transport of vaporized material can occur in either an open-flow or closed system.¹⁰

Applying an open-flow CVT method, RuO₂ single crystals with typical dimensions of 1-2 mm have been prepared by directly oxidizing Ru metal and using oxygen as a carrier gas¹¹ as shown in the reaction below:



Larger single crystals of RuO₂, with dimensions $\leq \sim 6\text{mm}$, have been produced by a similar open-flow CVT method, but utilizing polycrystalline RuO₂ powder or combinations of polycrystalline RuO₂ and Ru metal powder as a starting materials.¹²⁻¹⁴ Similar sized single crystals of RuO₂ have been made using a closed-system with RuO₂ as the starting material and HCl gas as the transport agent.^{15,16} However, the reproducibility of synthesizing single crystals of these sizes by CVT is unclear. Published results on the production of crystals with these dimensions came from two research groups in the 1980's, with no recent literature on the subject. There is only one reported example in the literature of an alternative approach to CVT to produce RuO₂

single crystals. In a novel preparation technique, lead ruthenate ($\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$) was oxidized to produce RuO_2 grains. Although the preparation time, 30 minutes, was much shorter than that required for CVT methods ($\sim 2\text{-}3$ weeks per gram of RuO_2 transported) the crystals produced were only on the order of 0.2 mm in diameter.¹⁷

In this chapter we present our work on synthesizing large RuO_2 single crystals by employing an open-flow chemical vapor transport method. The characterization of the single crystals with scanning electron microscopy (SEM) and single-crystal X-ray crystallography is presented here.

5.1.2 Approach II: Synthesis of Crystalline Thin Film (CrO_2)

The second approach presented in this chapter focuses on preparing CrO_2 supports by epitaxially growing thin films onto commercially available large rutile $\text{TiO}_2(110)$ single crystals (as shown in Figure 5.2). Thin film techniques such as this have allowed the preparation of model metal oxide surfaces without the growth and preparation of large single crystals. For example, thin films of $\beta\text{-MnO}_2$,¹⁸ anatase TiO_2 ,^{19,20} and $\alpha\text{-Cr}_2\text{O}_3$ ²¹⁻²³ have been grown in place of large-single crystals which are not commercially available.

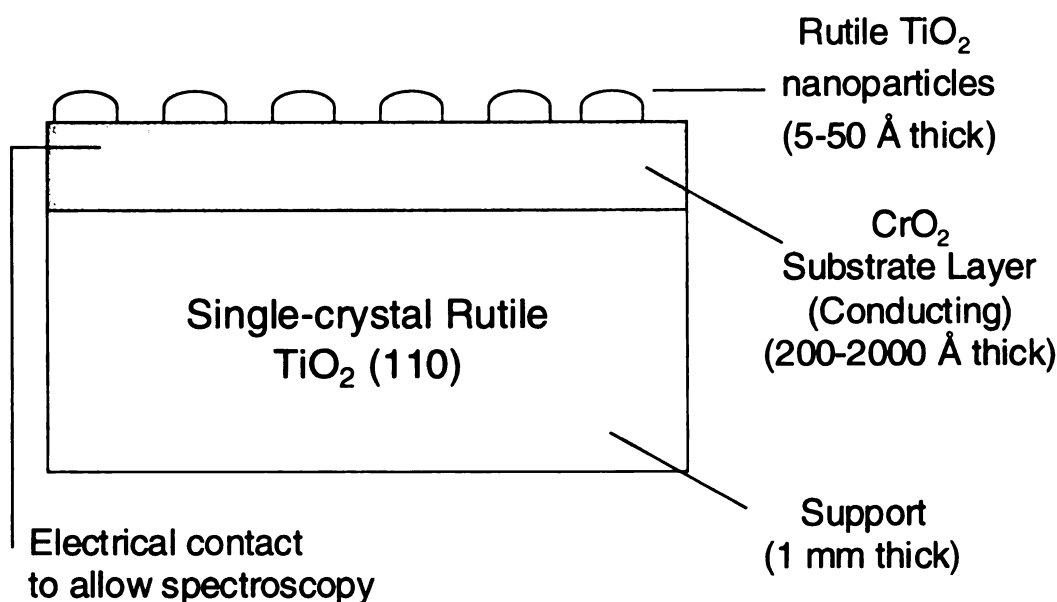


Figure 5.2 Schematic representation of metal oxide thin film approach to prepare a suitable CrO₂ substrate for rutile TiO₂ nanoparticles.

Chromium dioxide is difficult to synthesize because it is metastable at atmospheric pressures. It is often synthesized under high oxygen pressure conditions ($P > 10$ bar) by thermal decomposition of CrO₃. This process produces a fine powder with crystals no larger than ~ 0.5 mm.^{24,25} Approaches to create larger ordered CrO₂ surfaces via high pressure, epitaxial film syntheses have been investigated on rutile TiO₂ (100), (110), (210), and (001) surfaces as well as on the (0001) and (110) planes of Al₂O₃. X-ray diffraction (XRD) has indicated the substrates induce a texture in the CrO₂ layer, producing epitaxially orientated CrO₂ films on the TiO₂ surfaces.^{25,26}

Chromium dioxide films on TiO₂ surfaces have also been grown using a chemical vapor deposition (CVD) method developed by Ishibashi et al. as an alternative to high pressure routes.²⁷ In that work, scanning electron microscopy and reflection electron

diffraction suggested that CrO_2 films up to about 500 nm thick were deposited with epitaxial control on TiO_2 (100), (110), (111) and (001) substrate surfaces. However, the surface of the CrO_2 produced by this method was not examined in detail. Amorphous thin films of CrO_2 have been grown on glass and Si(110) substrates using oxidized Ti as a buffer layer. X-ray diffraction indicated textured, polycrystalline CrO_2 films.^{28,29} Li and coworkers have applied this CVD method to grow CrO_2 films on TiO_2 (100) for magnetic measurements³⁰⁻³² and also observed epitaxial CrO_2 films on TiO_2 (110).³³

In this chapter we present an examination of the surface morphology of CrO_2 grown on TiO_2 (110) single crystals using a modified version of Ishibashi et al's CVD approach. We have successfully grown epitaxial thin films of CrO_2 on TiO_2 (110) single crystal substrates at atmospheric pressure. Our studies provide insight into the growth characteristics, composition, and morphology of these films as indicated by scanning electron microscopy (SEM), powder XRD, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Additionally, the magnetic (magnetization) and transport (resistivity) properties of the CrO_2 films were examined and the results are compared to previously published work.

5.2 Experimental

Single Crystal Synthesis. Ruthenium dioxide single crystals were prepared using an open-flow CVT method.¹⁰ A pressure gradient was created within a specially designed quartz tube, which was encased inside a programmable furnace. The starting material, RuO_2 powder (99.9% purity, Alfa Aesar, Ward Hill, MA), was placed in one zone at 1150 °C. Oxygen flowing at a rate of $\sim 0.04 \text{ L}\cdot\text{hr}^{-1}$ was used as a carrier gas with

the deposition region in the second zone of the tube at 1000 °C. A synthesis typically lasted for 14 days.

Film Deposition. Chromium dioxide films were prepared using CVD inside a dual-zone programmable furnace. The starting material, CrO₃ (99% purity, Aldrich Chemical Company, Inc., Milwaukee, WI), was placed in the first zone at 260 °C. Titanium dioxide (110) single crystal substrates (7 × 7 × 1 mm, 99.99% purity, Superconductive Components, Inc., Columbus, OH) were ultrasonically cleaned in acetone, rinsed in H₂O, heated in oxygen at 400 °C for 24 hours and then placed in the second zone of the furnace at 400 °C. Oxygen flowing at a rate of ~0.1 L·s⁻¹ was used as the carrier gas for the decomposition products of CrO₃ which would subsequently form films of CrO₂ (CrO₃ → CrO₂ + 1/2O₂) on the TiO₂(110) substrates. Typical depositions ran for 8 hours.

Electron Microscopy. Images of the RuO₂ crystals and thickness analyses of the CrO₂ films were performed with a JSM-6400V SEM incorporating a LaB₆ electron source. Data were acquired with an accelerating voltage of 20 kV.

Single Crystal X-ray Crystallography. A Bruker SMART Platform CCD diffractometer was used for data collection. Several different sets of frames covering a random area of the reciprocal space were collected using 0.3° steps in ω at a detector-to-sample distance of ~5 cm. The SMART³⁴ software was used for data acquisition and SAINT³⁴ for data extraction. The absorption correction was done with SADABS,³⁴ and the structure solution and refinement was done with the SHELXTL³⁴ package of crystallographic programs. The structure was solved with direct methods. All atoms were refined anisotropically.

Powder X-ray Diffraction. Analyses of the CrO₂ films were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer operating at 50 kV/100 mA with a 1°/min scan rate, employing Ni-filtered Cu radiation in a Bragg-Brentano geometry.

XPS Analyses. A Perkin-Elmer Φ 5100 series XP spectrometer (base pressure 2.0×10^{-10} Torr) with an unmonochromatized Al K α ($h\nu = 1486.6$ eV) source operating at 300 W was used to acquire XP spectra. The spectrometer was calibrated using the binding energy (BE) of the Au 4f_{7/2} line at 84.0 eV with respect to the Fermi level. All XPS spectra were collected using a hemispherical mirror analyzer operating at a pass energy of 44.7 eV, and acquired at normal take-off angle (90° from the surface plane). After a Shirley-type background subtraction, the spectra were fitted using simple Gaussian-Lorentzian peak shapes. Observed BE's were referenced to the adventitious C 1s photoemission line at 285.0 eV and compared to reference XP spectra of CrO₂ powder (99.9% purity, EMTEC Magnetics GmbH) acquired under the same experimental conditions. Reference spectra of Cr₂O₃ (98+% purity, Aldrich) and Na₂Cr₂O₇, (prepared by heating Na₂Cr₂O₇·2H₂O (99.5% purity, Fisher Scientific) to 100 °C in vacuum) were also acquired for comparison. The atomic compositions were evaluated using sensitivity factors provided by the instrument manufacturer (Cr 2p = 2.427 and O 1s = 0.711).

AFM Analysis. Images were taken using a Digital Instruments Nanoscope AFM operating in contact mode in air using a standard silicon nitride probe. Micrographs were collected at several different positions on the surface to confirm that the CrO₂ layer was uniform on a macroscopic scale. The root-mean-square (RMS) roughness of the films was calculated using Nanoscope 4.1 software.

Magnetic and Transport Analysis. The magnetic susceptibility of the CrO₂ films was measured as function of temperature using a Quantum Design MPMS magnetometer with an applied field of 500 G. All measurements were made with the magnetic field oriented in the plane of the film. Resistivity measurements were made over a temperature range of 5-400 K, using conventional four terminal methods on the samples, mounted on a probe that was inserted into the same instrument.

5.3 Results and Discussion

5.3.1 RuO₂ Single Crystals

The RuO₂ single crystals produced by chemical vapor transport were dark purple, reflective, and needle-like in shape with typical sizes on the order of 2.0 mm × 0.14 mm × 0.14 mm (Figure 5.3). X-ray crystallography confirmed that the lattice parameters and symmetry were consistent with RuO₂ single crystals. The lattice parameters were calculated to be ($a = b = 4.4981$ Å, $c = 3.1134$ Å), which are in good agreement with reported literature values ($a = b = 4.49$ Å, $c = 3.11$ Å).³⁵ For further information regarding the crystal structure and refinement of RuO₂ refer to detailed tables in Appendix D.

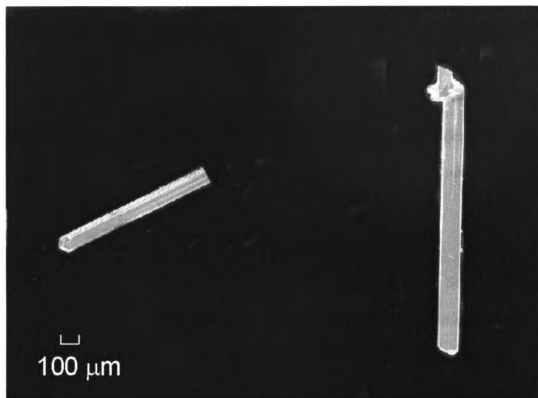


Figure 5.3 SEM image of RuO₂ single crystals. Dimensions of the largest crystals are typically 2.0 mm × 0.14 mm × 0.14 mm.

Although the RuO₂ single crystals produced from this work were not large enough to use as substrates (a sufficient size would be ~ 5 mm × 5 mm × 1 mm), the results in this study provide useful insight into the CVT mechanism and methods for improvement. In this work, CVT produced several small needles rather than a few large sized crystals. The growth of crystals also extended outside of the deposition zone. The generation of needle-like RuO₂ crystals is not uncommon and has been reported before.^{11,36} In our study, a typical synthesis resulted in ~15% of the starting material mass being

unaccounted for. This indicates that a loss of starting material was probably not a factor in the lack of larger single crystals of RuO_2 being produced. More likely, multiple nucleation sites within the quartz tube were favoring the growth of smaller sized crystals over larger ones. By using a seed crystal or a substrate of smaller surface area within the deposition zone, the growth of larger single crystals of RuO_2 may be obtained in the future. In addition, the evidence of crystals forming outside of the desired deposition zone indicates that the temperature gradient within the quartz tube needs to be more carefully controlled.

5.3.2 CrO_2 Films on $\text{TiO}_2(110)$ Single Crystals

The CrO_2 films produced were black and highly reflective. Scanning electron microscopy cross-section images of a typical CrO_2 film on a $\text{TiO}_2(110)$ substrate indicated an average thickness of approximately 850 nm, consistent with an average deposition rate of $1.8 \text{ nm}\cdot\text{min}^{-1}$. Supporting thickness measurements were also determined by AFM. During film deposition, small areas at the edge of the TiO_2 single crystal were covered by retaining clips. Once the deposition was completed and the films were removed from the furnace, the supporting clips were removed and the atomic force microscope was used to examine the "height" of the steps produced. The thicknesses of the films determined by AFM were consistent with the SEM analyses. All the powder X-ray diffraction patterns, a typical example of which is presented in Figure 5.4, showed features associated with both TiO_2 and CrO_2 (110) and (220) reflections. There is no evidence for orientations other than $\text{CrO}_2(110)$ or other chromium oxides.

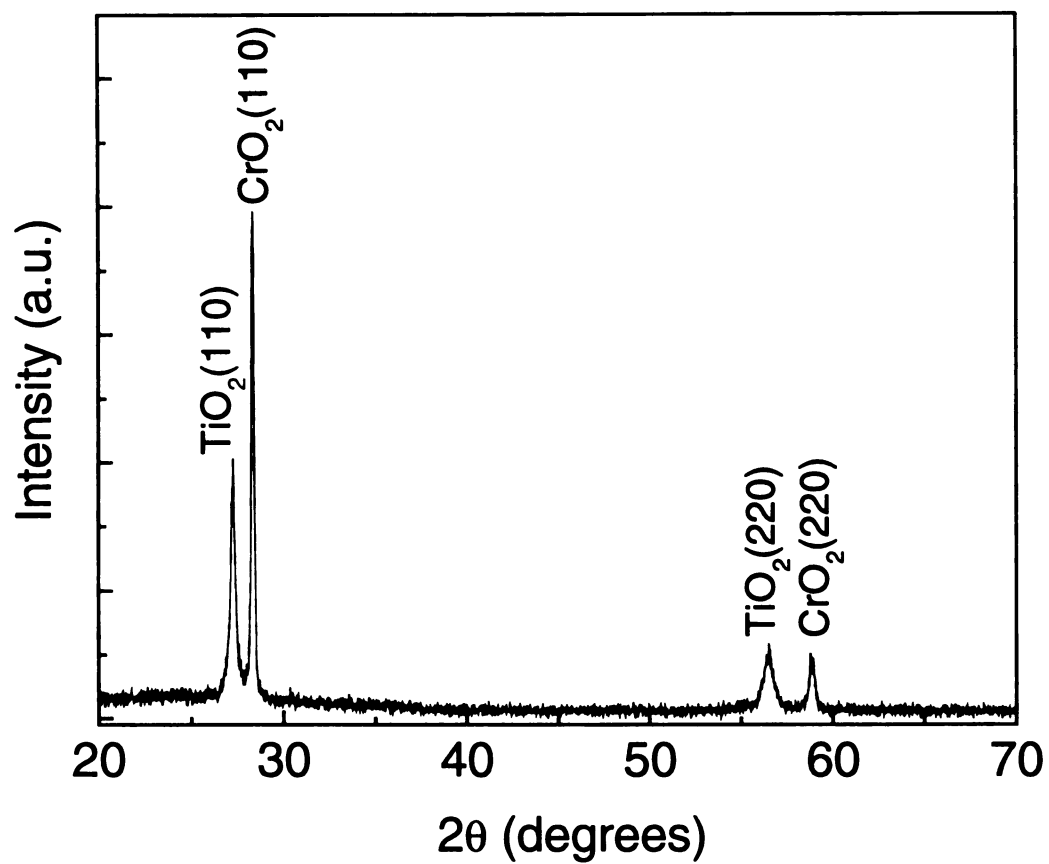


Figure 5.4 Powder XRD pattern of an 850 nm thick CrO_2 film on $\text{TiO}_2(110)$.

XPS Analyses. The composition and purity of the CrO_2 films on $\text{TiO}_2(110)$ were studied by XPS. Survey spectra, as shown in Figure 5.5, indicated only chromium, oxygen, and carbon were present on the surface of the films. Peaks associated with titanium are not evident, indicating that the films are continuous and, based on an estimate for the inelastic mean free path for the Ti 2p photoelectrons of 2.0 nm,³⁷ at least 6.0 nm thick. The minimum thickness inferred from the XPS measurements supports the AFM and SEM thickness values.

High resolution scans of the Cr 2p and O 1s regions of the CrO_2 film on $\text{TiO}_2(110)$ and a standard CrO_2 powder were acquired as shown in Figure 5.6. The peaks connected by a dashed line are those associated with CrO_2 . The BE's for Cr 2p and O1s peaks in the film and powder are in excellent agreement with each other and with values reported by Ikemoto et al.³⁸ as given in Table 5.1. Also shown in Table 5.1 are the BE's determined for other chromium oxide species, confirming that the oxide produced on our TiO_2 substrate could be uniquely identified. The measured BE's and spin-orbit splittings for the Cr_2O_3 (Cr (III)) and CrO_3 and $\text{Na}_2\text{Cr}_2\text{O}_7$ (Cr (VI)) oxides reported here are generally within 0.2 eV of analogous values in the literature.³⁸⁻⁴⁰ It is interesting to note that the chromium 2p peaks for Cr oxides do not follow a simple trend of increasing BE with increasing formal oxidation state. These effects have been remarked upon previously and attributed to differences in the crystal structure, ionic character and electronic properties of these oxides.^{38,41}

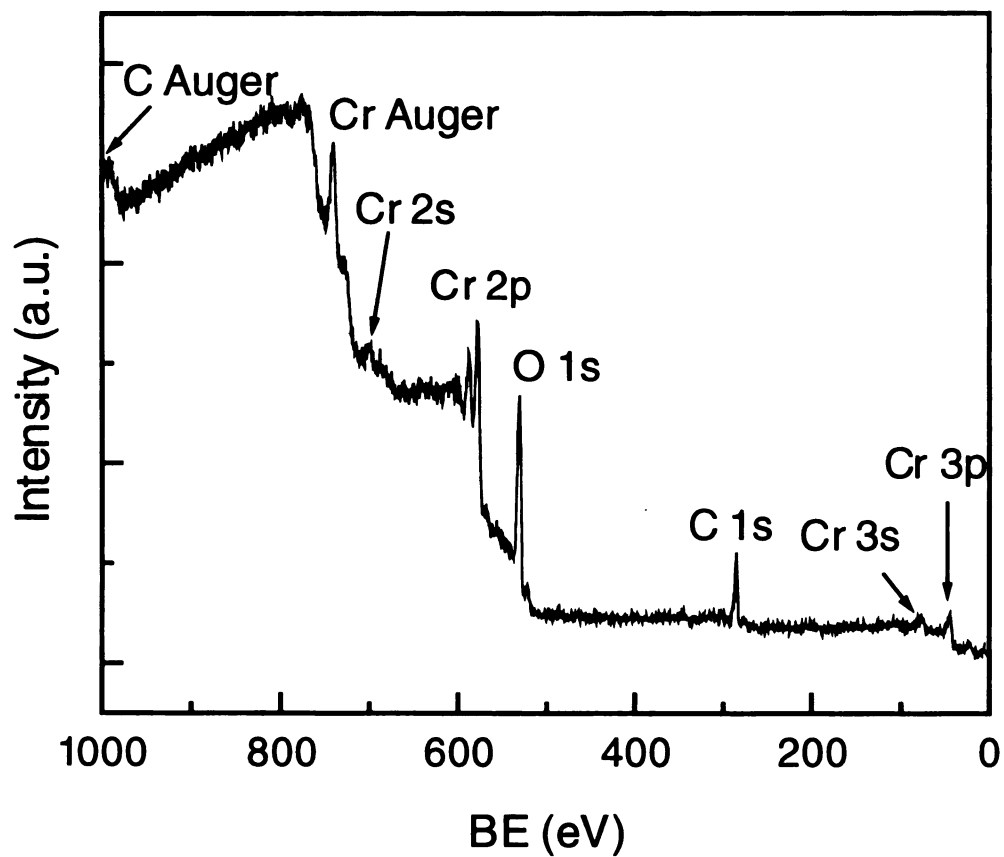


Figure 5.5 XPS survey scan of CrO_2 film on $\text{TiO}_2(110)$ (Al $K\alpha$ radiation). Note the absence of any features associated with TiO_2 substrate.

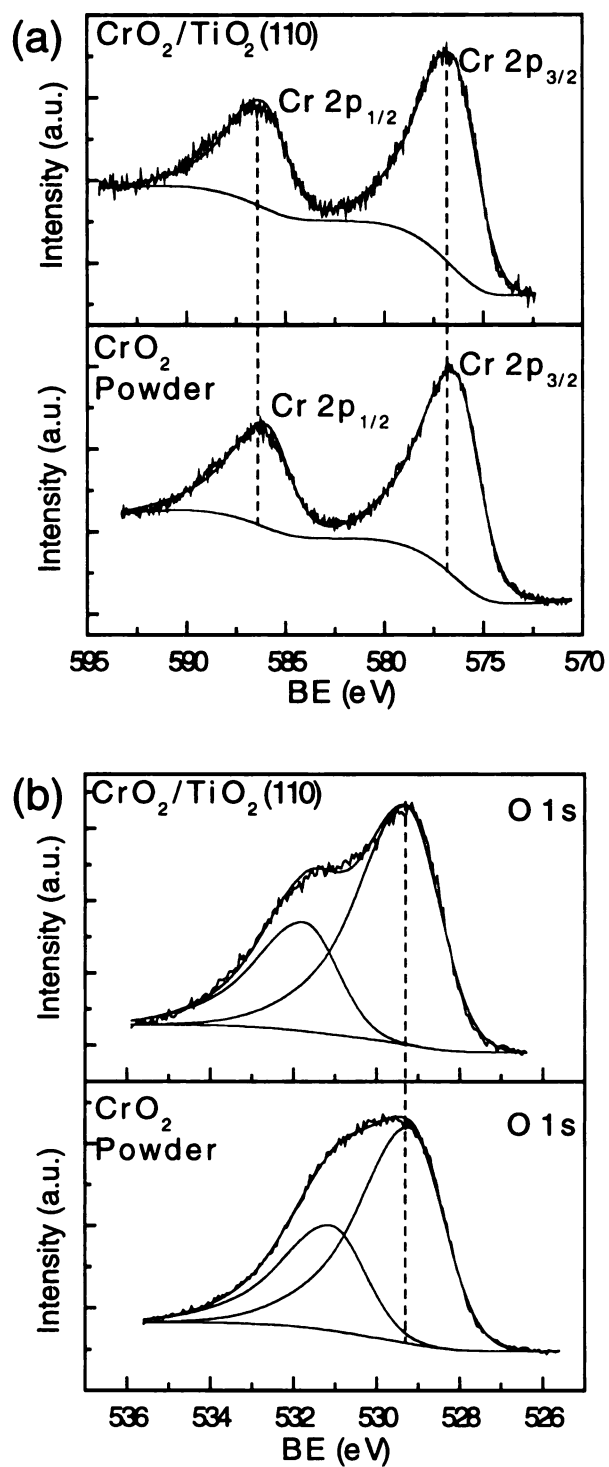


Figure 5.6 XPS comparison between $\text{CrO}_2/\text{TiO}_2(110)$ film and CrO_2 powder: (a) Cr 2p region and (b) O 1s region. For the Cr 2p region, dashed lines are drawn at 576.5 and 586.1 eV BE. For the O 1s region, a dashed line is drawn at 529.2 eV BE. The features connected by dashed lines correspond to CrO_2 .

Table 5.1 XPS binding energies (eV) obtained for CrO₂/TiO₂(110) films and other chromium oxides.^a

	CrO ₂ (110) Film	CrO ₂	Cr ₂ O ₃	CrO ₃	Na ₂ Cr ₂ O ₇
Cr 2p _{3/2}	576.6	576.4 (576.3) ^b	576.5 (576.8) ^c	578.3	579.8 (579.4) ^b
Cr 2p _{1/2}	586.2	586.0 (586.0) ^b	586.2 (586.5) ^c	586.0	589.0 (588.5) ^b
O 1s	529.3	529.2 (529.3) ^b	530.3 (530.5) ^c	529.9	530.5 (530.0) ^b

^a All values except those in parentheses were determined in the present study. ^b Data from the work of Ikemoto et al.³⁸ ^c Data from the work of Allen et al. (Their results have been corrected to the Au 4f_{7/2} as 84.0 eV).³⁹

The Cr 2p peaks of the CrO₂ film and powder, as shown in Figure 5.6 a, were noticeably asymmetric and broadened to the high binding energy side when compared with the Cr 2p peaks for Na₂CrO₇ and Cr₂O₃ (data not shown). Attempts were made to fit the Cr 2p peak envelope to simple symmetric peaks located at the BE's expected for Cr (IV) ($2p_{3/2} = 576.4$ eV) with a minor component attributable to Cr (VI) ($2p_{3/2} = 579.6$ eV). However, the quality of the fit was substantially worse than a single asymmetric peak due to Cr (IV). We therefore conclude that the CrO₂ peak shape is intrinsic to the material and likely associated with small energy electron-hole pair excitation across the Fermi level of this metallic material (so called Doniach-Sunjić lineshape).⁴²

The oxygen photoemission peaks for both CrO₂/TiO₂(110) film and CrO₂ powder (Figure 5.6 b) showed the presence of two components. These two components were fit with the same peak shape and FWHM (1.9 eV). The lower BE component, at 529.25 ± 0.05 eV BE, is associated with the chromium oxide species based on comparison to literature values.³⁸ The Cr/O ratio was calculated using the peak area for Cr 2p and the lower BE O 1s component, and was found to be 0.52 for the film and 0.60 for the powder. We estimate the error in these calculated ratios to be about ± 0.05 , determined largely by the errors associated with peak fitting. The calculated Cr/O ratios for the film and powder are in reasonable agreement with the theoretical value for CrO₂ of 0.50.

The higher BE oxygen component in the CrO₂ film and powder (Figure 5.6 b), located at about 532 eV BE, can be attributed to a surface contaminant. This was established by examining the O 1s region as a function of XPS analyzer take-off angle. By changing the take-off angle from 90° to 20° (Figure 5.7), the sampling depth is effectively decreased from approximately 4.5 nm to 1.5 nm. The intensity of the high BE

component of the O 1s envelope relative to the low BE CrO₂ O 1s peak, is greater at 20° than at 90°, indicating that this feature is localized in the near-surface region. Similar broadening of the O 1s region to higher BE for oxides of chromium has been reported previously and this feature is believed to be associated with adsorbed H₂O³⁹ or O₂.³⁸

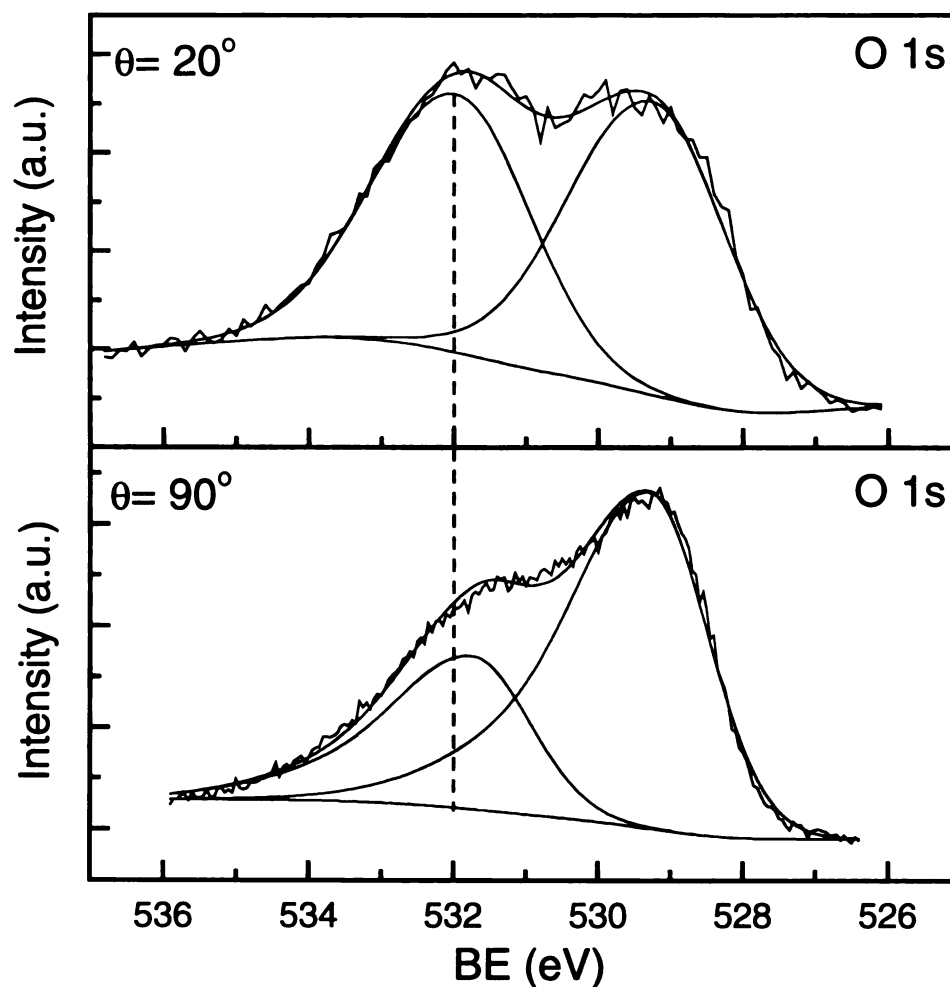


Figure 5.7 XPS comparison of O 1s region for CrO₂/TiO₂(110) film at two different take off angles (θ). Takeoff angle is defined as the angle between the surface plane and the electron energy analyzer acceptance axis. The dashed line is drawn at ~532 eV BE and is associated with surface H₂O.

Many metal oxides readily form a hydroxide layer on the surface when exposed to ambient air.⁴³ One example is Cr_2O_3 , where H_2O dissociatively chemisorbs and forms surface bridging and terminal OH groups even on a non-defective surface.^{21,22,44} Adsorbed OH and H_2O on the surface can be distinguished by the magnitude of the XPS chemical shift from the O^{2-} peak associated with the oxide. The peak positions of OH and O^{2-} are usually $+(1.1-1.5)$ eV BE apart. However, H_2O creates higher BE shifts, typically $>+3\text{eV}$ from the oxide peak.⁴⁵ For the CrO_2 film and powder studied here, the BE difference between the two O 1s peaks is about 2.7 eV. Based on this BE difference, we propose that the second oxygen component on the surface of the film and the powder is likely a surface H_2O species.

Morphology Investigation. Atomic force microscopy was used to investigate the morphology of the $\text{CrO}_2/\text{TiO}_2(110)$ films. It is known that the TiO_2 substrate is important in providing epitaxial stabilization of the CrO_2 phase.^{25,27,33} In Figure 5.8 (a), a $400\text{ }\mu\text{m}^2$ AFM image of a clean $\text{TiO}_2(110)$ single crystal is shown. The surface is uniform and a sectional height analysis across the surface indicates a flat substrate devoid of any noticeable surface features. The RMS roughness of the $\text{TiO}_2(110)$ substrate was calculated to be 1.5 nm for a $10\text{ }\mu\text{m}^2$ area within this image.

A typical AFM image of a $100\text{ }\mu\text{m}^2$ area of an 850 nm thick CrO_2 film on $\text{TiO}_2(110)$ is shown in Figure 5.8 (b). Individual grains on the surface can be resolved and their appearance is generally consistent with the rutile crystal structure of CrO_2 . Sectional height analysis of the film shows that the grains vary in size and height along the surface. The markers indicate the relationship between the topographical image and the section height analysis. On the CrO_2 film, grain sizes as large as ~ 1000 nm exist.

However, typical grain sizes found on the surface are approximately 200-300 nm in size. These grain sizes are larger or equal to those in the literature reported for CrO₂ films on TiO₂(100).^{30,46,47} The calculated RMS roughness of the film was 114 nm, an increase of two orders of magnitude compared to the initial TiO₂ substrate. Ranno et al. also noted large surface roughness of CrO₂ films grown by high pressure synthesis and reported variations in film thickness of 20-30%,²⁶ somewhat larger than our values of 10-15 %.

The surface roughness of the CrO₂ films may be a reflection of the deposition method. From the AFM images it may be concluded that many nucleation sites are present on the TiO₂(110) crystal surface, which would lead to the growth of grains of various sizes and, ultimately, a roughened surface. Alternatively, strain energy can accumulate rapidly with increasing film layer thickness, which might also result in an increase in surface roughness.⁴⁸

Methods to decrease the surface roughness, such as annealing the film or changing the deposition temperature of the substrate, were not investigated in this study. The temperature of the substrate must fall within 390-400 °C to allow for CrO₂ growth. Deposition at higher or lower temperatures will lead to the formation of other chromium oxides.²⁷ Post-annealing of the film after deposition at higher temperatures is also not possible: chromium dioxide decomposes to Cr₂O₃ at temperatures above 400 °C.^{25,27} Future investigations are underway to better control the surface roughness of CrO₂ films, and a further discussion can be found in Chapter 6.

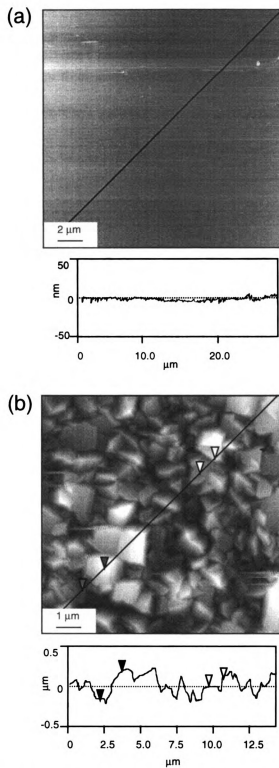


Figure 5.8 AFM surface morphology and sectional height analysis of (a) $\text{TiO}_2(110)$ single crystal ($400\ \mu\text{m}^2$ area) and (b) $850\ \text{nm}$ CrO_2 film on $\text{TiO}_2(110)$ surface ($100\ \mu\text{m}^2$ area).

Electrical and Magnetic Properties. The magnetic and electrical properties of these $\text{CrO}_2/\text{TiO}_2(110)$ films were also investigated. Figure 5.9 shows the electrical resistivity, ρ , for an 850 nm thick CrO_2 film on $\text{TiO}_2(110)$ as a function of temperature. The gross properties of CrO_2 films on $\text{TiO}_2(110)$ are similar to those of CrO_2 films grown on the $\text{TiO}_2(100)$ surface by CVD using CrO_3 ^{31,46} and CrO_2Cl_2 ⁴⁷ as precursors. Resistivity increased from $\sim 16 \mu\Omega\cdot\text{cm}$ at 5 K to $\sim 137 \mu\Omega\cdot\text{cm}$ at 300 K. An increase of resistivity of this magnitude is consistent with metallic behavior. These resistivity values are similar to those reported for CrO_2 films on $\text{TiO}_2(110)$ formed by high pressure synthesis.⁴⁹ However, it should be noted that our resistivity values should be regarded as approximate due to errors associated with measurement of the cross-sectional area of the $\text{CrO}_2/\text{TiO}_2$ film and the unknown effects of surface roughness.

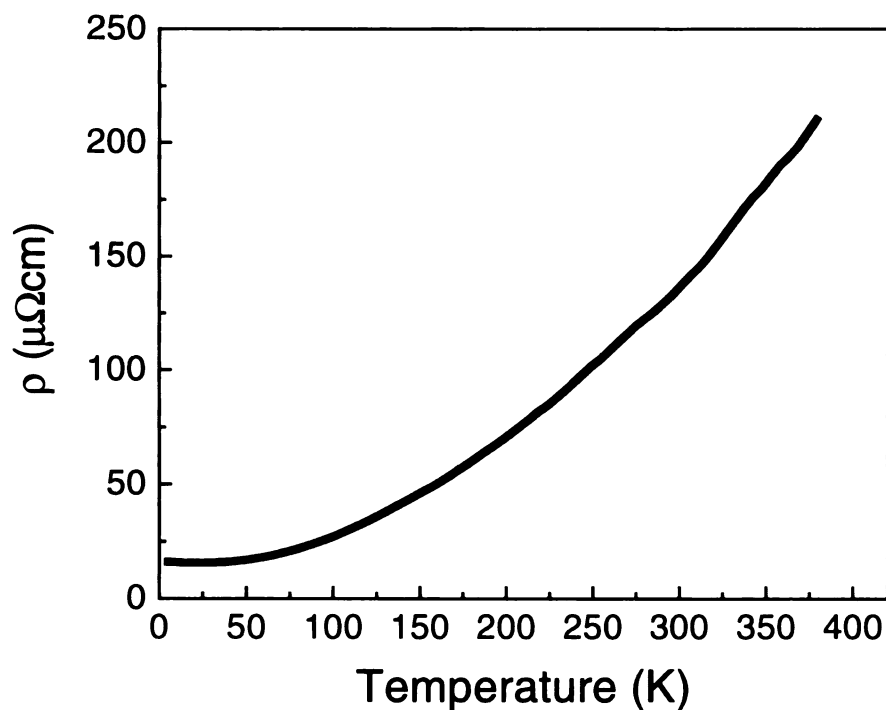


Figure 5.9 Resistivity vs. temperature of an 850 nm thick CrO_2 film on a $\text{TiO}_2(110)$ surface.

Measurements of the magnetic properties of the films indicated a clear ferromagnetic hysteresis and anisotropy along the *c*-axis of the films, (Figure 5.10) consistent with the assumption of a collinear relation between the crystallographic *c*-axis and the magnetic easy axis of CrO₂ single crystals⁵⁰ and CrO₂(100) films.^{30,31,47,51}

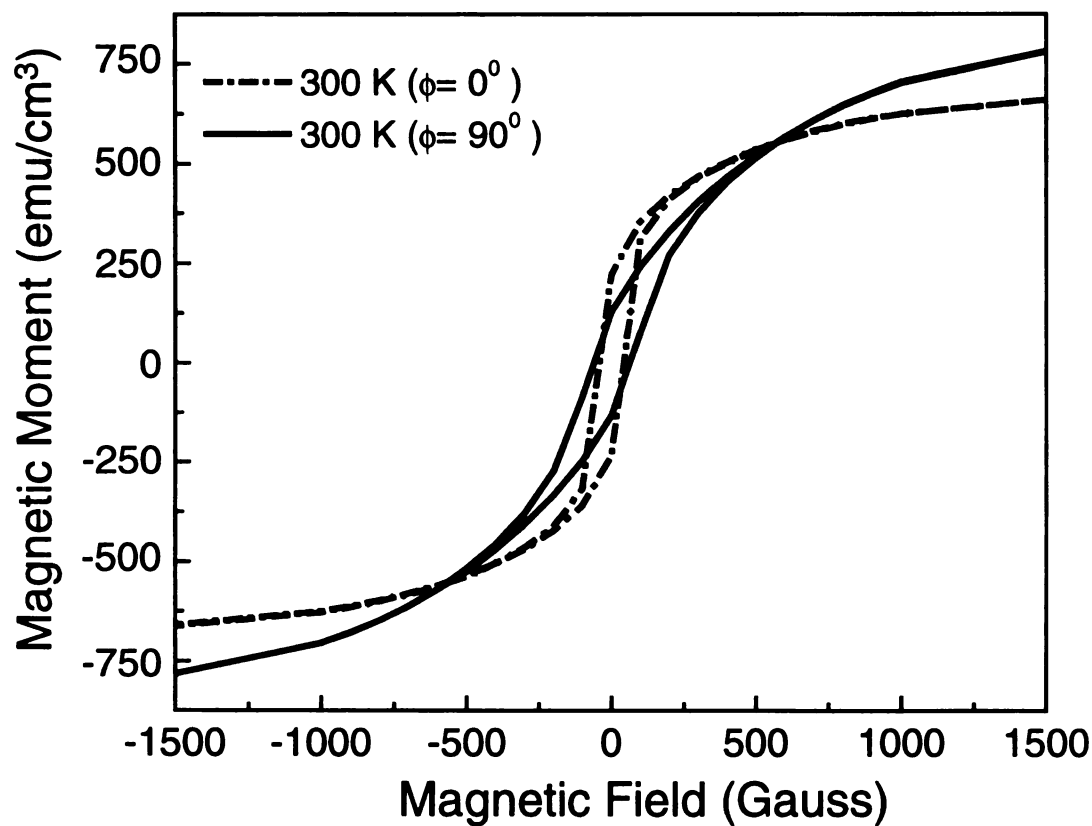


Figure 5.10 Hysteresis loops at $T = 300$ K of a 850 nm thick CrO₂ film on TiO₂(110) with the magnetic field applied at different parallel directions (ϕ) to the surface plane of the film. ($\phi = 0$ is with the magnetic field parallel to the *c*-axis, in the plane of the film.)

The spontaneous magnetization determined as a function of temperature in an applied field of 500 G, is presented in Figure 5.11. From these data, the Curie temperature was found to be ~ 398 K, which is in agreement with published results of CrO_2 films^{28,30,31,47,49} and bulk CrO_2 .⁹ Similar magnetization behavior has been also observed in $\text{CrO}_2(100)$ films grown by CVD^{30,31,47,49} but cannot be directly compared to our $\text{CrO}_2(110)$ films due different crystallographic orientations. To our knowledge, spontaneous magnetization measurements in (110) films have not been reported.

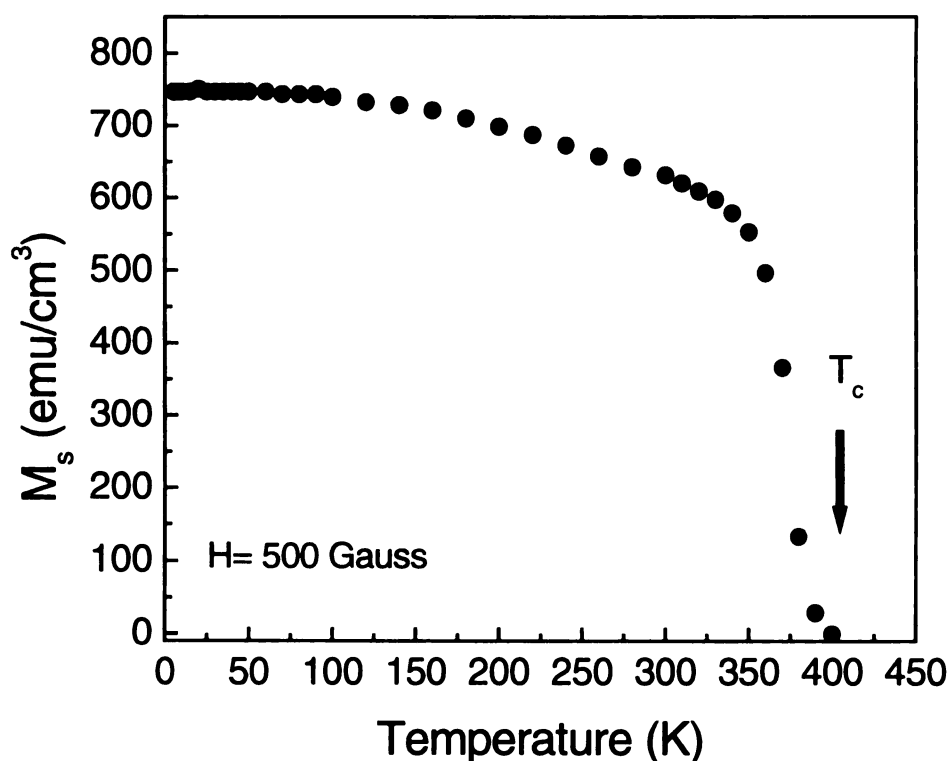


Figure 5.11 Spontaneous magnetization as a function of temperature for an 850 nm (110) oriented CrO_2 film in a 500 G field.

5.4 Conclusions

This chapter presented the results of two different approaches used to prepare suitable metallic oxide substrates for the epitaxial control of rutile TiO_2 nanoparticles. The first approach of trying to synthesize large single crystals of RuO_2 , produced needle-like crystals with dimensions ≤ 2.0 mm. X-ray crystallography indicated the needles were single crystals of RuO_2 with lattice parameters comparable to rutile TiO_2 . At this time, the dimensions of these crystals provide insufficient surface area to use as a substrate for nanoparticle deposition. Further experiments with modifications to the CVT method used in this study may produce crystals with larger dimensions.

The second approach to prepare crystalline metallic oxide substrates, via epitaxial growth of thin films, has successfully produced metallic chromium dioxide (110) films on $\text{TiO}_2(110)$ single crystal substrates. To the best of our knowledge, this is the first specific investigation of the growth, morphology, and bulk/surface composition of $\text{CrO}_2(110)$ films grown by simple chemical vapor deposition. The films were highly oriented with the (110) plane parallel to the $\text{TiO}_2(110)$ surface plane but exhibited a granular structure with grain sizes up to about 1 μm . Both powder XRD and XPS confirmed that no other bulk oxides are formed, but the surface is probably covered by a water layer. This CVD method has proven successful in growing $\text{CrO}_2(110)$ thin films and it is experimentally more accessible than a high pressure synthesis technique.

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Chapter 6

Conclusions and Future Work

The objective of this work described in this dissertation was to develop a method to create supported TiO₂ nanoparticles that were uniform in size and shape as a precursor to understanding their reactivity as a function of particle size. A nanosphere lithography (NSL) approach for patterning a surface with a monolayer of ordered mask spheres was utilized to synthesize different size and shape TiO₂ nanoparticle arrays on glass substrates. A systematic characterization of the TiO₂ nanoparticles as a function of size was undertaken using both microscopic and spectroscopic analytical techniques. In addition, the synthesis of conductive metal oxides to serve as epitaxial supports for the TiO₂ nanoparticles was investigated. In this chapter, a summary of the experimental results followed by a discussion of possible future directions will be presented.

6.1 Significance of the Results

Preparation of Monodisperse TiO₂ Nanoparticles using NSL. In the studies presented in this dissertation, it was determined that to obtain ordered TiO₂ nanoparticle arrays of uniform dimensions, mask assembly had to be carefully controlled. The self-assembly of polystyrene spheres was dependent on the coefficient of variance of the sphere diameter (polydispersity), hydrophilicity of the substrate, and rate of solvent evaporation. Control of these parameters produced ordered hexagonally close-packed monolayer arrays with domain sizes as large as 100 μm^2 . By simply changing the concentration of the sphere solution, bilayers of spheres could be deposited, although the

size of the ordered domains decreased. Autocovariance analysis and particle counting methods proved to be useful means of providing detailed quantitative evaluation of mask quality, statistical evaluation of nearest neighbor distances and the degree of order within a given area of a mask.

The monolayer and bilayer masks were used to produce two distinct TiO_2 nanoparticle arrays. Atomic force microscopy (AFM) indicated that nanoparticles were uniform in size and shape and that the interparticle spacings within the nanoparticle arrays were in agreement with geometric predictions based on the projected free space between a hexagonally close-packed array of spheres. However, the measured particle diameters were larger than predicted and the nanoparticles exhibited an apparent circular profile. In addition, a new periodic particle array was observed, derived from areas of square packed spheres that had deviated from the typical hexagonal packing observed within the mask.

X-ray photoelectron spectroscopy (XPS) confirmed the surface composition of the nanoparticles corresponded to TiO_2 with a minor concentration of Ti^{3+} states present, presumably associated with oxygen defects on the surface of the nanoparticles. The optical absorption edges of the nanoparticles were blue-shifted compared with single-crystal rutile and possessed a significant tail extending into the visible region, consistent with small particles or high defect levels.

The apparent increase in diameter of the nanoparticle arrays from predicted values was analyzed in detail as a function of nanoparticle size and correlated with an investigation of the influence of AFM tip radius on the observed nanoparticle profiles. The radius of curvature for standard AFM tips ($r = 20\text{-}60\text{ nm}$) was found to distort the

measured in-plane shape and dimensions of the nanoparticles (for particles < 386 nm in diameter), but not the out-of-plane height. Using an etched Si probe ($r = 5\text{-}10\text{ nm}$), tip convolution was reduced and a linear relationship between particle diameter, a_{sl} , and mask sphere diameter, D , was observed. The relationship linking these two dimensions was calculated to be $a_{sl} = 0.36D$ for particles ranging from 36-386 nm in diameter. The apparent nanoparticle diameters were still larger than geometric predictions, implying that the particles were diffusing under the projected free space between a hexagonally close-packed array of spheres. Regardless, the out-of-plane height of the TiO_2 nanoparticles could be varied from $\sim 5\text{-}25\text{ nm}$ independent of the nanoparticle diameter simply by varying the deposition time.

Further investigation of the morphology of the TiO_2 nanoparticle arrays by AFM revealed that the nanoparticles exhibited apparent layer-by-layer growth. In addition, the shape of the nanoparticles appeared to change as a function of particle size. For 386 nm TiO_2 particles, the nanoparticles were triangular in shape, as predicted from geometric models. However, as the dimensions of the particles were reduced, the particles converted from a triangular to circular profile, with an intermediate hexagonal structure. The concentration of Ti^{3+} states as a function of particle size was analyzed by XPS and indicated that the $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio for the TiO_2 nanoparticles increased with a decrease in particle size. This observation is consistent with the change in morphological structure of the TiO_2 nanoparticles and suggests that the smallest nanoparticles may undergo a substantial degree of reconstruction driven by an increase in the amount of Ti-O surface coordination.

Substrates for Epitaxial Control. Raman spectroscopy hinted that the TiO₂ nanoparticle arrays on glass were rutile, but the evidence remains somewhat inconclusive. Glass substrates are not expected to offer epitaxial control, a means by which the substrate could stabilize a desired crystallinity of TiO₂ nanoparticles. Therefore, alternative (conductive) metal oxide substrates that adopt the rutile crystal structure and have similar lattice parameters to rutile TiO₂ (RuO₂, CrO₂) were synthesized, with the goal of utilizing them to influence the crystallinity of TiO₂ nanoparticles produced from NSL.

Using a chemical vapor transport method, needle-like crystals of RuO₂ with 2 mm maximum dimensions were produced in this work. At this time, these dimensions were considered to offer insufficient surface area to use as substrates for nanoparticle arrays. In addition, chromium dioxide substrates were prepared by epitaxially growing CrO₂ thin films on rutile TiO₂(110) single crystal supports using a chemical vapor deposition (CVD) approach. The CrO₂ films were continuous, highly (110) textured, and exhibited similar ferromagnetic and metallic behavior to bulk CrO₂ powder measurements. The CrO₂ films appeared to be stabilized by a hydroxide-like layer, as evident from XPS analysis, but were relatively rough with a root-mean-square roughness (RMS) of ~114 nm for a 850 nm thick film.

6.2 Possible Future Directions

The research presented in this dissertation provides a basic foundation for creating monodisperse, supported TiO₂ nanoparticles. Unlike traditional solution methodologies, the TiO₂ nanoparticles produced are non-aggregated, uniform in size and shape, and are

amenable to surface characterization. The knowledge gained from this work establishes a starting point for controlling the crystalline structure and dimensions of TiO_2 nanoparticles, with the ultimate goal of understanding how the surface morphology of the particles correlates with particle size and reactivity. Upon this basic framework, a variety of different directions can be pursued to expand on both the basic understanding and applications of these TiO_2 nanoparticle arrays. In addition, the success of NSL for TiO_2 , indicates that this technique may be applicable to other interesting metal oxides.

We have demonstrated the feasibility of fabricating TiO_2 nanoparticles of various dimensions simply by manipulating the size of the mask spheres and deposition duration. To date, the smallest TiO_2 particles produced in this work (using a monolayer mask) were ~36 nm in diameter. However, these are not in the size regime where quantum size effects are expected to occur for TiO_2 . In principle, TiO_2 nanoparticles as small as 3-5 nm can be produced from commercially available polystyrene spheres. Additionally, further reduction of size and control of TiO_2 nanoparticle shape may be achieved by changing the evaporation angle during deposition. This can lead to vastly different nanostructures and can extend the flexibility of the NSL method substantially.¹

Although AFM was able to probe the structure of the TiO_2 nanoparticles, detailed structural studies will require an intrinsically higher resolution technique than AFM. Direct investigations of metal oxide surfaces by high resolution scanning tunneling microscopy (STM) are becoming an increasingly important method for relating surface structure to chemical reactivity.² Characterization of TiO_2 nanoparticles using STM, however, has not found widespread application to date, largely due to the experimental difficulties associated with the imaging of unsupported or insulating particles. Typical

STM measurements of TiO_2 surfaces are done on reduced rutile single crystals, which contain purposely-introduced oxygen vacancies.³⁻⁷

The use of a conductive substrate such as CrO_2 and RuO_2 would allow for STM investigations of the intrinsic TiO_2 nanoparticle surface without the need to purposely create oxygen defects. Ruthenium dioxide and chromium dioxide remain the best candidates for TiO_2 nanoparticle supports, as they are not only conductive but also have similar lattice parameters to rutile TiO_2 , offering the chance for epitaxial stabilization of the nanoparticles. It is believed that crystalline nanoparticles are essential to ensuring reproducible surface properties from particle-to-particle. Ultimately, this work would require further development of the RuO_2 and CrO_2 supports to provide large, relatively smooth surface areas for TiO_2 nanoparticle arrays. Synthesis of ruthenium dioxide thin films as substrates may be a more successful approach than growing large single crystals. $\text{RuO}_2(110)$ films can be grown in a variety of ways, including direct oxidation of $\text{Ru}(0001)$ single crystals,⁸ molecular beam epitaxy,⁹ or metal organic chemical vapor deposition on $\text{TiO}_2(110)$ single crystals.^{10,11}

An improvement in the quality of CrO_2 substrates may be achieved by a detailed analysis of the change in surface roughness and composition with a variation in film thickness. Recently it has been suggested that deposition of CrO_2 in the CVD process occurs through an intermediate oxide, Cr_8O_{21} , found in the thermally produced “crust” on CrO_3 .¹² We have produced and isolated gram quantities of Cr_8O_{21} as confirmed by powder x-ray diffraction.^{13,14} Preliminary results using Cr_8O_{21} as the precursor in CVD are promising. X-ray photoelectron spectroscopy provides evidence that CrO_2 films can

be grown on $\text{TiO}_2(110)$ single crystal substrates. The binding energies of the Cr 2p and O 1s levels are in agreement with CrO_2 bulk powder, as shown in Table 6.1.

Table 6.1 XPS binding energies (eV) for CrO_2 film on a rutile $\text{TiO}_2(110)$ single crystal made from Cr_8O_{21} precursor.

	Film	CrO_2 Powder
Cr 2p _{1/2}	576.4	576.4
Cr 2p _{3/2}	586.0	586.0
O 1s	529.6	529.2

The surface roughness of the CrO_2 films also decreased considerably, as evident from the AFM image presented in Figure 6.1. RMS roughness values were ~ 4.6 nm for films produced using Cr_8O_{21} compared to ~ 114 nm for films produced from CrO_3 by CVD methods. Additionally, Cr_8O_{21} may be used in UHV conditions since it is significantly less hygroscopic than CrO_3 . Unlike atmospheric pressure CVD, the molecules under UHV conditions exhibit molecular flow and should allow for a more uniform thin film growth and better masking.

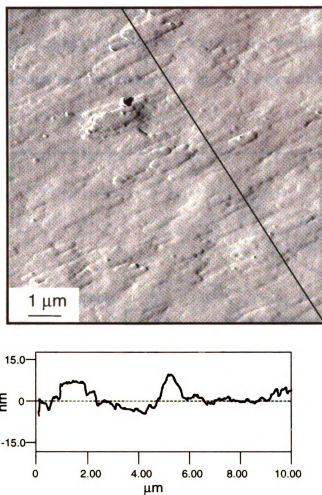


Figure 6.1 AFM 100 μm² area image (height mode) of a CrO₂ film on a rutile TiO₂(110) single crystal substrate. The film was produced by CVD in dual-zone furnace, with O₂ flowing at a rate of ~0.1 L·s⁻¹. The precursor, Cr₈O₂₁, was held at 260 °C and the substrate at 400 °C.

An important longer-term component of the work is to study the photocatalytic behavior of the TiO_2 nanoparticle arrays. Initially, methylene blue may be a suitable molecule upon which to examine the photoreactivity of the TiO_2 nanoparticles as the degradation can be monitored using simple UV-Vis absorbance spectroscopy.¹⁵⁻¹⁸ A continuous flow system, such as the one shown in Figure 6.2, could be used to monitor the change in dye absorbance as a function of time during UV or visible irradiation.

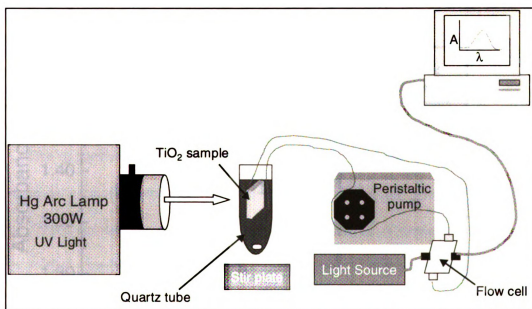


Figure 6.2 Experimental continuous flow apparatus to monitor the photocatalytic reactivity of TiO_2 nanoparticles.

Preliminary work using the experimental apparatus shown in Figure 6.2 indicates that TiO_2 nanoparticles photocatalytically degrade methylene blue, and suggests that they are more reactive than a rutile TiO_2 single crystal as shown in Figure 6.3. In the absence of TiO_2 , methylene blue photooxidizes resulting in decolorization. However, the presence of a TiO_2 nanoparticles enhances the rate of photooxidation. The increase in

reactivity for the TiO_2 nanoparticles compared to the single crystal is not believed to be attributed to surface area effects; estimates indicate that the total surface area of the nanoparticle arrays is significantly less than the total area of the single crystal. Other factors, such as pH, temperature and oxygenation of the aqueous dye solutions¹⁹ may influence the overall rate of this process.

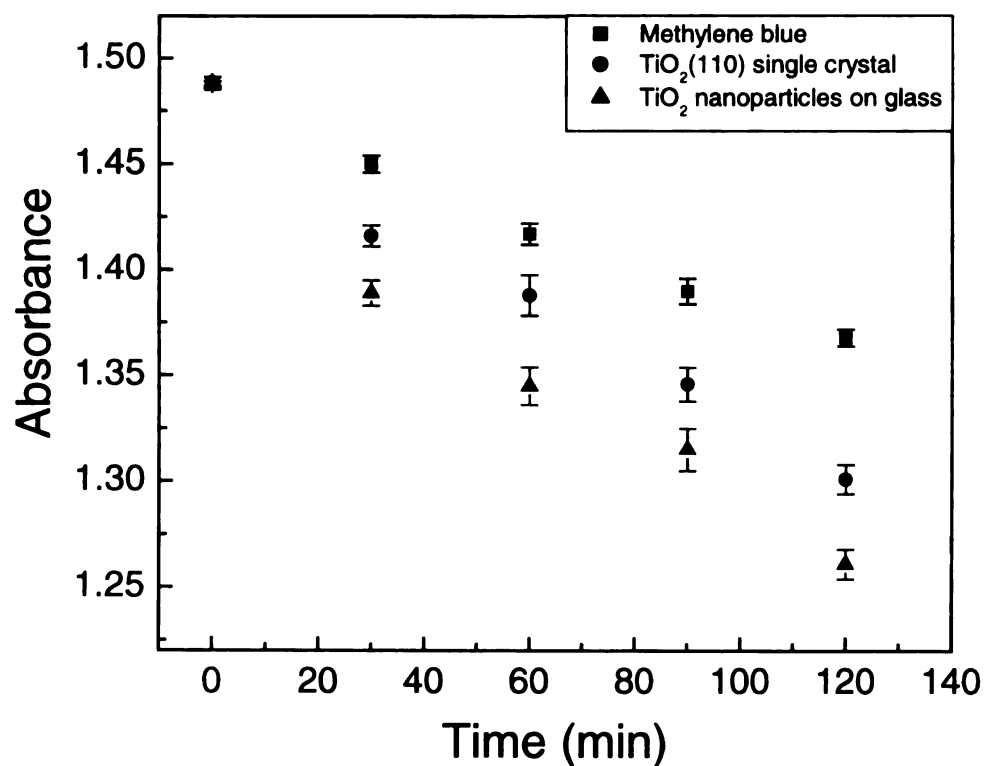


Figure 6.3. Comparison of the degradation of methylene blue dye for a rutile $\text{TiO}_2(110)$ single crystal and a ~ 150 nm particle diameter TiO_2 nanoparticle array.

The size dependent reactive, magnetic or electronic properties of other metal oxides such as RuO_2 , and CrO_2 may be interesting to explore using NSL. However, the thermal stability of polystyrene spheres currently used to make mask templates by NSL, limits deposition of material to near room temperature (substrate temperature $<100\text{ }^\circ\text{C}$). The synthesis of other metal oxides may require heating of the substrate, for example to promote decomposition of CVD precursors or improve crystallinity/composition within the nanoparticles. An alternative approach may be to use monolayer and bilayer masks built from self-assembled silica spheres.²⁰ Colloidal crystals built from silica spheres are stable to at least $500\text{ }^\circ\text{C}$ without melting.

6.3 Outlook

The experiments conducted in this dissertation have illustrated that the simple methodology of nanosphere lithography can be applied to make nanoparticles of metal oxides. These are the first detailed studies of any metal oxide nanoparticles made by this method. The diameter and height of the particles can be tuned relatively easily. The particles are produced as adherent arrays on solid supports and, as such, they provide the ideal systems upon which to test the role of surface chemistry in the properties of nanoparticles and can act as models for probing quantum size effects. The range of properties exhibited by metal oxides is varied and includes metallic conductivity, semiconductivity, superconductivity, ferromagnetism, piezoelectric susceptibility, catalytic reactivity and photocatalytic behavior. Although this thesis has concentrated on the synthesis of TiO_2 nanoparticles, it has demonstrated that the NSL technique has great

potential in elucidating size-reactivity-property relationships in many other nanometer scale oxide particles.

6.4 Literature Cited

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APPENDICES

Appendix A

X-ray Photoelectron Spectroscopy (XPS) Calibration Spectra

To ensure the calibration of the X-ray photoelectron spectrometer, calibration spectra for both the Al K α and Mg K α anodes were taken at high and low binding energy (BE) using the Cu 2p_{3/2}, and Au 4f_{7/2} regions, respectively. The Au 4f region was analyzed using a gold foil sample (0.25 mm thick, 99.99% purity, Aldrich) which was rinsed in ethanol prior to analysis. The Cu 2p region was analyzed using a copper foil sample (0.025 mm thick, 99.98% purity, Aldrich). No sample preparation, such as sputtering of the Cu film, was done prior to its analysis. The Cu metal peak could be distinguished in the XPS, despite oxygen contamination present on the surface as indicated by the small peak in the Cu 2p region at ~1.5 eV higher BE than Cu metal. The peaks in the Au 4f and Cu 2p regions were fit using a simple Shirley background subtraction with simple Gaussian-Lorentzian peak shapes and compared with known literature values. This appendix shows typical calibration spectra for the Al K α and Mg K α anodes.

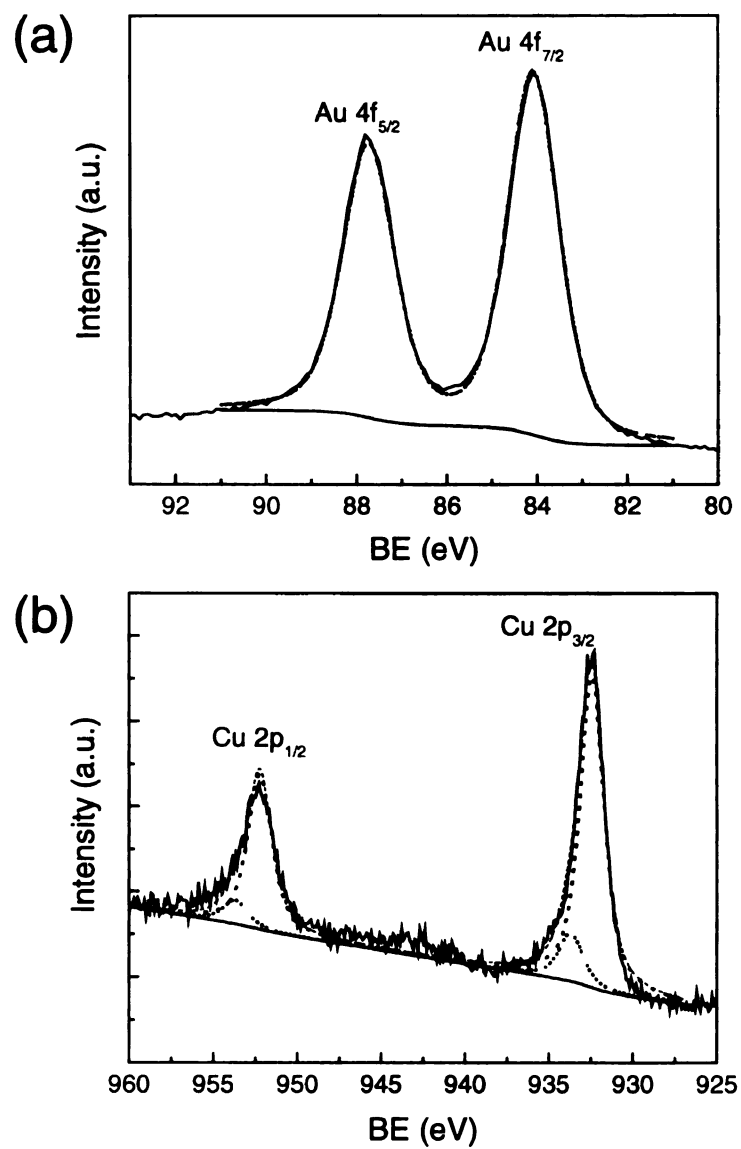


Figure A.1 XPS Calibration spectra for Al K α anode: (a) Au 4f region, and (b) Cu 2p region.

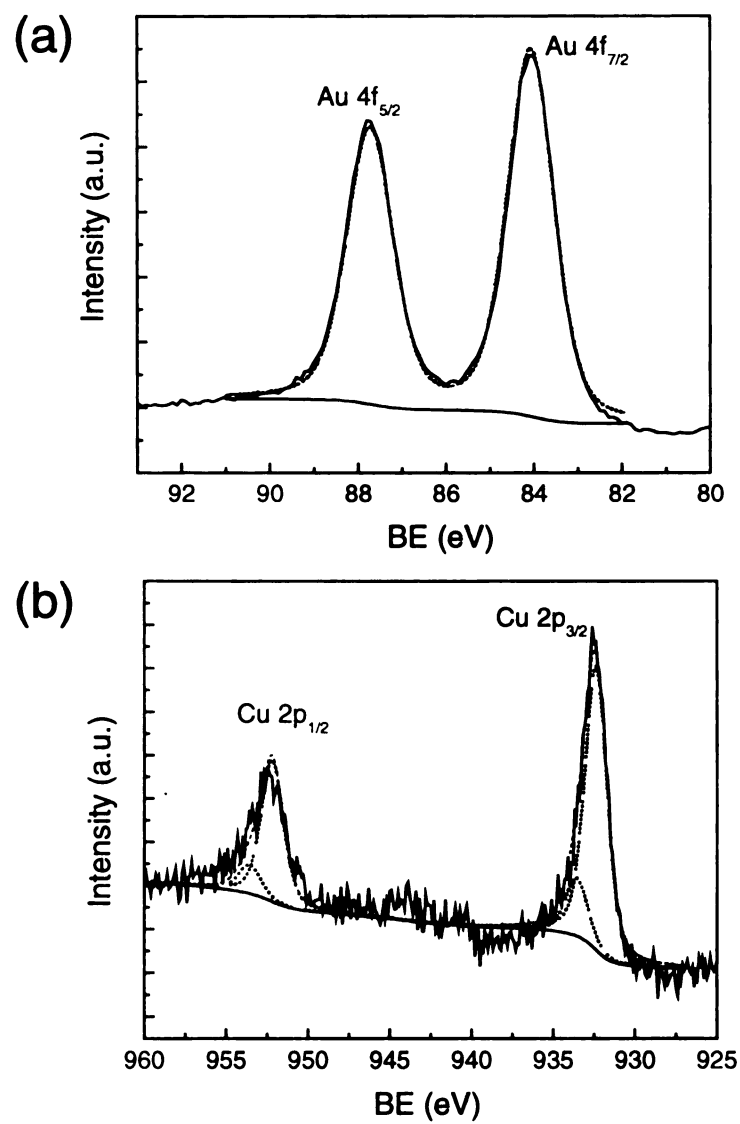


Figure A.2 XPS Calibration spectra for Mg K α anode: (a) Au 4f region, and (b) Cu 2p region.

Appendix B

Calculation of Polystyrene Sphere/Water Proportions for Monolayer Mask Assembly

The polystyrene sphere supplier provides the original concentration of the particles as

$$\eta = 6\omega/(\pi\rho\phi^3) \times 10^{12} \text{ particles/mL} \quad (\text{B.1})$$

where ω is the percentage of solid polystyrene, ρ is the density of the polystyrene and ϕ is the diameter of the spheres in microns. With this information, the concentration needed to obtain a monolayer over area A (100 mm^2) can be determined.¹ A polystyrene particle will occupy an area of

$$A_p = \pi (\phi/2)^2 \quad (\text{B.2})$$

Using this value and the area of deposition, the number particles that will cover an area, N_p , can be calculated as shown below:

$$N_p = A/A_p \quad (\text{B.3})$$

This value is then divided by the volume of water ($10 \text{ }\mu\text{L}$) used in the deposition. This will yield the concentration of spheres a portion of the stock solution should be diluted to.

$$\eta^* = N_p/C \quad (\text{B.4})$$

For example, a stock solution of 420 nm polystyrene spheres contained 1.54×10^{12} particles/mL. A diluted concentration of 420 nm spheres, η^* , was calculated to be 7.2×10^{10} particles/mL.

Typically the concentration, η^* , is doubled as multilayers may form at the edges of an aqueous drop, which will decrease the concentration of spheres in the interior region. To achieve bilayers, the calculated concentration is typically tripled.

B.1 Literature Cited

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Appendix C

Autocovariance Data for Generated Masks with Different Degrees of Order

Models of different types of sphere packing were generated and imported into the Scion Imaging Software¹ to confirm if this method could be used to distinguish order and disorder in a mask. Tetragonal packing, hexagonal packing, random packing, point defect, domain boundaries, ordered areas with large vacancies, and variations in the gray scale were evaluated. Fast Fourier transforms (FFT) and autocovariance analyses (AC) were performed on generated images.

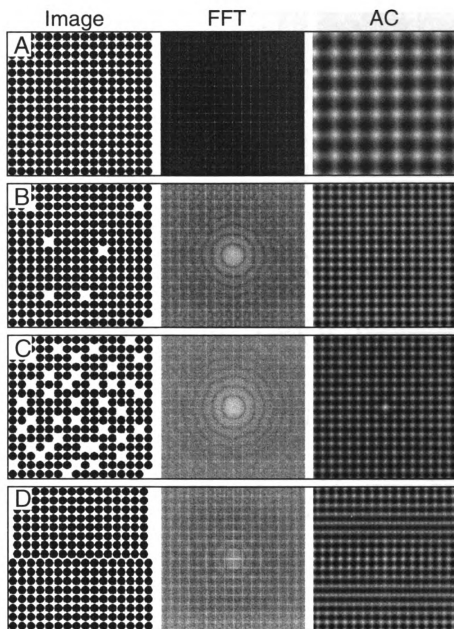


Figure C.1 Tetragonal close-packed array of spheres: (a) ordered area, (b) few point vacancies, (c) large concentration of point vacancies, and (d) two ordered domains with lattice mismatch (dislocation).

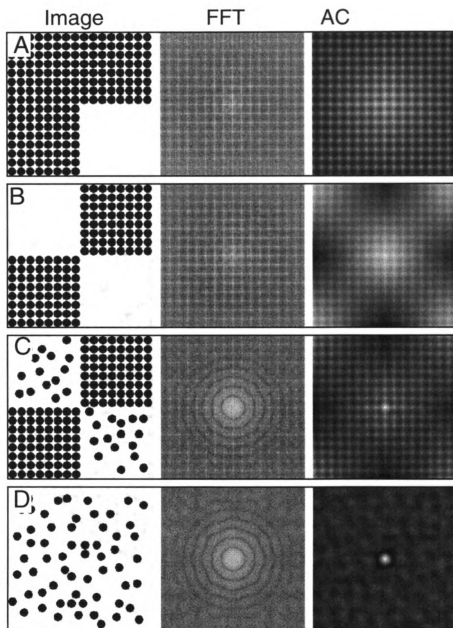


Figure C.2 Tetragonal close-packed array of spheres: (a) large ordered area with vacant region in corner, (b) regions with ordered and vacant areas of equal size, (c) regions with ordered and randomly ordered areas of equal size, and (d) randomly ordered spheres.

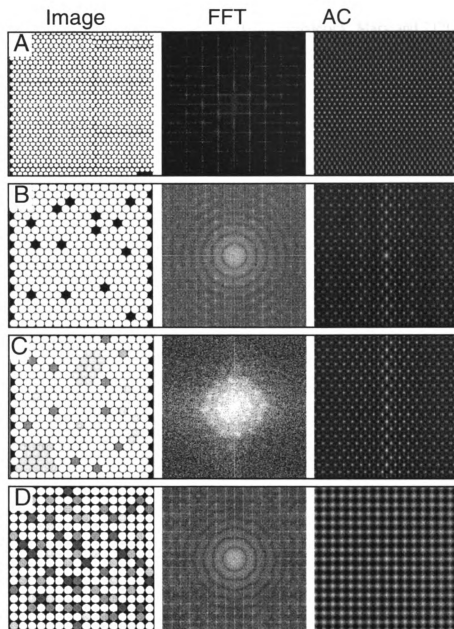


Figure C.3 Hexagonal close-packed array of spheres: (a) large ordered area, (b) ordered area with point vacancies, (c) ordered area with different gray scale for some of the spheres, and (d) ordered area with a larger variance in the gray scale shading of spheres.

C.1 Literature Cited

- (1) SCION Imaging Software, v. 4, Scion Corp.: Frederick, Maryland 21701, 2000.

Appendix D

Single Crystal X-ray Crystallography Data for RuO₂

Table D.1 Crystal data and structure refinement for RuO₂.

Formula	RuO ₂
Formula weight	133.07
Temperature	173K
Wavelength	0.71073 Å
Space group	P4 ₂ /mnm (#136)
Unit cell dimensions	a = 4.4981 (6) Å b = 4.4981 (6) Å c = 3.1134 (6) Å
Volume	62.993(17) Å ³
Z, Calculated density	3.508 Mg/m ³
Absorption coefficient	5.882 mm ⁻¹
F(000)	60
Crystal size	2.0 mm x 0.14 mm x 0.14 mm
θ range	6.41 to 27.14°
Limiting indices	-5 ≤ h ≤ 5 -5 ≤ k ≤ 5 -3 ≤ l ≤ 3
Reflections collected/unique	531 / 46
R _{int}	0.0296
Completeness to θ _{max}	97.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	46 / 0 / 9
Goodness-of fit on F ²	1.183
Final R indices [I > 2σ(I)]	R1 = 0.0337 wR2 = 0.0750
R indices (all data)	R1 = 0.0376 wR2 = 0.0772
Largest diff. peak and hole	1.400 and -0.387 e ⁻ /Å ³

^a $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma(wF_o^2)^2]^{1/2}$

Table D.2 Atomic coordinates ($\times 10^4$) for RuO₂.

	x	y	z
Ru	5000	5000	0
O	1952(12)	1952(12)	0

Table D.3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RuO₂.

	U11	U22	U33	U23	U13	U12
Ru	5(1)	5(1)	0(1)	0	0	0(1)
O	8(3)	8(3)	0(3)	0	0	-1(4)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + \dots + 2hka^*b^*U12]$

Table D.4 Selected bond distances for RuO₂.

Bond distances ($\text{\AA}$)	
Ru –O (1)	1.939 (7)
Ru –O (2)	1.991 (5)
Ru –O (3)	1.991 (5)
Ru –O (4)	1.991 (5)
Ru –O (5)	1.991 (5)
Ru –O (6)	3.1134 (6)
Ru –O (7)	3.1134 (6)
Ru –O (8)	1.991 (5)
Ru –O (9)	1.991 (5)