PLASMA APPLICATION FOR SYNTHESIS OF NOVEL NANOSTRUCTURES AND MECHANICAL PROPERTIES INVESTIGATION

By

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ABSTRACT

PLASMA APPLICATION FOR SYNTHESIS OF NOVEL NANOSTRUCTURES AND MECHANICAL PROPERTIES INVESTIGATION

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Today, nanomaterials are receiving increasing attention, as they exhibit exciting and useful attributes that can be employed across applications and disciplines range from electronics to drug delivery. This dissertation focuses on two disparate projects, both related to plasma-synthesized nanocrystals. The two projects highlight the unique properties of nanocrystals, and their sustainable synthesis using gas phase approaches. These methods apply non-thermal plasma reactors for nanocrystal synthesis. First, we introduce a plasma-based gas phase method for Gold nanoparticle (AuNPs) synthesis. Second, we use plasma-synthesized Silicon nanocrystals (SiNCs) in bilayer and composite structures with a commonly used elastomer, to investigate the mechanical behavior of the structures in a first-of-its kind investigation.

There are many applications for AuNPs due to their interesting optoelectronic properties, such as tunable optical absorption and plasmonic resonance behavior. While synthesis and stabilization of colloidal AuNPs is well-established, new synthesis routes can lead to enhanced versatility of applications for AuNPs, particularly if the methods allow avoidance of solution processes or surfactants. In Chapter 2, we introduce a plasma-based synthesis of AuNPs, using a consumable gold wire and a radiofrequency power source. The AuNPs are monodisperse, with an average diameter of 4 nm. While production yield is low, the narrow size distribution of the AuNPs and the avoidance of solution processing in this method are promising for future syntheses of metal NPs based on plasmas.

Next, a comprehensive analysis of the mechanical behavior of SiNC/PDMS systems, using plasma-produced SiNCs has been performed. Chapter 3 details our experimental methods combined with modeling to estimate the mechanical behavior of thin layers of SiNCs on PDMS, as deposited directly onto the PDMS from non-thermal plasma reactor. For the first time we estimated the mechanical behavior of thin films of SiNCs by using the onset of bifurcations as an indicator of

their modulus. Next, reaching towards luminescent nanocomposites for applications in luminescent devices, we investigated the optical and mechanical behavior of blended SiNC/PDMS nanocomposites. The results from these investigations, reported in Chapter 3 and Chapter 4, have shed light for the first time on the interactions between SiNCs and PDMS both in bilayer and composite structures, pointing to future optoelectronic and opto-mechanical device applications with predictable properties. Finally, in Chapter 5, we share ongoing projects which will be finalized soon, as well as detailing future work surrounding these ideas. We share our parametric study to uncover the various effects of surface functionality, SiNC layer thickness, and PDMS modulus on the resulting SiNC thin film. Concurrently, we probed the formation of wrinkles and cracks on SiNC film surfaces, which were deposited on pre-stretched PDMS using a finite bending configuration, to examine how instabilities on the thin films can be predicted.

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CHAPTER 1

INTRODUCTION

The focus of this dissertation is synthesis and use of nontoxic nanomaterials for a variety of applications. Nanomaterials such as nanocrystals are critical for a range of novel applications ranging from biological treatments and diagnostic procedures to devices such as light-emitting devices (LEDs), solar photovoltaics, and wearable sensors. There are two main thrusts to the research: one focuses on new gas-phase routes to freestanding, surfactant-free gold nanoparticles, including a novel plasma reactor. The other explores the optical and mechanical behavior of plasma-synthesized silicon nanocrystals. This introductory chapter sets the stage for discussing the subsequent research by providing a background on plasmas, the history and use of gold nanoparticles, and the prior work on studying the mechanical behavior of thin films of silicon nanocrystals.

1.1 Introduction to Non-thermal Plasma

Today, many research studies have been dedicated to investigating the synthesis and use of nanocrystal-based materials, including those processed in the liquid phase [83, 122, 164]. While liquid-phase synthesis and/or surface modification has yielded exceptional results for some nanocrystalline materials, there are limitations imposed by solution processing. For example, the temperature of liquid phase synthesis methods are limited by the boiling points of solvents [83]. This can hamper the formation of some nanocrystals due to the required high crystallization temperatures, though some approaches have been successful for materials such as silicon nanocrystals [36, 63, 64, 189]. Additionally, liquid-phase synthesis and/or surface modification processes necessitate disposal procedures for the solution wastes and by-products which are timeconsuming and are not environmentally sustainable. In contrast, gas phase approaches do not require organic solvents during the synthesis process and are capable of achieving nanocrystals from high-temperature-crystallization materials. There are two classes of gas phase synthesis methods, differentiated according to the thermal equilibrium during the process. Thermal equilibrium syntheses include flame synthesis [83, 158], thermal pyrolysis in furnaces [129], laser pyrolysis [83, 91] and thermal plasmas [142]. In this class of gas phase synthesis, the entire system achieves a relatively high temperature (e.g. gas species, excited species, and synthesized nanomaterials). During many thermal-equilibrium processes, the produced nanoparticles have reduced charging and a large degree of agglomeration. Some liquid phase post-processing steps are often be required in this regard. Also, higher temperature thermal plasma increases the chance of broad size distribution [83]. Gas-phase processes that are not in thermal equilibrium (such as non-thermal plasmas) are the alternate class of method for nanoparticle synthesis. In non-thermal equilibrium we have heavy gas species and ions that are close to room temperature, while free plasma electrons (which have negligible mass in comparison) can achieve temperature between 1000 to 50000 K [83, 107]. Collisions between plasma electrons and molecules in gas flow dissociate and ionize gaseous precursors, producing highly reactive components [83]. Non-thermal plasmas have several of advantages including ligand-free, high-purity final products. High melting point materials can be synthesized due to highly exothermic reactions just at the surfaces of the forming nanoparticles. In non-thermal plasmas, synthesis of very small nanoparticles (with sizes below 10 nm and size distributions around 10-20% std. dev.) are possible. Diffusion loss to the walls, together with nanoparticle agglomeration, are negligible due to negative charges of surface of the reactor walls as well as at the surfaces of nanoparticles - both of these are the result of the high kinetic energy and collision frequency of electrons with surfaces in the plasma. Additionally, nanoparticle growth occurs over a particle residence time on the ms time scale [3, 83, 107]. These attributes make nonthermal plasmas an interesting substitute for liquid phase synthesis.

In general, nonthermal plasmas are classified by low ionization fraction. In radiofrequency (RF) plasmas, such as the ones used in this dissertation, ions are generated by the applied rf field. This field causes the free electrons to accelerate to high speed. The number of free electrons exponentially increases in the plasma and few of these electrons are able to exchange energy with heavier gas species, such as precursor molecules [83]. Most of the energy provided to the plasma

also absorbed with electrons since they have higher mobility compared to ions. The densities of electrons and ions remain approximately equal due to the principle of quasineutrality in the plasma, except near the walls (this small region of non-neutrality is called the plasma sheath) [18, 92]. The difference between speed and temperature of electrons and ions in the plasma is what establishes the condition of non-thermal equilibrium, and is also the cause of the negative charging of surfaces (*i.e.* walls and nanoparticles) in the plasma [25, 83].

In the non-thermal plasma, nanoparticles will be charged to negative potentials in the order of $k_B T_e/2e$. By considering the typical temperature of electrons, individual nanoparticles will have a charge of up to few volts. As an example, a typical particle flowing in the plasma with diameter of around 1 nm carrying a single electron will have a negative potential of -1.4 V [83, 136]. In order to validate a charge balance between electron and ion currents reaching the surface of the nanoparticles, it is essential to note that nanoparticles of different sizes will charge to approximately the same steady state potential.

Bouchoule et al. [17, 83] proposed a three-steps mechanism for nanoparticle growth in nonthermal plasmas. Although the repulsion between negative charges prevents nanoparticles from agglomeration, the smaller particles at earlier stage of growth (nanoparticles with size less than 1 nm) usually have no charge and their aggolomeration is one of the main mechanisms for nanoparticles growth. First, initial clusters of precursor fragments generate at nucleation stage, forming protonanoparticles. Second, since the nanoparticles emerging from the first stage are mostly less than 1nm in size and has no charge, larger particles grow quickly through the coagulation of initial neutral small clusters [83]. This step continues up to point that all of nanoparticles have single charge. Finally, the growth of nanoparticles continues by reaction of precursor on their surface.

Non-thermal plasma reactors can operate under reduced pressure or atmospheric pressure. These reactors can include various components and characterization tools including the reaction chamber, vessels for precursor injection [83], gas processing pipelines, analysis ports, and the nanomaterial collection system (often by impaction or diffusion). The reaction chamber can be modified over a vast range for flow-through and batch processing requirements.

This dissertation research employs plasma reactors for nanomaterials synthesis in two separate projects. A background on alternate methods provides useful context. In the next section we briefly review prior methods for fabrication of noble metal nanoparticles, pertinent to the chapter on gold nanoparticle synthesis using a novel non-thermal plasma reactor. Then we briefly talk about silicon based- nanomaterials for electronic, sensor, and optoelectronic applications, especially nanoparticles produced by non-thermal plasmas. In addition, we introduce poly(dimethylsiloxane) (PDMS) as a stretchable substrate with some unique physical properties that make it suitable for probing the mechanical behavior of silicon nanoparticle layers. Finally, we review some existing mechanical models for estimating the mechanical properties of a thin film of semiconductor layers on a flexible substrate.

1.2 Gold Nanoparticles

Gold nanoparticles (AuNPs) are one of the oldest forms of nanostructures, with medical applications dating back to 1618 [15]. Today scientists are especially interested in Localized Surface Plasmon Resonance (LSPR), a phenomenon of unique optical shape-dependent property with quantum features, which results from the small size of these structures in less than 10nm. LSPR is an optical property which occurs when a noble metal nanoparticle interacts with a photon[43]. Depending on the metal, particle size, particle shape, and photon energy, the free electrons in the nanoparticle can undergo resonant oscillations and amplify or otherwise modify the electromagnetic field nearby. LSPR has two main consequences. First, the electric field near the particle's surface is greatly enhanced; second, the nanoparticle's optical absorption has a maximum at the plasmon resonant frequency (which is dependent on metal, size, and shape). The enhancement decreases quickly with increasing distance from surface of the particle. LSPR occurs at visible wavelengths for the noble metal nanoparticles including AuNPs [21, 71, 90, 98, 101, 147, 198]. The LSPR effects (both for emission and absorption) from AuNPs can be used in many applications including as biological labels, therapeutic cancer treatments, solar photovoltaics, near-field and electron microscopy, and more [47, 70]. In addition to uses centered around their LSPR, metal nanoparticles can be used to catalyze the growth of anisotropic semiconductor nanostructures such as silicon nanorods (SiNR) [63]. These anisotropic structures offer novel and shape/size-dependent optoelectronic properties, and so the catalysis offered by AuNPs and others adds to their attractive properties.

1.2.1 History of AuNP synthesis

Among the synthesis methods for AuNPs production, many involve wet chemistry-based approaches, which require ligands and other solution-phase modifiers to the naoparticle surfaces [101, 121]. Solution based syntheses are among the earliest methods for formation of gold nanostructures and are still used today[20, 35, 39, 49, 54, 101, 171, 197]. In general, AuNPs in solution phase produced by reduction of chloroauric acid. In these methods the naoparticle growth happens step by step from molecular precursors (also called bottom-up), leading to better control on the shape and size distribution of AuNPs in the final product. In the solution-based routes, the AuNPs end up solubilized in water or other solvents. We endeavored to eliminate the possibility of contamination from these liquids and extend the uses of AuNPs by synthesizing the AuNPs in the gas phase. This will open up a new approach for AuNPs synthesis and reduce both product contamination as well as reduce the need for solution disposal after-process. Our research builds on prior work to synthesize AuNPs in the gas phase, particularly aiming towards a synthesis method that permits easy integration of the AuNP product into subsequent reaction steps without interruption of process parameters. We review these pre-existing methods below, and in Chapter 2 we introduce our new plasma-based method.

1.2.2 AuNP formation in the gas phase

Other work has led to gas-phase, solvent-free synthesis routes to AuNPs. There are several options for synthesis in the gas-phase, including inert gas condensation of Au vapor in a chamber, spark-ignition AuNP generation, sputtering techniques, and hot-wire synthesis. Here we detail the hot-wire synthesis method, which has demonstrated promise in multi-step reaction procedures.

[15]. This approach is similar to other gas-phase methods in that it requires a gas flow and a heat source for generating the AuNPs. Since the metal wire is heated via electrical resistance, the average background gas temperature will not increase except in the area locally close to the resistive element. Under the right conditions of gas flow, pressure, and suplied electrical current, the evaporated metal atoms reach supersaturation upon leaving the metal wire surface, and rapidly nucleation of nanoparticles begins. Gas drag then carries the AuNPs downstream for collection or further use. The big advantage of the hot wire method is that according to previous studies, background gas has small effect on property of metal nanoparticles. Peineke et al. described that the hot wire method is suitable for all metals which have vapor pressure of higher than (3.75*10-5)Torr) at the melting point. According to this guideline, gold (with a vapor pressure of 1.5*10-5Torr) does not meet this requirement. However, as Boies *et al.* reported [15], gold can be used if the source is an electroplated wire structure. For example, they had success using a Platinum (Pt) (99.5%, trace metal, Aldrich) wire with 0.5 mm in diameter as the core. The gold as the outer shell was deposited via electroplating by the ProPlate Company in Minnesota. Studies have shown that hot wire method with a coaxial gold source can produce AuNPs with less than 10 nm average diameter [15, 16]. Figure 1.1 depicts the schematic diagram of hot wire gold nanoparticle formation method as developed by Boies et al. This method is promising as it results in AuNPs entrained into the gas flow – but had only been reported at atmospheric pressure prior to our work. For coupling into a low-pressure reactor for possible multi-step reactions including non-thermal plasmas, we were interested to explore this method as an AuNP catalyst source at lower pressure. We were also interested in other methods for AuNP synthesis at lower pressure.

Our work on a reduced-pressure approach to the hot wire synthesis of AuNPs is detailed in Chapter 2, alongside our introduction of a plasma-based synthesis of AuNPs, using a consumable gold wire and a radiofrequency power source. In our plasma method, the AuNPs are mono-disperse, with an average diameter of 4 nm, offering some improved properties as compared to our attempt at a low-pressure hot wire synthesis route. Notabely, this size range is one of the most interesting for optoelectronic and LSPR functionality for AuNPs. As shown in that chatper, although the



Figure 1.1: Hot wire synthesis of AuNPs as developed by Boies *et al.*

production yield is low, the narrow size distribution of the AuNPs and the avoidance of solution processing in this method are promising for future syntheses of metal NPs based on plasmas.

1.3 Silicon Nanoparticles

The other focus of this dissertation is on deployment of silicon nanoparticles onto and within polymer substrates for evaluation of optical and mechanical properties of these bilayered and hybrid macroscale structures. Silicon has been a dominant material in the field of electronics over the last half century or more, due to its semiconducting electronic behavior, optical band gap at 1.1 eV, its natural abundance, its low cost, and its relative nontoxicity. Despite the long history of use in transistors, traditional solar photovoltaics, bulk silicon has poor emission behavior. Due to its indirect band gap, silicon requires that photon emission and absorption processes involve a momentum-balancing phonon [107]. This disadvantage limits the applications of bulk silicon as a potential material for host of optoelectronic devices including emissive applications, although doping, alloying, and combination of bulk silicon into hybrid structures with other direct band gap semiconductors has allowed some device development in the area of optoelectronics. [75].

However, since the late 1980s, new discoveries on the behavior of nanoscale silicon have revealed that optical processes become much more efficient when the silicon becomes quantumconfined, meaning its size becomes small enough that electron-hole combination processes are affected. In particular, when the silicon nanostructure size shrinks to approximately the Bohr exciton radius (around 5 nm), the electron and hole wavefunctions can exceed the nanostructure's physical size. This widens the band gap, relieves some of the quantum selection rules governing the recombination processes, and improves the efficiency of photon processes for the relaxation of the exciton. This is manifested in size-tunable photon energy and increased photolumienscence (PL) efficiency. Many studies have been probed the PL and other optical properties of silicon nanocrystals (SiNCs), leading to their application in optoelectronic devices, microelectronics, and solar photovoltaics [5, 26, 32–34, 39, 107, 139, 167].

In the last few decades many advancements on influence of surface conditions on the luminescence properties of quantum confined SiNCs have emerged [107, 176, 199]. In particular, passivating the SiNC surfaces with organic ligands has been demonstrated to improve their PLQY. There are various approaches to this, including solution-phase thermal hydrosilylation, UV- and white-light-initiated hydrosilylation, and gas-phase methods including using furnaces and lowenergy plasmas [5, 37, 76, 105, 106, 150, 189].

The wide range of applications for luminescent SiNCs had been limited by the lack of a simple, fast, and inexpensive synthesis approach [107]. Liquid-phase approaches, including synthesis in inverse micelles [187] synthesis in high temperature supercritical solutions,[42] the oxidation of metal silicide,[135] and the reduction of Silicon tetrahalides and other alkylsilicon halides,[8] are mostley time consuming processes. These methods usually have low production rates. Gas-phase methods including the pyrolysis of silane in furnace flow reactors, [94, 107, 127] the decomposition of silane through laser light irradiation (photolysis),[12] and laser pyrolysis using high power infrared lasers [107], all may yield faster processing times. Although these methods have faster production time, are prone to particle agglomeration. In order to deagglomerate the final clusters,further post processing is necessary. These post processing steps might diminish quantum confinement properties [107]. However, non-thermal plasma processes as among the most promising, due to the rapid, facile synthesis and tight control over SiNC properties correspond to the easily adjustable reactor parameters such as pressure, reactor dimensions, supplied power, and gas species.

SiNCs experience an interesting journey during synthesis in a non-thermal plasma reactor. One of the earliest reports regarding the particle heating in plasmas dealt with micron-sized particles that were injected into argon plasmas [38]. For $0.5-3 \mu$ m, they measured particle temperatures that were 75 k above the gas temperature [38]. The propsed model is that the heating of the particles are due to electron-ion recombination and the main cooling event is due to radiation and coduction at the surface of the particles.

Despite a low overall gas temperature, SiNCs can reach elevated temperatures, as pointed out by *Daugherty et al.* and *Mangolini et al.* [38, 107]. These investigations considered the effects of electron-ion recombination at SiNC surfaces, other reactions between neutral gas species with SiNC surfaces, radiative cooling processes, and gas conduction cooling processes. Results indicate that the SiNC temperatures can spike to several hundred Kelvin higher than the gas temperature. These spikes are responsible for the crystallization of the SiNCs. These works also revealed that bigger nanoparticles require higher temperatures for their crystallization. Significantly, smaller particles will gain higher energy (corresponding to higher spike temperature) due to exothermic recombination events on their surfaces[107]. *Kramer et al.* [84, 85] studied the differences between nanoparticle heating and cooling events at atmospheric pressure and low pressure respectively. Since gas conduction is faster in atmospheric pressure, SiNCs produced at atmospheric pressure experienced higher spikes of temperature and fast cooling successively. However, in low pressure environment, cooling is much slower and SiNCs experience higher average temperature after successive heating and cooling events.

One of the major attractions of nonthermal plasmas compared to other gas-phase methods is their ability to produce quantum-confined, luminescent SiNCs that are smaller than 5 nm [83]. Studies have shown that decreasing residence time in the reactor produces smaller particles [55, 83]. Synthesis of SiNCs with tunable sizes between 3 nm and 6 nm and residence time of 2 ms and 7 ms, respectively, in a capacitively coupled plasma (CCP) has already been reported more than a decade ago [107]. One important consideration is that the large surface-to-volume ratio for nanoparticles of all types means that efficient luminescence processes require a surface with few defects. For many materials this is accommodated by ligand attachment at the surfaces, a process which is intrinsic to their synthesis in the solution phase. With plasma-produced SiNCs, as-produced hydrogen-coated nanoparticles have a high density of defects and thus a low PL yield. With air exposure, an oxide layer at the shell of these plasma-produced SiNCs enhances the luminescence efficiencies. Even more improved luminescence for plasma-produced SiNCs can be achieved via passivation of the SiNCs by surface-functionalization with organic compounds, such as alkene organic ligands. This covalent bonding at the surfaces of the SiNCs helps to achieve solution PL quantum yields (QYs) as high as 60% [79, 105]. Our work on using plasma-produced SiNCs in bilayer and hybrid polymer structures (3) includes surface functionalization using a corresponding procedure, and application of these surface-modified SiNCs.

Andthony *et al.* [7] pointed out that the injection of hydrogen H_2 downstream of the synthesis

plasma also improves the quantum yield of the resulting SiNCs [83]. The improvement has been confirmed by electron paramagnetic resonance (EPR), with lower surface defects in SiNCs produced using H_2 injection. [133]. These prior discoveries built the foundation of our approach to synthesis and surface-modification of SiNCs, as will be discussed in subsequent chapters.

1.3.1 SiNCs on Flexible Substrates: Polydimethylsiloxane (PDMS)

In Chapter 3 and Chapter 4, we introduce methods for investigating the SiNCs both on top of and embedded within polydimethysiloxane (PDMS), a commonly-used flexible/stretchable elastomer. We anticipate these structures to find applications in the next generation of gas sensors, solar panel devices beyond traditional architectures, LEDs, and other flexible microelectronics[26]. Previously, luminescent SiNCs have been used exclusively in traditional rigid devices - but flexible, stretchable devices offer exciting opportunities. Recently, the Plasmas and Nanomaterials Laboratory (PNL) performed a study on the aging properties of SiNCs on PDMS [104]. Keeping the synthesis parameters constant, SiNCs were deposited directly out of the plasma reactor into thin-film layers on the PDMS and onto bulk Si wafer substrates and/or glass using inertial impaction through a slit-shaped orifice [3, 5, 68]. This impaction results in a different thin film morphology on the rigid substrate, as observed using electron microscopy [104]. The reason behind this morphological difference is under investigation, however, is likely attributed to the difference in elastic properties of the PDMS as compared to the rigid substrate. In chapter 4 we introduce a *in situ* method for measuring mechanical properties of SiNCs and PDMS as a bilayer system.

PDMS belongs to a class of polymeric compounds that are commonly referred to as silicones. PDMS is by far the most widely used organosilicon compound polymer [1]. PDMS also has distinctive flow properties. PDMS is inert, non-toxic and non-flammable. Its applications span a wide range, including in contact lenses and medical devices, additives in beauty products, foodrelated industries as a foam prevention agent, adhesives, replica molding, micro-nanofluidic and membranes, and more [24]. Moreover, PDMS is a useful functional polymer material in academic experimental research and industrial applications due to its unique properties including reasonable thermal stability, high transparency, low surface free energy and excellent biocompatibility which provides a wide range of other applications for medical device development and health monitoring sensors [24].

PDMS is a viscoelastic polymer. Its viscosity is a function of temperature. During long flow times and high temperatures, it acts like liquids with high viscosity, however, in low temperature it acts like a rubber-like material. Viscoelasticity is a common form of nonlinear elasticity for a wide range of polymers [46]. The elastic behavior of PDMS mostly depends on the concentration of cross-linking agent used during the curing process. PDMS can conform to various types of surfaces during the curing process. Obviously this feature makes PDMS a tunable material for a wide range of experimental applications including, microelectromechanical systems [111, 145]. Mostly, the cross-linked cured version of PDMS as a rubber-like material, has a solidified form and is extensively used for stretched, bent, compressed and other type of stress-based deformation experiments [185]. Generally, PDMS has a low elastic modulus which enables it to be easily deformed and results in the a rubber-like behavior [78, 96]. The shear modulus of PDMS changes with preparation conditions, and consequently varies between the range of 100 kPa to 3 MPa. This topic will be discussed further in chapter 3 and chapter 4.

1.3.2 Mechanical properties of SiNCs, deposited as thin films

To date, nanoparticles have been used for variety of applications. However, there is a noticeable lack of knowledge regarding the mechanical behavior of layers of nanoparticles, especially the layer's ability to bend, stretch and deform when deposited on a flexible substrate. The mechanical behavior upon deformation of a substrate will cause instabilities in deposited thin film structures, including in layers of nanoscale particles. Additionally, when nanoparticles are mixed within polymers, they can affect the nanocomposite's mechanical behavior. Combining the mechanical properties of a polymer-based materials such as PDMS, with the tunable optical, electronic, and estimated mechanical properties of SiNCs could lead to the introduction of a new class of highly

flexible technologies utilizing multi-layer and composite architectures including wearable sensors and foldable LEDs, among others. [10, 11, 156]. In order to be able to practically design devices with such a new level of flexibility, the mechanical properties of the substrate and thin film layers should be investigated individually and together as a system.

Large deformations such as uniaxial compression, equibiaxial compression, pure shear, finite bending, and unbending are attracting interest as methods to estimate the mechanical behavior of materials [14, 40, 143, 144, 153]. In addition, uniaxial tensile testing can reveal information about the mechanical behavior of nanocomposites. Chapter 3, Chapter 4, and Chapter 5 discuss our efforts to apply uniaxial tensile testing, bifurcation analysis, and theoretical modeling frameworks to estimate the mechanical properties of nanocomposites based on SiNCs and of SiNC thin films deposited on PDMS directly from the gas phase.

In chapter 3 we discuss a novel technique for measuring the mechanical properties of thin film of nanocrystals, especially SiNCs, due to their vast ranges of application and growing market for future device development, deposited on PDMS as a flexible substrate. This method further can be applied for other nanostructure thin films and flexible substrates. In Chapter 4 we investigate the mechanical properties of a composite structure, SiNC clusters embedded in PDMS for luminescence solar concentrator and other flexible optical devices. In Chapter 5, we introduce a parametric study to investigate the dependence of various parameters, including, thickness of the film, modulus of the substrate and surface functionality of SiNCs on the mechanical property of the thin film in a bilayer system. Later in Chapter 5 we also report our study of another class of surface instability, which arises as a result of unbending of SiNC layers as deposited on an initially pre-stretched PDMS system. In summary, these results shed light on the mechanical behavior of SiNCs, dependent on their surface functionality, both in nanocomposite and in bilayer structures. This work contributes to the future applications of SiNCs in flexible, bendable, and stretchable manifestations.

CHAPTER 2

AUNP SYNTHESIS: A PLASMA-BASED APPROACH

Portions of this work were published in the journal "Plasma Processes and Polymers" in July 2019 and reproduced here. This article was also featured on the front cover of the July 2019 issue of the journal.

PLASMA PROCESSES AND POLYMERS



Figure 2.1: An overview of gold nanoparticle synthesis

2.1 Introduction

Metallic nanostructures have proven to be among the most flexible nanomaterials owing to the synthetic control of their size, shape, composition, as well as the resulting tunable optical properties[72]. Gold nanoparticles (AuNPs) are among the oldest forms of engineered nanostructures, with medical applications dating back to the early 17th century. AuNPs are broadly attractive across disciplines, and are used for applications such as medical theranostics, Surface Enhanced Raman Spectroscopy (SERS), optoelectronic device enhancements, and as seeding sites for other materials such as silicon nanowires [43, 61, 72, 97, 159, 170, 190].

Most synthesis methods of AuNP production involve wet chemistry-based approaches[20, 35, 49, 54, 73, 101, 121, 171, 197]. In solution-based routes, the AuNPs typically end up solubilized in water or other solvents using surfactants, which is useful for some applications – but this can also increase contamination for many post-processing purposes. To eliminate the possibility of contamination in post-synthesis reactions and applications, there is interest in routes for synthesizing the AuNPs in the gas phase. Pre-existing methods in gas phase include inert gas condensation, spark ignition, plasma sputtering, and hot wire synthesis[15, 81, 117, 132, 137, 161]. Recently, several groups have turned to flow-through plasma synthesis of metallic NPs and nanostructured films[28, 29, 86, 188, 197]. The advantages to these plasma-based methods are a relatively narrow size distribution and continuous synthesis. Here we introduce a new method for making AuNPs based on a radiofrequency (rf) plasma together with a consumable Au electrode for synthesis of monodisperse AuNPs with an average diamter of ~4nm. We compare this method with a low pressure hot-wire technique for AuNP synthesis, finding that while the hot-wire method has a higher yield of AuNPs, the plasma-based route produces NPs with a smaller size dispersity. This approach adds to the versatility of plasma reactors for nanomaterials synthesis.

2.2 Experimental Details

We used a non-thermal radiofrequency (RF) plasma reactor for AuNP synthesis. Figure2.2 shows a schematic view of this reactor. The plasma is initiated via RF power (13.56 MHz) supplied via a matching network to a copper coil around a quartz tube (2.54 cm O.D. and 20 cm length). The grounded electrode is a pure Au (99.99) wire threaded coaxially within the tube, which is also the source of Au for the AuNPs. We flowed Argon (Ar) gas through the reactor at flowrates between 600-1200 standard cubic centimeters per minute (sccm) and used orifice plates downstream of the



Figure 2.2: Photograph and schematic of plasma-based AuNP synthesis. Insets show TEM images of AuNPs.

reactor to modulate the pressure between 60-220 Torr. The pressure beneath the orifice was <10 Torr.

We varied the power to the external coil between 5-15W (nominal), upon which the gas surrounding the Au wire began to glow. To confirm that the Au wire acts as the ground, we attempted to operate the reactor without the coaxial wire – with no success at initiating a plasma. We placed a TEM grid (Lacey Carbon Film Cu 300 mesh from TedPella[®]) at the exit of orifice for collecting and analyzing the AuNPs. Figure 1 shows a schematic diagram of our process, and Fig2.1 shows a list of samples and corresponding parameters we explored for the plasma method, including pressure, power, and discharge length.

We sought to compare our plasma method with an alternate technique, similar to the previouslyreported hot-wire AuNP synthesis technique at atmospheric pressure reported by *Boies et al.* [15], but operated under reduced pressure of 10 Torr. Our hot-wire setup consisted of a glass tube with a Platinum (Pt) wire electroplated with Au (0.5 mm thickness) and connected to a DC power supply. The electroplated Pt-Au wire was threaded via an electrical vacuum coupler feedthrough into a

Sample	Pressure (Torr)	Flowrate (sccm)	Power (W)	Reactor Length (cm)	AuNPs	Orifice Size (mm)
1	220	1200	5	20	Yes	1
2	180	900	10	20	Yes	1
3	239	1200	10	20	Yes	1
4	117	1200	5	10	Yes	2
5	120	600	25	20	Yes	1
6	91	600	10	20	No	2
7	60	1200	15	20	No	3

Table 2.1: Reaction parameters for plasma-based AuNP synthesis

sealed glass vacuum reactor tube and connected externally to a DC power supply. The glass reactor tube was a three-way heavy-duty quartz glass (2.54 cm O.D. and 12.7 cm length) which was fused to a flexible stainless steel flange to prevent it from breaking during experiments. Ar was used as a background gas for carrying AuNPs towards the reactor exit, with flowrates between 300-1200 sccm and reactor pressure from 2-30 Torr, depending on gas flowrate and orifice size. DC power was supplied to the Pt-Au wire, resistively heating the gold at the surface and causing evaporation. The gold atoms entered the gas phase and condensed to form AuNPs. Figure 2 shows a schematic view of this reactor.

2.3 **Results and Discussion**

We measured the diameter of the plasma-produced AuNPs with Transmission Electron Microscopy (TEM) and Scanning TEM (STEM). TEM images showed individual AuNPs deposited onto the grid at the exit of the reactor (Fig.2.4a-d). Both bright field and dark field images (Fig2.4) show that the collection grid is covered with individual AuNPs. A higher-magnification image shows lattice spacing, with the [2 0 0] plane identified (Fig.2.4c). We performed Fast Fourier Transform (FFT) analysis of an individual AuNP to measure the crystal lattice spacing (Fig.2.4d).



Figure 2.3: Schematic and photograph of hot-wire AuNP synthesis, including inset table of reaction parameters.



Figure 2.4: Imaging of AuNPs using transmission electron microscopy (TEM). (a) Bright field and (b) dark field low-magnification images of AuNPs collected on carbon fiber TEM grid; (c) higher-magnification TEM image of single Au NP with [2 0 0] crystallographic plane identified as based on (d) FFT of the same AuNP.

We performed STEM combined with Energy Dispersive X-ray Spectroscopy (EDS) to further confirm the presence of Au and to measure possible contamination – which we did not observe



Figure 2.5: (a)STEM imaging confirms crystalline AuNPs, with inset showing the scanning line for EDS analysis. (b) EDS confirms the composition of the AuNP.

Fig.2.5[188, 190, 193]. The EDS peaks aside from Au are from Copper (Cu) and Carbon (C), both likely from the carbon-coated copper TEM grid we used. We did measure some trace Oxygen (O), which is likely the result of normal atmospheric contamination during sample loading.

We used high resolution TEM (HRTEM) to measure the average diameter of the AuNPs. Figure 2.6 shows a chart of AuNP diameter (error bars reflect standard deviation) that we found for various reactor conditions as listed in Figure 2.1.

The AuNPs have narrow size distribution with average diameter below 5 nm, regardless of the reactor conditions we tested (including pressure, RF power, and reactor volume). While the parameters we tested did not yield a major change in AuNP diameter, the small NP size is within a promising range for use as plasmonic resonators and in other applications[45, 60, 175].



Figure 2.6: AuNP average diameter and standard deviation of various samples from Table.2.1, as measured from TEM images

To understand the physical process during AuNP synthesis, we used SEM to image the gold wire before and after the plasma synthesis under the conditions for Sample 2 (900 sccm Ar, 10 W supplied RF power). Figure 2.7 shows the SEM images. Roughness at surface of the Au wire after the plasma indicates physical destruction via the plasma process.


Figure 2.7: (a) SEM image of the consumable Au wire surface before plasma exposure. (b) SEM image of the Au wire surface after plasma exposure (conditions as for Sample 2 in Table2.1), showing noticeable roughness. (c) Higher magnification of SEM image of the Au wire after the plasma process.

We hypothesize that the cause of AuNP production is related to the increased wire temperature during the plasma process. During the process, the wire glows as though it is heated, and when we increased the power to the plasma we saw eventual melting of the wire. By inserting a thermocouple lead into the plasma during the reaction, we were able to measure the gas temperature within a few seconds of extinguishing the plasma (RF interference prohibited direct measurement during the reaction), with temperatures around 400K. This is far from the melting poing of gold (1337 K), consistent with the nonthermal nature of this plasma. However, resistive heating from the supplied RF as well as electron/ion recombination at the wire could lead to increased wire temperature. Due to the higher pressure of our reaction (100-300 Torr) operated at RF we do not suspect ion sputtering to be a major cause of AuNP formation, since any ions produced are likely to have low energies.

While the plasma-based method was promising regarding the AuNP size distribution, the mass yields were low – in fact while collection of NPs on a TEM grid was facile, we were unable to collect enough AuNPs for an accurate weight measurement. For comparison, we also performed AuNP synthesis using the hot-wire method under low-pressure conditions (1-10 Torr), as described in the Experimental Details section. Here we compare these two methods. In the hot wire method, we applied a narrow range of DC power to the Au-Pt wire (10-15 W) and the system pressure was lower than plasma-based method (several Torr versus 100-200 Torr for the plasma-based method). The rate of production was lower for the plasma-based method, as confirmed with the TEM results from each method under the same collection time. The hot-wire method produced AuNPs with a broad size distribution and larger average diameter (see Fig.2.8). By comparison, the plasma-based method yields AuNPs with a smaller average diameter and narrower standard deviation, which is attractive as many applications for these NPs rely on size-dependent properties.



Figure 2.8: (a,b) TEM images of AuNPs as synthesized using plasma-based method (Ar: 900 sccm, pressure: 180 Torr) and the hot-wire method (Ar: 900, DC power: 12 W) respectively. (c) Average AuNP diameter and standard deviation for the plasma-based method (circular symbols, Samples 1 and 2 from Fig.2.1) and the hot-wire method (square symbols, Samples 3 and 4 from Fig.2.3) as measured using TEM image analysis. AuNP, gold nanoparticle; DC, direct current; TEM, transmission electron microscopy

The lack of size control for the plasma method deserves comment. We explored a wide range of plasma powers and gas flowrates, and did not see a pronounced change in average AuNP diameter. In line with our hypothesis that the plasma process for AuNP synthesis is thermally driven, we did not see any size change as a function of power. At low powers, the wire was not heated sufficiently to lead to AuNP production. However, the thin wire equilibrated in temperature rapidly – so once we supplied enough power for AuNP synthesis, increasing the power led to the wire melting, not to increased AuNP vapor and size: the available power range was small due to this, and did not

allow for size control. We also did not see a flowrate dependence. In other flow-through plasma synthesis reactors, the size of the resulting nanoparticles is dictated by the residence time of the nucleates/particles in the plasma[28, 58, 87, 107, 197]. However, in our process, the pressure and flowrate were not decoupled (due to using orifice-based pressure control) and any increase in flowrate caused also an increase in pressure, reducing the effect of flowrate on the residence time. Furthermore, the long residence times for our process (due to the higher pressure) meant that we were not dynamically altering AuNP formation by changing the gas flowrate. When we tried to reduce the pressure and thus the residence time, we were not able to synthesize AuNPs.

We also calculated the residence time (RT) of the AuNPs in the reactor. This calculation is based on Equation 2.1 below. The RT (described below) roughly estimates the time each particle travels in the plasma and thus can give an idea of how long the particle has to grow. This equation accounts for fluid velocity and steady flow conditions through the orifice. This equation shows that pressure and flowrate have a direct effect on a particle's RT. These results show a loose correlation between the size of the AuNPs and their RT, as we dicussed above in this section. Table 2.2 shows calculated RT for particles characterized in Table 2.1.

$$ResidenceTime(RT) = (((\pi * R^2) * L * ((P/Patm))))/((F(sccm)) * 60)$$
(2.1)

Sample	Pressure (Torr)	Flowrate (sccm)	Power (W)	Reactor Length (cm)	AuNPs	Orifice Size (mm)	Residence Time
1	220	1200	5	20	Yes	1	0.120
2	180	900	10	20	Yes	1	0.1652
3	239	1200	10	20	Yes	1	0.1376
4	117	1200	5	10	Yes	2	0.087
5	120	600	25	20	Yes	1	0.2182
6	91	600	10	20	No	2	0.3975
7	60	1200	15	20	No	3	0.0409

Table 2.2: Comparing plasma-based and hotwire methods

Despite the success at synthesizing AuNPs using the hot-wire method and some control over size via process parameters, we were discouraged by material costs (namely, the Pt core wire),

experimental constraints, and difficulties associated with the reactor geometry, as well as the wide size distribution of the AuNPs. The plasma technique is a more direct, lower-cost method for AuNP synthesis and gas-entrainment, although the production yield is also low enough to prompt future studies on how to improve on this method.

Here, we presented a gas phase method which is based on an RF plasma to synthesis AuNPs. We also produced AuNPs by hotwire method under vacuum and compared these two methods. For either method, it is critical to understand the conditions during AuNP growth so that the method can be extended to other noble metals, and to aid future processes based on specific AuNP properties (for example, Si nanorod growth based on supersaturation of a eutectic alloy of Au and Si using the AuNPs as seeds). Reaching toward future experiments using these combined gas-phase processes, we performed preliminary experiments to analyze the AuNP temperature during formation, the gas temperature during the plasma process, and employed methods to analyze the gas composition with future use in estimating the electron temperature in the plasma. Those results are summarized in this section.

Based on results presented earlier in this Chapter, future experiments on anisotropic semiconductor nanostructure growth in the PNL will use the plasma-based AuNP synthesis route. As a preliminary step towards this objective, we performed experiments to determine the exact nature of AuNP production in this method as we briefly discussed earlier [83, 84]. In one experiment, we attempted to able to measure the ion density in the plasma using an electrical probe which is installed in the plasma reactor. This theory has been applied in experiment as well [19, 84, 109]. A function generator is connected to a variable frequency power supply through a capacitor. The probe is powered at RF frequencies (< 13.56 MHz) and chopped – during the "signal-off" phase, the capacitor is discharged by the plasma ion flux to the probe. The rate of discharge is proportional to the ion density (which is equal to the electron density under the assumption of quasineutrality in the plasma) [19, 83, 84, 134]. Our experiments with electrical probe measurements are ongoing, due to complications with the lower-frequency power supply which led to many false starts. While our probe measurements are on hold until we can obtain more robust and reliable equipment, we plan to use this method in the future as a means to estimate the plasma characteristics during AuNP synthesis.

We also used Optical Emission Spectroscopy (OES) to investigate different excited species and their relative intensities in the plasma system which helps to calculate species concentrations and can give an idea of the electron temperature during the reaction. In OES measurements, a spectrometer collects all emitted light from the plasma (ultraviolet and visible light). The lines are indicative of various atomic transitions from excited-state species in the plasma. The ultimate objective in this study was to then use a computer code to estimate the concentrations of various species and the electron temperature during the process, based on comparing these characteristic line intensities. Figure 2.9 shows a sample of OES from the Ar plasma with the gold central ground electrode, including a trace addition of H₂ gas for use in calculating electron temperature[19, 84, 109]. The data in fact was inconclusive. We hoped to see a line from Au, if in fact we had generated any excited-state Au atoms during our process. However, either the process was not energetic enough to excite the Au atoms/clusters that coagulated during AuNP synthesis, or else the densities were too low to observe. Characteristic lines from Au are expected at 406.511 nm, 460.750 nm, 479.273 nm, 627.817 nm and 751.073 nm (from NIST Atomic Spectra Database Lines Data website). Additionally, we hoped to use the trace H_2 that we added to the plasma as a means to estimate the electron temperature, but we were also not able to clearly see evidence of the H₂ optical emission, making that calculation impossible. It is interesting that the two spectra with and without H₂ (red and blue, respectively) are qualitatively different from one another - and so the addition of H₂ even at low concentration (1 sccm) was sufficient to shift the emission from the Ar plasma.

In Figure 2.9 we used a 340-1050 nm Ocean Optics USB spectrometer to run the AuNPs plasma reactor with using H_2 .

2.4 Conclusion

We presented a new gas phase method which is based on an RF plasma to produce AuNPs in a more sustainable path. For comparison, we also produced AuNPs by hot wire method at low



Figure 2.9: OES test for Plasma-Based AuNP synthesis, 340-1050 nm spectrometer with Hydrogen(red) and without Hydrogen(blue)

pressure. This new plasma-based approach results in a smaller average size and smaller overall distribution of sizes per sample, as compared to the hot wire method. Among the challenges presented by this method are a low production yield and invariant particle diameter, based on the parameters we tested, although the average AuNP diameter of 4 nm is suitable for many applications. Future work will explore methods to increase the production.yield as well as control the AuNP diameter using the plasma method, along with efforts to employ this facile technique to synthesis of other metallic NPs.

CHAPTER 3

ESTIMATING THE MECHANICAL PROPERTIES OF SINC LAYERS ON PDMS

Portions of this work have been published in the journal "Nanoscale" in March 2019 and are reproduced here.

3.1 Introduction

As flexible devices become more prevalent, it is increasingly important to measure and predict the mechanical properties of active device layers, including thin films [9–11]. Nanoscale components, such as nanocrystals, can be incorporated into mechanically flexible devices.[10, 152] Silicon in its nanocrystal form has semiconducting and photoluminescence properties which make it a promising material for technologies like microelectronics[103, 140, 163], photonics[50, 103], solar-photovoltaics[95, 166], memory devices[146], biosensors, and light emitting devices[6, 7], as well as other applications involving polymer matrices.[115, 173] Using silicon nanocrystals in these applications is particularly attractive considering the natural abundance and non-toxicity of silicon. In most of the aforementioned applications, silicon nanocrystals (SiNCs) are deposited on rigid substrates. Depositing a SiNC film onto stretchable or flexible substrates opens up possibilities for new device development and modifications[179]. While the opportunity of designing these devices is exciting, it also highlights the need for an innovative way to estimate mechanical properties for these systems.

Substantial work has been done by various groups on studying the mechanical properties of nanocrystalline materials, both in the elastic [57, 191] and plastic [62, 172, 180, 181, 184] regimes. Some works also discuss the significant differences in mechanical properties of nanocrystalline material from their bulk counterparts [57, 62, 172, 181, 182, 184, 191, 196]. These testing techniques, while powerful in estimating the material properties for a large variety of nanocrystalline materials, inherently require the destruction of the samples or the plastic deformation of the material. This is in conflict with the scope of this work, which is focusing on non-destructive techniques to estimate elastic behavior of thin layers of nanocrystals on deformable substrates. These combined systems limit *in-situ* measurement of the layers' mechanical properties such as elastic modulus. This necessitates finding an appropriate method to understand and predict the response of not just the nanocrystal layers during deformation, but of the whole elastomer-nanocrystal layer system. Indeed, *in-situ* evaluation of mechanical behavior is crucial for thin layers, for which interactions between the substrate and the thin film can be as important as the properties of the thin film itself. To

our knowledge, such *in-situ* evaluation of the mechanical properties of SiNC layers on elastomers has not been previously reported.

Prior *in situ* studies on nanoscale materials have employed microscopy during uniaxial tensile testing to observe deformation under applied loads [181, 183, 184]. Barring the specialty equipment necessary for these experiments, a promising option that has been used in the last two decades to estimate material properties of thin films is to measure the onset of instability patterns on the surface of the thin film due to different loading conditions [30]. This technique has the advantage of being simple, inexpensive, and non-destructive; furthermore it can be applied to any type of thin layer deposited on a deformable substrate. Because of its flexibility, this method has been employed to estimate mechanical properties of several isolated thin films [157, 168, 178] or multilayered structures [77, 102, 125, 162]. All of these studies focused on applying homogeneous deformations, namely uniaxial tension or compression, to the system. However, other types of nonhomogeneous loading conditions, such as bending, can also lead to the formation of instabilities. In the past, several studies have focused on developing a theoretical framework to describe the onset of instabilities on the surface of rectangular blocks subject to finite bending [31, 40, 41, 44, 51, 52, 143, 144, 153, 169]. The framework developed in these works focused only on finite bending deformation for a homogeneous block. These early predictions have also been recently confirmed by experimental work [51, 52]. In the last decade, a few studies focused on predicting bifurcations during finite bending of multi-laminated structures, specifically in bilayered systems, both theoretically and experimentally [143, 144].

A recent study on the optical and structural properties of SiNCs on polydimethylsiloxane (PDMS) performed at PNL and demonstrated the formation of instabilities on a nanocrystal film deposited on a prestretched elastomer [104]. Combining the onset of instabilities with the predictions from the theoretical modeling framework described, we evaluate the mechanical properties of the SiNC thin film deposited on an elastomeric substrate. This theoretical framework can further be applied to different combinations of nanocrystals and elastomers, for *in situ* measurement of mechanical properties of such bilayered systems.



Figure 3.1: Steps from plasma deposition to finite bending. SiNCs are deposited through a slitshaped orifice onto PDMS, which is then bent to observe formation of wrinkles on the SiNC surface. (a) Photograph of plasma reactor. (b) Schematic diagram of reactor and SiNC synthesis. (c) SiNC/PDMS sample illuminated with UV light, demonstrating photoluminescence. (d) Finite bending applied with a lab-designed apparatus.

3.2 Methods

Here we take a novel approach to evaluate the mechanical properties of thin films of nanocrystals on an elastomeric substrate. A PDMS-SiNC bilayer was used as a model to present the framework. First, we inertially impacted a uniform film of SiNCs on PDMS. Then, we applied a finite bending deformation to the system until instabilities formed on the surface coated with the SiNCs, noting the critical angle at which the instabilities appeared. Finally, we applied a theoretical modeling framework to describe the bilayer system. See Figure. 3.1 for an overview of our process.

3.2.1 PDMS fabrication

To prepare the PDMS as substrates for this study, a Dow Corning heat-cured prepolymer PDMS 184-kit Sylgard Elastomer with curing agent catalyst was used with a 10:1 weight ratio of base to curing agent catalyst. Changing this mass ratio will result in PDMS substrates in different stiffness. In other words, curing agent ratio will determine the mechanical properties such as shear modulus of the PDMS polymer after curing process. This topic will be discussed in Chapter 5. This mixture was stirred vigorously with a mechanical stirrer until air bubbles formed, and placed under vacuum for 10-15 minutes to remove the trapped air. The mixture was then weighed and poured into a petri dish of 85 mm diameter and was cured for 120 minutes at 60°C by placing on a hot plate to form PDMS with an average thickness 2.5 mm. When PDMS cured, the thickness at the edge of the container is alittle bit higher, due to surface tenssion of fluid during the curing process. After curing, the PDMS was cut in rectangular sections according to our requirements and then attached to two metallic handles with Gorilla[®] Super Glue as shown in Figure.3.1b and d.

3.2.2 Plasma synthesis of SiNCs

We produced the SiNCs using a nonthermal plasma reactor as has been reported previously[76, 80, 83, 104, 107]. This reactor, as presented in Figure 3.1, consists of a pyrex tube through which we flow 94 sccm (standard cubic centimeters per minute) of Argon (Ar) and 16 sccm of silane (SiH₄, 5% in Ar), as well as 50 sccm of H₂ through the sidearm for surface passivation. Radiofrequency (RF) power at 13.56 MHz was supplied to dual ring electrodes encircling the reactor, and the pressure was kept constant in the range of 3.75 to 3.85 Torr using a slit-shaped orifice. Obviously changing the size of the orifice, will change the operating pressure of this reactor. The standoff distance between the orifice and the substrate was ~4 mm. In this study, we keep the standoff distance constant to presevre same impaction for SiNCs deposited on the flexible substrate. The downstream pressure was ~0.500 Torr. We also mesured the pressure in the middle of the reactor, using a side arm in the same height as for the side arm desgined for Hydrogen line. This middle pressure was ~1.250 Torr. The nanocrystals were deposited on thin films by inertial impaction directly out of the reactor onto

the substrate[6, 48, 69, 124]. One of the assets of this synthesis method is the room-temperature process and ability to directly deposit SiNCs without post-processing steps or solvents, even on temperature-sensitive substrates such as PDMS. The PDMS samples were made (as described in Sec. 3.2.1), attached to a pushrod, and placed under the orifice downstream of the reactor. The SiNCs were deposited by rastering the substrate back and forth beneath the orifice to achieve a uniform film of SiNCs on the PDMS. Figure 3.1b shows a work-flow schematic of the reactor and deposition of SiNCs on the PDMS. The rastering duration was 20 minutes with each back and forth movement lasting 3 seconds, resulting in a SiNC layer thickness of ~4.5 μ m.

3.2.3 Silicon nanocrystal film characterization

The thickness of the sample was measured by scanning electron microscope (SEM) imaging of a cross-section of the sample generated using a focused ion beam (FIB). Figure 3.2a shows an SEM image of the sample, and Figure.3.2b shows the FIB-generated cross section for thickness estimation. To decrease charging effects and improve the image quality of the SiNC film, a thin layer of Platinum (Pt) (~ 6 nm) was deposited via Ar plasma sputtering prior to imaging. To perform a reasonable FIB cross sectioning, we need to roughly estimate the thickness of the film prior to milling and final imaging. As we mentioned in previous section, we started our FIB milling with an estimation of 4.5 μ m. The speed of FIB cross sectioning depends on the thin film structure and its thickness. The FIB image presented in Figure 3.2 took around 10 mins. Another challenge in this thickness measurement was due to similarity of contrast of PDMS and SiNCs. In other word, due to the existing Silicon in the structure of PDMS and SINCs, the contrast at the interface of PDMS, as the substrate and SiNC layers, as the thin film, is negligible and need high resolutiom for confirming proper estimation of the interface as presented in Figure 3.2. X-ray diffraction (XRD), shown in Figure 3.3a, confirms the formation of crystalline nanoparticles. Transmission electron microscopy (TEM) was performed on the SiNCs using a JEOL 2200 instrument, showing individual NCs (Figure.3.3b). The TEM sample was prepared by tapping the TEM grid on the surface of the sample to collect some of the SiNCs. The size of the SiNCs was measured using

TEM image analysis, giving an average SiNC diameter of ~3.7 nm.



Figure 3.2: SEM and FIB cross-sectioning of the SiNC layer. The thickness is estimated to be (~4.50 μ m). (a) SEM image showing the surface of the SiNC layer on PDMS, including the FIB-milled area (inset). (b) Higher magnification SEM image of the FIB-milled area demonstrating the thickness of the SiNC layer.



Figure 3.3: (a) X-ray diffraction confirmed formation of SiNCs. XRD for SiNCs shows crystal reflections at 2θ values 28.3, 47.3 and 56.1 degrees consistent with the (111), (220), and (311) planes of silicon. (b) TEM image confirming the formation of SiNCs: black circles highlight individual SiNCs. The inset shows FFT of the correspondig SiNCs of the TEM image.

3.2.4 Uniaxial tensile test

We applied a standard uniaxial tensile test to evaluate the mechanical properties of the PDMS. A rectangular sample of PDMS was mounted on a custom built uniaxial tensile test machine and four black dots were applied on it as fiducial markers. Figure 3.4 shows a PDMS mounted to the load cell for performing unaxial tensile test. The sample was then stretched cyclically for 5 cycles from a configuration with a 10g pre-load (reference configuration) until a 20% deformation was achieved. The sample was stretched between two clamps, one of which was attached to a load cell to measure the force on line with the applied deformation. The strain rate used during the tensile test was 0.1 mm/s. The force from the load cell was converted to engineering stress by calculating the average cross-section area of the sample in the reference configuration. A Hitachi KP-M2AN CCD camera was used to capture and feed the image of the fiducial markers during uniaxial stretch into LabVIEW.



Figure 3.4: The stress machine loaded with a colored PDMS and dots depicted on the PDMS, dislocation of dots will be recorded by a digital camera



Figure 3.5: (a and b)A schematic diagram of proposed aparatus for finite bending measurement desgned by *Solid Work* software and (c) Alluminum cast aparatus designed at PNL

3.2.5 Finite bending experiment

We designed a finite bending apparatus similar to the one used previously by Roccabianca et al.(2010)[143]. A schematic diagram of this aparatus shown in Figure 3.5. Two mainparameters in this design are slenderness ratio ($\Lambda = l_0/h_0$) which is the ratio of width to thickness of the sample in cross section, and thickness ratio ($H = h_0^{NC}/h_0^P$) which is the ratio of thickness of the SiNC layer by that of the PDMS before finite bending (see Fig. 3.6a for reference). The third dimension is taken to be 8-10 times larger than l_0 to achieve a plane-strain condition on the cross section.In other words, due to the size ratio of third dimension to the other two dimensions of the substrate, the third dimension does not have an impact on the formation of surface instabilities. Here (and in all following equations) the superscript 'P' refers to the PDMS and 'NC' refers to the SiNCs.





Figure 3.6: PDMS sample in the finite bending apparatus. (a) Side view, showing sample (with handles) in the finite bending apparatus. (b) Top view showing formation of bifurcations.

The bilayer PDMS/SiNC system was put in the finite bending apparatus (see Fig.3.6) and progressively bent until the SiNC film underwent bifurcation, at which point the critical angle was recorded. Due to higher critical angles of bifurcation observed for samples with higher slenderness ratios, deformation was applied by hand instead of using the apparatus. The onset of bifurcations was detected by direct visual inspection, and the critical angle was measured using analysis of photographs of the side view of the sample. Each measurement was performed three times to ensure accurate and reproducible readings.

3.2.6 Modeling bifurcation in elastic layered structures

The following sections pertaining to theoretical modeling of the behavior of the bilayer system were largely executed by M. Sinha and Dr. S. Roccabianca, our collaborators on this project. For completeness they are included here.

Roccabianca et al. (2010), formulated a theoretical framework to study incremental bifrucations due to finite bending of an elastic incompressible multilayered block[143]. This theory was developed for an N-layered system for Mooney-Rivlin type of material. The authors also performed some experiments in bilayered structures that confirmed their theoretical predictions. Here, we employ a similar theoretical modeling framework for the bilayered system to estimate the ratio of mechanical properties of SiNC thin film to that of PDMS.

3.2.6.1 Finite bending

The finite bending deformation is prescribed such that the reference configuration is rectangular and described in a Cartesian coordinate system, and the deformed configuration is a sector of ring described in a cylindrical coordinate system (see Fig. 3.7).



Figure 3.7: Reference and deformed configurations for the PDMS-SiNC bilayer. The bilayer deforms from the Cartesian coordinate system in the reference configuration (e_1, e_2, e_3) to a cylindrical coordinate system in the deformed configuration (e_r, e_θ, e_z) . Specifically, a plane at constant x_1^0 transforms to a plane at constant r (dashed line), and a plane at constant x_2^0 transforms to a circular arc at constant θ (dashed-dotted line). Since the out of plane deformation is taken to be zero, we have $x_3^0 = z$.

Briefly, the finite bending deformation can be described, within both the PDMS and the SiNC layers, by the following deformation gradient F[143]

$$\boldsymbol{F} = \frac{l_0}{2\bar{\theta}r} \boldsymbol{e}_r \otimes \boldsymbol{e}_1^0 + \frac{2\theta r}{l_0} \boldsymbol{e}_\theta \otimes \boldsymbol{e}_2^0 + \boldsymbol{e}_z \otimes \boldsymbol{e}_3^0, \qquad (3.1)$$

where l_0 is the overall width of the sample and $2\bar{\theta}$ is the angular deformation of the sample. We consider the volume of the system to be conserved and the two layers to be perfectly bonded. Therefore, we can apply the interface condition $r_o^{NC} = r_i^P$, where r_o^{NC} and r_i^P are the outer radius of the SiNCs layer and the inner radius of the PDMS, respectively. This allows us to write,

$$r_o^{NC}(h_0^{NC}, h^{NC}, \alpha) = r_i^P(h_0^P, h^P, \alpha),$$
(3.2)

where h_0^m and h^m represent the thickness of each layer before and after bending (m = NC, P), and $\alpha = 2\overline{\theta}/l_0$. To predict all geometrical characteristics of the deformed state, we consider all the layers to be equilibrated. Briefly, we define the Cauchy stress in each layer as,

$$\boldsymbol{T} = -\pi \boldsymbol{I} + \boldsymbol{F} \frac{dW}{d\boldsymbol{C}} \boldsymbol{F}^{\mathrm{T}},\tag{3.3}$$

where $C = F^{T}F$ and I are the right Cauchy-Green deformation tensor and the identity tensor, respectively, and W and π are the strain energy function and the Lagrange multiplier for each layer, respectively. We have employed the neo-Hookean strain energy function to describe both layers, defined as $W = \frac{\mu_0}{2}(trC - 3)$. Note that we are defining two constitutive equations, one for the PDMS layer as a function of the material parameter μ_0^P , and one for the SiNC layer as a function of the material parameter μ_0^{NC} .

For the layers to be equilibrated, the equilibrium equation in absence of body forces is required to be satisfied within each layer. Furthermore, boundary conditions of zero traction are applied at the innermost and outermost surfaces, as well as an interface condition of perfect bonding between the two layers.

3.2.6.2 Bifurcation analysis

The loss of uniqueness of the plane-strain incremental boundary value problem has been investigated for multi-layered structures in previously published work[143]. Here we have adapted the formulation to fit our application for a bilayered system of PDMS and SiNCs. Briefly, for each layer, we seek to solve the incremental counterpart of the equilibrium, div (Σ) = 0, where $\Sigma = \dot{S}F^{T}$ is the incremental first Piola-Kirchhoff stress tensor, and the first Piola-Kirchhoff stress and the Cauchy stress tensors are related by $S = TF^{-T}$ for incompressible materials. Here, and in the following, we use a superimposed dot to represent incremental quantities. The linearized constitutive equation for each layer is given by

$$\Sigma = -\dot{\pi}I + \mathbb{C}L \tag{3.4}$$

where \mathbb{C} is the fourth-order tensor of instantaneous elastic moduli and L = grad u is the gradient of incremental displacement u(x). We consider bifurcations to be represented within each layer by an incremental displacement field in a separable-variables form, as described by Roccabianca et al. (2010). For incompressible isotropic elastic materials, one can write \mathbb{C} as a function of two incremental moduli, namely μ and μ^* . For neo-Hookean materials subject to finite bending in plane strain condition, the elastic moduli can be written as

$$\mu = \mu^* = \frac{\mu_0}{2} \left[(\alpha r)^2 + (\alpha r)^{-2} \right]$$
(3.5)

Finally, the incremental boundary value problem is completed by a set of boundary and interface conditions. Specifically, zero normal and shear incremental stresses at the innermost and outermost layer, zero incremental shear stress and incremental radial displacement at the boundary $\theta = \pm \bar{\theta}$, and continuity of incremental stresses and displacements across the interface. To calculate the angle that satisfies the bifurcation condition, θ_{cr} , we employed the compound matrix method, as described in a previously published study [144].

3.3 Results and Discussion

Experimentally, the critical angles of bifurcation were measured for nine samples by performing the finite bending experiment described in Sec. 3.2.5. The values, reported in Table 3.1, have been obtained for three experimental groups, characterized by a slenderness ratio $\Lambda = 2$, 3 and 5, each group formed by a total of three samples (see Fig. 3.8).



Figure 3.8: Critical angles of bifurcation evaluated as a function of ratio of material properties for a PDMS-SiNC bilayer sample. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. All curves have been calculated for a thickness ratio *H* included in the range 0.0013–0.0018. Each line represent a different value of slenderness ratio, $\Lambda = 2$, black solid line; $\Lambda = 3$, black dashed line; $\Lambda = 4$, dark gray solid line; $\Lambda = 5$, dark gray dashed line; $\Lambda = 6$, light gray solid line. The insert represents a schematic of the bilayer and defines the slenderness ratio.

Slenderness ratio, Λ	Critical angle, θ_{Cr}	Material parameters ratio, $\bar{\mu}_0$
2	47.33 ± 3.21	1.90 ± 0.13
3	71.33 ± 1.53	1.85 ± 0.05
5	130.67 ± 3.21	1.68 ± 0.04

Table 3.1: Critical angles of bifurcation for different slenderness ratios, expressed in degrees. Angles are reported for $\Lambda = 2$, 3 and 5.

Employing the model described in Sec. 3.2.6, we evaluated the critical angle of bifurcation for the bilayered structure, shown in Fig. 3.8 and Fig. 3.9. Specifically, after fixing the overall geometry of the sample, namely the thickness ratio H and the slenderness ratio Λ , we calculated the value of the angle representing the onset of bifurcation for each value of the neo-Hookean material parameters ratio, defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. In both Figures, we considered $\bar{\mu}_0$ to be included



Figure 3.9: Plotting points from the experiments on graph obtained by numerical calculations. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC} / \mu_0^P$. Shown here are points obtained for $\Lambda = 2$, 3 and 5. Insert shows an instability on the surface of a sample with $\Lambda = 2$.

between 0 and 100, however a pilot study showed that the value of the critical angles plateaus for values of $\bar{\mu}_0$ included between 10^2 and 10^5 (data not shown). Furthermore, the same pilot study showed that the critical angle of bifurcation is independent of the thickness ratio *H*, if *H* is included in the range 0.0013 – 0.0018. The experimental value measured in this study is included within that range, specifically *H* = 0.0017 on average for the nine samples.

Figure 3.8 shows the variation of the critical angle of bifurcation for varying values of the slenderness ratio, specifically for Λ included in the range 2 to 6. For a fixed value of $\bar{\mu}_0$, which is represented by a vertical line in the graph, an increase in the slenderness ratio results in a later appearance of the bifurcation, namely a higher value for the critical angle. This trend is consistent with previously published results[143, 144].

Figure 3.9 shows how we employed the onset of bifurcation to estimate the mechanical properties

of the SiNC layer. Briefly, for each value of slenderness ratio considered in the experiments, we calculated the correspondent theoretical sets of bifurcation angles. Then, the critical angle measured experimentally was employed to uniquely identify the corresponding $\bar{\mu}_0$. The experimental value of the critical angle fixed the abscissa of the point in the $\theta_{cr} - \bar{\mu}_0$ plane, represented in Fig. 3.9. Then, we imposed that the experimental point belonged on the bifurcation threshold curve calculated for the corresponding slenderness ratio, which in turns fixed the ordinate of the point which is $\bar{\mu}_0$. The value estimated for each experimental group, namely for each value of slenderness ratio considered, is reported in Table 3.1. A vertical dashed line in Fig. 3.9 represents the average value of $\bar{\mu}_0$ for all the experimental data, which is 1.81 ± 0.12 . We then estimated the value of $\mu_0^P = 190$ kPa by fitting the data collected from the uniaxial tensile test, as described in Sec. 3.2.4. This gave us a value for the neo-Hookean material coefficient for the SiNC layer of μ_0^{NC} 345 ± 23 kPa. The neo-Hookean material constant is analogous to the shear modulus for low values of applied strain.

This finding is a clear indicator that the mechanical properties of this materials system are determined by the interactions between SiNCs within the NC layer and between the NC layer and the PDMS. Direct measurements of the mechanical properties of individual silicon nanocrystals via microscope-guided nanoindentation have yielded elastic moduli around 170 GPa,[53] several orders of magnitude higher than our measurement of the shear modulus for the SiNC layer on PDMS (assuming incompressible behavior, shear modulus is ~1/3 of the elastic modulus). Others have produced elastic/Young's modulus estimates for single SiNCs between 70-170 GPa.[82, 119, 149] This range of values (~20-60 GPa for shear modulus) is also consistent with mechanical measurements of thin ribbons of crystalline silicon on PDMS [82]. By contrast, our value of 345 kPa for shear modulus is far lower, and is consistent with the higher porosity of our nanopowder layer as compared to bulk silicon. For example, Gross *et al.* showed that increasing porosity of powder hydroxyapatite coatings leads to decreasing elastic modulus - further, regardless of porosity, the coatings exhibited values of elastic modulus more than 35x smaller than the modulus of single-crystal hydroxyapatite. [59, 192] Similarly, the Young's modulus of aluminum foams is between 10^{-1} and 10^{-3} the value of Young's modulus of solid aluminum, depending on porosity.[2] Finally,

previous results have shown that increased porosity significantly decreases the Young's modulus of polymer thin films deposited on PDMS, when measured by employing mechanical instabilities[155]. The porosity of our layers was difficult to ascertain with high accuracy. However, a preliminary density measurement provided us with a value near the limit for close-packed randomly oriented rigid spheres (volume fraction 0.64). While we did not probe the effects of porosity in this proof-of-concept investigation, the porosity of the SiNC layer is tunable by adjusting reactor properties,[48, 69] and future work will be devoted to determining the relationship between layer porosity and mechanical properties. This versatile method is broadly applicable to extract the mechanical properties of nanoparticle layers on elastomer substrates regardless of material, layer thickness, and density. Our results also offer a unique opportunity in the future to investigate how the NC surface functionality (organic ligand coating, inorganic shell, *etc.*) influences the mechanical behavior of the NC films.

3.4 Conclusion

In conclusion, we have used a new method based on the onset of bifurcation to estimate the mechanical properties of thin layers of nanocrystals on PDMS by coupling the experiment and theoretical modeling. In general this method, opening up new possibilities for estimating, and controlling the mechanical behavior of nanoparticle layers on stretchable or bendable device technologies, leveraging both the unique optoelectronic properties of nanoparticles together with the mechanical versatility offered by these films.

Finally, the results obtained from this experiment are exciting since previous attempts in investigating instability formation due to finite bending in a multilayered structure were limited to structures with elastomeric layers only. Here we have reliably shown formation of instabilities in thin SiNC films deposited on PDMS as a flexible substrate. This brings opportunities to study and develop constitutive models which are better suited to such constituents, in addition to other experimental methods that can perform non-destructive and *in-situ* measurements of this class of multilayer systems. This versatile method is broadly applicable to extract the mechanical proper-

ties of nanoparticle layers on elastomer substrates. In Chapter 5 we apply same methodology to investigate a parametric study regarding the influence of a few properties of the SiNC layer and the PDMS and how they affect the mechanical properties of the SiNC thin films. Also this method, regardless of material, layer thickness, and density can be applied for a range of nanomaterial films and substrates.

CHAPTER 4

OPTICAL AND MECHANICAL BEHAVIOR OF SINC-EMBEDDED PDMS SLABS

4.1 Introduction

Luminescent nanocrystal inclusions in polymer hosts have received considerable interest recently, in particular due to their promise in novel optoelectronic device applications such as photovoltaics based on luminescent solar concentrators (LSCs), electrochromic windows, and more [23, 65, 89, 115, 116, 141, 165, 174, 186]. The combination elastomeric behavior of polymers together with the tunable optical absorption and emission from these nanocomposites also opens avenues to stretchable and flexible manifestations of these same applications, as well as wearable electronics such as biosensors for health monitoring systems, and more. While many groups have studied the optical behavior of these nanocomposites, their mechanical behavior is not well understood, although a few recent studies have made advances in uncovering the effects of the nanocrystal inclusions [23, 66]. Modifications to the mechanical behavior of the polymers upon inclusion of the nanocrystals is especially important for elastomeric polymers with intended use in flexible or stretchable applications. The inclusions can change the overall mechanical properties of the composites, depending on a range of factors such as the nanocrystal concentration, dispersion within the host polymer, the nanocrystal surface properties, and more. Going beyond informing the deformability of the composites, tests on the mechanical properties of the composites can also provide information about the interaction between the inclusions and the polymer, and the ways in which applied stretching or bending can affect the other physical properties of each.

A particularly compelling materials system is silicon nanocrystals included in polydimethylsiloxane (PDMS). Silicon nanocrystals (SiNCs) are made from an abundant and nontoxic material, and exhibit exciting tunable optical properties such as photoluminescence[3, 5, 27, 36, 107, 113, 114, 154, 160, 194]. PDMS is a commonly-used silicone-based elastomer used in biomedical, industrial, microfluidic, and optoelectronic applications [27, 88, 99, 110, 112, 123, 131, 148, 151, 177, 195]. As a host for nanocrystals, PDMS offers easy fabrication, tunable mechanical behavior, biocompatibility, and high translucency in ultraviolet through near infrared spectral range [93]. Recently SiNCs embedded in polymers such as polymethyl(methacrylate) (PMMA) and PDMS have been proposed as agents for LSCs, solar cells, UV-blocking layers, and more due to the NCs' absorbance in the ultraviolet (UV) – blue spectral range and efficient emission at red-near infrared (NIR) wavelengths. Understanding the influence of the SiNCs on the mechanical behavior of the composite NC/polymer system as a whole is important for designing future applications based on this materials system, as well as other NC/polymer combinations.

A recent report by *Chen et al.*indicated a modified rupture stretch and mechanical properties (tensile strength and Young's modulus) for SiNC-infused PDMS, depending on the surface functionality of the SiNCs. That group also demonstrated the UV-blocking ability of the SiNC/PDMS composite system, highlighting the multifunctionality of these materials. We sought to further characterize the influence of surface termination on the mechanical properties of SiNC/PDMS composites by using uniaxial tensile testing to evaluate the neo-Hookean coefficient of the composite system, depending on both nanoparticle concentration within the nanocomposite and nanoparticle surface functionality as modified using a solution-phase thermal hydrosilylation technique. The neo-Hookean coefficient is analogous to the shear modulus of a material, at low values of applied strain. Our results indicate that, while all nanocomposites exhibited photoluminescence (PL), the SiNC concentration and surface functionality play a profound role in the mechanical properties of the composite.

4.2 Experimental Work

4.2.1 Plasma synthesis of SiNCs

SiNCs were synthesized with a non-thermal low-pressure plasma reactor as described previously [7, 13, 22, 56, 104, 107, 118, 120, 126]. The reactor consists of a pyrex tube with dimensions of 0.25" OD at the reaction zone, expanding to 1" OD in the plasma effluent. Dual ring electrodes bearing radiofrequency (RF) power at 13.56 MHz encircled the tube, with power delivered at 30W via a lab-built impedance matching network. Argon (Ar, 96 standard cubic centimeters per minute, sccm) and silane (SiH₄, 5% in Ar, 16 sccm) are flown through the reactor at a pressure of 3.6-3.8 Torr as controlled using an orifice near the exhaust. Hydrogen gas (H2, 50 sccm) is injected just below the onset of the expansion region in order to provide more thorough surface passivation

[7]. SiNCs are nucleated and grown during the reaction and collected at the reactor exhaust onto stainless steel mesh filters. The filters were weighed before and after the reaction to measure the weight of SiNCs collected, which was on average 3.2mg for the 12 minutes collection time used for each batch. A section of the mesh filter was removed for FTIR analysis, before the remaining mesh filter loaded with SiNCs was placed into a test tube, capped with a rubber septum, and flushed with N2 to ensure an inert atmosphere.

4.2.2 Functionalization of SiNCs

Thermal hydrosilylation was performed for all F samples using a nitrogen-purged Schlenk line [106]. The SiNCs were mixed with a dried and degassed solution of 5:1 v/v mesitylene and 1-dodecene (Aldrich) and sonicated for 5 minutes. The resulting cloudy yellow solution was transferred via cannula to a round-bottom flask with a refluxer and heated in a sandbath heater to 205-210°C for 2-hours. Following this process, the SiNC solution became clear indicating surface stabilization with the dodecyl ligands. The resulting solution was dried under N2/vacuum for 24 hours at a temperature of 60°C to evaporate the residual solvent mixture. 12 mL hexane was added to the round bottom flask and sonicated for 5 minutes to ensure proper redispersion. Next, 2 mL of the solution was placed in a vial for PL spectroscopy and the remaining 10 mL was ready for nanocomposite formation.

4.2.3 PDMS preparation

We made the PDMS using a previously documented method [110]. A Dow Corning heat-cured 184 Sylgard Elastomer PDMS kit was used with a 10:1 w/w ratio of base to curing agent. The SiNCs with known mass and concentration in hexane were added to the PDMS pre-polymer solution. The mixture was stirred vigorously and then placed in a vacuum desiccator to remove any air from the mixture and most of the hexane evaporated during this process. The resulting composite mixture was poured into an aluminum mold with a rectangular shape and defined dimensions. The PDMS-SiNCs composite was cured on a hot plate at 60 °C, typically reaching final cure in 3 hours. Once the samples were cured they removed using tweezers.

4.2.4 Uniaxial tensile testing

We performed a standard uniaxial tensile test as reported previously to evaluate the mechanical properties of the plain as well as the nanocrystal infused PDMS [154] A rectangular sample was mounted on a custom built uniaxial tensile test machine and four black dots were applied on it as fiducial markers. The sample was then stretched cyclically for 5 cycles from a reference configuration, until a stretch of 1.2 was achieved [154]. This stretch is equivalent to a tensile strain of 20%. The sample was stretched between two clamps, one of which was attached to a force transducer to measure the force on line with the applied deformation; simultaneously, the deformation was measure by tracking the fiducial markers using a CCD camera (Hitachi KP-M2AN). The strain rate used during the tensile test was 1 mm/s. The force was converted to Cauchy stress by evaluating the average cross-section area of the sample in the reference configuration, and the change in cross section for the deformed configuration. The samples were then stretched in the same setup at a strain rate of 1 mm/s until rupture.

4.3 Results

4.3.1 SiNC characterization and nanocomposite formation

SiNCs were produced using a nonthermal plasma technique, as reported previously and describeed in the Experimental Details section below [5, 104, 107, 154]. We characterized the SiNCs using xray diffraction (XRD) and transmission electron microscopy (TEM) (Fig. 4.1). The average size of a single SiNC was estimated using TEM image analysis to be ~4 nm in diameter and confirmed to be around ~3.7 nm using Scherrer broadening analysis of the XRD peaks [56, 154]. In formation of the nanocomposites, we considered two separate surface treatments: non-functionalized SiNCs (NF, which have a native hydride coating from the plasma synthesis process), and functionalized SiNCs (F, which have alkylated surfaces following a thermal hydrosilylation process with 1-dodecene as



Figure 4.1: SiNC Characterization: XRD (a) shows crystallographic reflections for nanosized silicon. Gray lines are the actual data and the black trace is the peak fit. TEM imaging (b) indicates spherical nanocrystals and lattice spacing consistent with crystalline silicon. Inset shows FFT of image.

functionalizing ligand and then dried). Photographs of the NF and F samples are shown in Figure 4.2a-b under room light and ultraviolet (UV) excitation, demonstrating visible red luminescence. PL spectra from solutions of NF SiNCs and F SiNCs are presented in Figure 4.2. Solution PL quantum yields from these samples were 1.6% and 54%, respectively, as measured using an Ocean Optics, Inc. USB2000 spectrometer and integrating sphere and excited using a 395nm LED excitation source. The NF and F samples were mixed into a small volume of hexane (12 mL, of which 10 mL was used for fabricating the nanocomposites) and then added to the PDMS pre-polymer solution and the curing agent – 1:10 w/w ratio for all samples – then vigorously mixed using a mechanical rotary stirrer for 1 minute. Air bubbles and residual hexane were removed using vacuum desiccation and the PDMS was poured into casts and cured at 60° C (more details in Section 4). We examined two different concentration samples with the prefix L- and H-. Specifically we characterized 4 sample sets and one control: L-NF, L-F, H-NF, H-F, and PDMS (no nanocrystal inclusions).



Figure 4.2: SiNCs in solution, (a) photographed in room light and b) under UV excitation Shown are hexane, NF, and F samples from left to right. (c) PL spectroscopy shows much brighter luminescence for surface-functionalized (F) SiNCs as compared to nonfunctionalized (NF) SiNCs in solution.

4.3.2 Nanocomposite characterization

4.3.2.1 Photoluminescence

Photographs of representative control PDMS and nanocomposite slabs in room light and under ultraviolet (UV) excitation are shown in Figure 4.3a-b. We also measured PL quantum yields from the nanocomposites, which are plotted in Figure 4.3c. These PL QYs underscore the high optical quality of the nanocomposites, at 1.2% and 16% on average for H-NF and H-F samples.

4.3.2.2 Microscopy

Based on PL and visual inspection, it was not evident how the SiNCs were dispersed within the PDMS. To investigate the dispersion of SiNCs in the nanocomposite, we first assigned a specified spatial Cartesian coordinate system (Figure 4.4a) to each slab, sliced the slabs to obtain thin cross-sections, and then performed microstructural analysis using a Nikon AIRsi Confocal Laser Scanning Microscope (CLSM), in which thin slices can be imaged with white light as well as



Figure 4.3: (a) Photographs of SiNC/PDMS nanocomposites in room light and (b) under UV excitation (c) shows the average PL QY of SiNCs in hexane and in the nanocomposites, with error bars reflecting the standard deviation of the measurements.

imaged at selected optical wavelengths using a laser excitation at 405 nm. The CLSM allows visual detection of the SiNCs and clusters of SiNCs, which are otherwise difficult to discriminate from the PDMS matrix using traditional optical or electron microscopy. The confocal nature of the instrument allows depth resolution of the luminescent features as well, so that one can view a composite 2-D image of 80 imaging planes (in X-Z, slice depth along the Y direction, Figure 4.4b, or a 3-D depth-resolved map of the dispersion (Fig.4.4c). For this 3-D map, the position of each SiNC cluster is represented in its physical location within the map as well as using color-coding for depth. Based on this 3-D representation we found that, regardless of surface functionality, the SiNCs are clustered together to some degree. This optical measurement technique is resolution-limited, and so we were not able to visualize the degree of unclustered dispersion of the NCs within the sample, but the results are important as they demonstrate the differences in clustering behavior of the samples.

Figure 4.5 shows representative composite images for each sample type, all acquired under identical microscope settings. The depth of each image is $\sim 60 \mu m$, and the representative images in



Figure 4.4: (a) For reference during microscopy, we assigned each nanocomposite the same coordinate system, (b) A single CLSM image of a slice is shown and (c) the depth-resolved composite image (scale inset), demonstrates the distribution of small clusters within the sample slab.

Figure 4.5 are a composite of 80 separate depth scans along that 60µm thickness. Visual inspection of the CLSM images indicates an increase in number of SiNC clusters at higher concentrations (HF and HNF) as compared to the lower concentration samples, which is not surprising. To quantify any differences between the samples, we analyzed the cluster size for each sample type using a particle counting/volume algorithm via the ImageJ processing platform. We analyzed 3-4 individual images from different individual samples for each sample type using this algorithm to build a comprehensive picture of the SiNC dispersion characteristics.

The results are plotted in Figure 4.6 using a box plot to display the five-number summary of the data. First, we note that the smallest cluster size for our data was resolution-limited, and so the lower bounds of each sample set are nearly identical. These lower bounds represent not the true smallest cluster sizes but instead the smallest size that is resolvable using the CLSM instrument and the processing algorithm. Aside from the increase in number of clusters, the data suggests that



Figure 4.5: Representative CLSM images of the SiNC/PDMS nanocomposites



Figure 4.6: SiNC cluster size statistics based on image processing from the CLSM images. 3 separate images were analyzed for each sample type. A key to the data representative is shown as inset.

the average cluster size and median cluster size do not significantly depend on the concentration of SiNCs in the polymer, at least over the concentration range we investigated. This indicates that

for the SiNC concentrations that we studied, the mixing and curing procedure we used is sufficient to ensure relatively uniform dispersions. In other words, the distance between clusters within the polymer host at our "high" concentration of SiNCs is still so large that the cluster formation and dispersion is largely unaffected. It is worth noting, however, that the larger particle concentrations sometimes required slightly modified PDMS curing procedures, namely extended time on the hot plate. At the 0.12 wt% concentration, which is modest by nanocomposite standards, the SiNC clusters still seemed to interfere with the curing process to some degree, occasionally leading to longer required curing times. Next we examine the effect of surface functionality of the SiNCs on the dispersions. One notable difference between NF and F samples is the average cluster size. Visual inspection of the CLSM images indicates that the clusters for the NF samples were larger than for the F samples. The median cluster sizes as measureable using CLSM were nearly equivalent, between F and NF samples, but the spread of data (both the interquartile ranges and the outlying points) was larger for NF samples at both low and high concentrations. The mean cluster size of the SiNCs in the PDMS, represented by the X symbols in the plot, is also larger for the NF samples as compared to the F samples at both concentrations, although the discrepancy appears smaller at the lower concentration. This finding is consistent with the fact that surface functionalization causes a greater separation between individual SiNCs as well as improved integration with the monomer chains before polymerization.

4.3.2.3 Mechanical properties of the composite

To test the effect of the concentration and surface functionality of the SiNC inclusions on the nanocomposite mechanical behavior, we used uniaxial tensile testing and a material model to estimate a characteristic mechanical parameter, and we also quantified rupture stretch. The resulting stress-stretch data (Figure 4.7a) can be analyzed to extract the neo-Hookean coefficient (μ , with the dimension of a stress) based on the following equation for Cauchy stress (ϕ):

$$\phi = \mu * (\lambda^2 - (1/\lambda)) \tag{4.1}$$


Figure 4.7: Mechanical properties of the nanocomposites. (a) shows a representative plot of Cauchy stress vs. stretch data for each sample type. From this data, (b) we extracted the neo-Hookean coefficient for each sample, showing a distinct reduction for the higher-concentration sample. (c) the rupture stretch was unaffected by the SiNC inclusions.

where λ is the applied stretch. Figure 4.7b shows the estimated neo-Hookean coefficient of each sample, with standard deviations plotted as error bars. The rupture stretch, shown in Figure 4.7c, has a value of 2 for all samples including the control PDMS. However, the results for μ (Figure 4.7b) tell a different story: while the μ values for the L-NF and L-F samples are within the statistical variation of the control PDMS, the H-NF and H-F samples both exhibit a reduced μ , correlating to a reduced stiffness. This reduction is most prominent for the H-NF samples.

4.3.2.4 Discussion

These results have significant meaning. From an optical standpoint, inclusion of surface-alkylated SiNCs in PDMS via this procedure leads to brightly emissive nanocomposites with PL QYs around 16%, pointing to the promise of this materials system going forwards. The non-functionalized SiNCs still result in emissive nanocomposites, but the PL QY of these is quite low (~1-2%) and is difficult to measure at the lower concentration we studied. For optically emissive nanocomposites, using the surface-functionalized SiNCs is critical. The CLSM images make it clear that clustering of SiNCs within the PDMS is prevalent across sample type. Preventing this clustering effect using modified nanocomposite fabrication procedures or by tuning the surface of the SiNCs by using other organic ligands with alternate terminal groups are promising routes to explore, for even

higher-efficiency photoluminescence from the nanocomposites. For example,*Hill et al.* revealed that the ligand terminal group greatly influenced the dispersion of SiNCs in a PMMA host [65]. This calls for a comprehensive investigation of the interaction between the ligand termination and the resulting dispersion of SiNCs in PDMS.

Mechanically, our first conclusion is that inclusion of SiNCs at very low concentration (0.03 wt%) in the PDMS does not appear to influence either the rupture stretch or the modulus of the PDMS nanocomposites. At low concentration, the SiNC cluster sizes within the nanocomposites were widely dispersed, and despite a change in average cluster size between NF and F samples, the low concentration did not influence the overall mechanical behavior of the nanocomposites (although it did lead to bright PL in the case of the LF samples). Second, at higher concentrations both the NF and F samples demonstrated a significant reduction in the neo-Hookean coefficient μ and the reduction is more prominent for the NF samples. When compared with the nonexistent change in μ for the lower concentration samples, this indicates that the modulus of the nanocomposites depends both on the surface functionality and on the SiNC concentration in the nanocomposite.

We were cognizant of the fact that mixing the SiNCs into the PDMS prepolymer solution might be one cause for the large cluster sizes and the reduction in modulus. To test this hypothesis we also used a shear mixer (FlackTek SpeedMixer at 3000 rpm, 1 minute) for mixing H-F samples into PDMS. Our uniaxial tensile testing results and CLSM imaging from the samples prepared using shear mixing do not indicate any significant deviation from the samples prepared as described above. This points to solubility as the major cause for cluster formation and modified μ for the nanocomposites, rather than incomplete mixing. The reason behind the reduction in the neo-Hookean coefficient for the high-concentration composites is cause for further consideration. Previously, we estimated μ for non-functionalized SiNC layers deposited on PDMS and found a value of 345 kPa, approximately twice the value for PDMS. While the parameters influencing this value are undoubtedly complicated, we can at least use it as an approximation for the modulus of the SiNC inclusions in the composites. Our CLSM imaging confirmed that a large fraction of SiNCs are not individually dispersed within the PDMS matrix but instead are grouped together in clusters up to several hundreds of nm in diameter and thus have a high amount of self-same interaction rather than exclusively interacting with the matrix, and so considering their modulus within the nanocomposite as being similar to the modulus of SiNC layers is a reasonable approximation for the purposes of our analysis. Here, we can base our discussion around that value of μ as estimated previously. Our first approach to estimating the theoretical modulus of the composite employed the standard theory of mixtures, in which the μ values for the host and inclusion are treated as unchanging. The volume fraction of the mixture is used to weight the two μ values, as

$$\mu_{COMP} = \mu_{PDMS} * \phi_{PDMS} + \mu_{NC} * \phi_{NC} \tag{4.2}$$

where, μ (COMP), μ (PDMS) and μ (NC) are the moduli of the composite, PDMS and SiNC respectively, and ϕ (PDMS)and ϕ (NC)are the volume fractions of PDMS and SiNC (calculated for each sample type using ImageJ). Based on the previous equation, the composite is expected to exhibit a modulus of 190.59 kPa, which is nearly identical to the modulus of PDMS (190 kPa) on its own. From the theory standpoint, this is logical due to the very low volume fraction of SiNCs (calculated theoretically at 0.1% for the high concentration samples). However, our measured value of μ in both the functionalized and non-functionalized samples was lower than the modulus of PDMS on its own. Even using the more sophisticated Mori-Tanaka approach [13, 120], the theoretical mixture modulus was near the value for PDMS.

Recognizing this discrepancy, we also considered the possibility that the μ of the PDMS matrix itself may be altered by the presence of the SiNCs at higher concentration. The clusters of SiNCs are large enough to conceivably interfere with cross-linking between polymer chains, in effect countering the concentration of cross-linking agent and reducing the modulus of the PDMS [22, 126].

Considering this, we can work backwards from our measured μ for the composites, assuming the SiNC modulus as estimated in our prior work, and allow μ PDMS to change. Using this approach, we calculated that the PDMS modulus for the H-F samples was ~40% lower than the PDMS without SiNCs, and for the H-NF samples it was even more dramatically altered, ~70% lower than for PDMS alone. Based on established trends for the mechanical properties of PDMS as a function

of cross-linking agent concentration, this would mean that by including SiNCs (F and NF) in the PDMS at a concentration of <1% causes an effective change in the cross-linking ability of PDMS equivalent to reducing the curing agent:prepolymer ratio to 1:12 and ~1:18, respectively, for the H-F and H-NF samples [118].

4.4 Conclusions

We measured the luminescence and neo-Hookean coefficients of SiNC/PDMS nanocomposites based on concentration and surface functionality. The PL QY from the nanocomposites is high at 16% for the samples made with surface-functionalized SiNCs, and still measurable at 1-2% for the samples made with non-functionalized SiNCs at higher concentration. Our experiments indicate that the mechanical behavior of luminescent SiNC/PDMS nanocomposites depends on both the nanocrystal concentration within the PDMS as well as the surface functionality of the SiNCs. At low concentration (0.03 wt%) the SiNC inclusions do not influence the rupture stretch nor the neo-Hookean coefficient of the nanocomposites, regardless of surface functionality. However, at higher concentration (0.1 wt%) there is a statistically significant reduction in the neo-Hookean coefficient. This is in contrast to the report by *Chen et al.* [23], who found similar PL results for their SiNC/PDMS nanocomposites but reported a reduction in Young's modulus (~three times µ at low applied strain and assuming a Poisson's ratio of 0.5) and the tensile strength of hydrogenated (NF) samples but an increase in both for decyl-capped SiNCs in PDMS. We do not expect that the difference between decyl- and dodecyl-capped SiNCs should have such a profound impact on the mechanical properties of the nanocomposites, neither at low nor at higher concentrations. Further, the PL results from our study largely concur with their findings. Thus, these conflicting results point to the importance of further characterization and an improved understanding of the exact mechanisms of interaction between nanocrystals, their surface functionality, and manufacturing procedures during fabrication of nanocomposites using elastomers such as PDMS.

CHAPTER 5

FUTURE

5.1 AuNP Application for Silicon NanoRods (SiNRs) Sythesis

Throughout our experiments on synthesis of AuNPs, our overarching objective was to fabricate SiNRs with aspect ratio (AR) (Length/ Diameter) of 2-7. If successful, this work would introduce a brand-new plasma-based flow-through approach to continuous synthesis of SiNRs. Similar anisotropic SiNR growth in a fluid suspension was achieved by Heitsch *et al*, which used a ligand-assisted solution-phase method, based on Au-seeded solution-liquid-solid (S-L-S) growth [63]. Our focus is on translating this approach from solution to the plasma, which can avoid solvent use and could lead to wide tunability of the SiNR properties such as structure, AR, and surface in a continuous nanomanufacturing method.

For plasma-based SiNR growth, we sought to build on existing methods and use seeded growth based on AuNPs. In Chapter 2, we reviewed different methods for fabrication of AuNPs and introduced our plasma-based method which provides a new opportunity for fabricating SiNRs based on multi-stage reactor design. Figure 5.1 shows a schematic diagram for the proposed multi-stage reactor for producing AuNP-assisted SiNRs. The ultimate goal of this reactor is continuously making gold nanoparticles and then using them as the seed catalysts for growing SiNRs and continuously, using the plasma as energy source. For our preliminary trials, we constructed several iterations of this reactor. The concept was based on multi-stage reactors, with the first stage used for AuNP synthesis, and a subsequent plasma stage for growth of SiNRs using a supersaturated eutectic mixture method.

This reactor consists of gas cylinders connected to quarter inch tubing coming to MFCs and tubes, non-thermal RF plasma, electrical circuit for matching the power and stainless steel tubing for gas lines [107]. AuNPs are produced in the first stage using the hot-wire or plasma-based approach. After producing the AuNPs, in the second step these particles enter the second stage RF plasma (operated at 13.56 MHz and with supplied powers ranging from 5 to 40 W), tuned with a lab-constructed impedance matching networks including an adjustable capacitor, inductor coil, and air gap. SiH₄ was provided by a SiH₄/Ar mixture cylinder (1% SiH₄-99% Ar) as injected into the reactor from a 0.5-inch O.D. sidearm at flowrates between 5 and 50 sccm. The eutectic alloy

temperature for the Au/Si alloy is 363°C, and so we sought to explore the parameters necessary to reach this temperature by adjusting reactor parameters such as power, gas flowrate, overall pressure, and reactant partial pressure.



Figure 5.1: (a) Schematic Diagram for SiNRs synthesis (b) early stage experimental set up with hot wire method (*Courtesy R.J.Anthony*)

We modified the early stage design shown in Figure 5.1 by adding the Silane from an elevated side arm between the two stages. The early design added silane in the middle of the second stage, as presented in Figure 5.1, depicted in Figure 5.2. After using the reactor for ~ 20 mins, a thick film deposition of Silicon formed in the side arm and on the main reactor tube, preferentially on the injection side. We hypothesized that effective mixing of the AuNP-Ar flow from the first step and Silane from the second stage did not take place, causing the SiH₄ to remain spatially segregated, decomposing into film growth near the side arm for adding the Silane between two steps. This modification greatly reduced the gas mixture homogenization problem, and eliminated the preferential film growth near the side arm. We collected the reaction products at the bottom of the second stage in the reactor, and performed TEM characterization to investigate possible SiNR



Figure 5.2: High flowrate of AuNP-Ar from the first step(600-1200 sccm) and low flowrate of SiH₄ from the side arm did not mix properly in the second step of the reactor



Figure 5.3: Modified hotwire AuNP reactor for sythesis SiNRs

growth. Surprisingly the microscopy showed a widely size-dispersed set of silicon nanoparticles with both crystalline and amorphous structures. We had expected to see some mix of AuNPs, whether the SiNR growth had happened or not, as we were certainly injecting AuNPs into the

second stage. EDS provided some proof for AuNP from the first step collected after the second step of adding Silane without turning on the RF plasma in second stage. We focused on the form of the plasma, which included a filamentary structure (constricted region of high plasma density) during the second reaction. Other reports have indicated that, in argon/silane plasmas, the plasma density and temperature spikes reached by the nanoparticles in the plasma are related [3, 84, 109]. We hypothesized that the constricted plasma filament caused sufficient power density to in fact coalesce the smaller SiNCs typically produced under the same pressure/flow/power conditions but with a diffuse plasma. While Si nanoparticles exhibit size-related melting point depression [67, 108], the larger crystalline Si nanoparticles we observed had diameters >10 nm, indicating that they reached temperatures in excess of 1300 K. Not only this is higher than the eutectic alloy temperature we were seeking to reach, it also exceeds the melting temperature of gold. Our hypothesis was that by passing through the filamentary region, the AuNPs were re-evaporated (explaining their disappearance before collection on the TEM grid) and the SiNCs were coagulated and recrystallized. The solution we proposed was to eliminate the filament using gas flowrates.

We were able to stop the filament in the reactor by controlling the gas species flowrate inputs to the second stage (in particular, by keeping the SiH₄ flowrate <5 sccm) and by controlling the power to the plasma (Rf power limited to the range of 5-15 Watts). Photographs of this second-stage plasma with filament present (a) and the diffuse plasma (c) achieved using limited power and reduced SiH₄ flowrate are presented in Figure 5.4. Unfortunately, though, we probed a wide range of parameters within the confines of avoiding the filamentary plasma, we never observed anisotropic growth from this reactor configuration.



Figure 5.4: (a) Filament formation associated with high plasma density (b) High plasma density resulted in wide size range of Silicon nanoparticles with both crystalline and amorphous structures. (c) Controlling the SiH₄ flowrate and RF power stoped fillament and resulted in narrow size distribution for Silicon nanoparticles

As presented previously, the plasma-based method works with wider ranges of experimental parameters, compared to the hotwire method. Thus, we next attempted to combine plasma-synthesized AuNPs and SiNR growth. Figure 5.5 shows a schematic picture of the projected dual-plasma reactor. Future work will involve exploring the full range of capabilities of this dual-stage reactor.



Figure 5.5: Schematic of dual-plasma reactor for AuNPs-SINRs simultaneous synthesis

5.2 Modulus of SiNC Layers on PDMS: Parametric Investigation

5.2.1 Introduction

In-situ investigation of mechanical properties of nanomaterials in form of thin films is one of the challenging obstacles in advancement of nanotechnology and nanomaterial fields. There are many studies dedicated to plastic properties of individual nanoparticles in crystalline and amorphous forms [100]. Nanoindentation experiments and other physical probe-based techniques can be used to evaluate single-nanocrystal deformation in elastic and plastic regime. These techniques generally require especial microscopy techniques like tunneling electron microscopy. However, as these approaches are mostly irreversible and/or destructive, there is a significant interest in non-destructive methods for evaluating properties of thin films, especially for layers of nanocrystals on elastomeric substrates. The future of electronics strongly relies on advancement in mechanical flexibility, sustainability and biocompatibility of electro-optical sensors, health monitoring systems,

photovoltaic devices, displays, and functional coatings. We recently introduced a novel *in-situ* approach for estimating mechanical properties of luminescent SiNCs deposited on flexible substrates by measuring the onset of instabilities in the SiNC layers on PDMS under finite bending deformation as reported in Chapter 3. This study revealed a neo-Hookean coefficient (μ , analogous to shear modulus at low stress/strain) of a 4.5 μ m thick SiNC film to be 345 ± 23 kPa, which is significantly smaller than the young modulus of a single SiNC at the value of 170 GPa. There are many parameters that could influence the mechanical behavior of the SiNC layers on PDMS, including layer thickness, surface functionality, and mechanical properties of the PDMS substrate. In order to reveal some of these interrelationships, we investigated these parameters regarding their influence over the mechanical properties of SiNC layers on PDMS. Our results indicate that the layer of SiNCs and PDMS parameters exert competing influences on the mechanical properties of the SiNC layers. For example, we found that reducing the stiffness (reducing μ) for PDMS leads to a decrease in μ for the SiNC layer. However, the relationship is not monotonic. Unraveling the connection of these parameters on the physical, mechanical, and optical properties of the SiNCs will allow advancement for predictive engineering of nanomaterial thin films, for stretchable and flexible devices.

5.2.2 Experimental work

We prepared the PDMS in lab using a Sylgard prepolymer PDMS 184-kit and curing agent catalyst produced by Dow Corning. The PDMS mechanical properties depend on the prepolymer PDMS kit-184/curing agent catalyst ratio and curing conditions during PDMS preparation. We produced a range of substrate with same geometrical shape and dimensions (defined earlier in Chapter 3 as slenderness ratio). For experiments designed around modifying the SiNC layer, the prepolymer:curing agent ratio was 10:1, as before. For experiments to test the dependence of SiNC layer modulus on PDMS modulus, we altered this ratio to produce PDMS slabs with lower moduli. With a higher fraction of curing agent, the modulus of the resulting cured PDMS increases. [78]. We attempted to increase the modulus for this study by using a 7:1 ratio of prepolymer to curing agent,

but our experiments revealed that the critical angle required for bifurcation onset was too large to measure practically. Instead we reduced the amount of curing agent, using ratios of 10:1, 12:1, and 20:1 for this parametric study. We used the same method for evaluating μ for the substrates as discussed earlier in Chapter 3 and Chapter 4. For performing this parametric study, we chose a 3/1 slenderness ratio for our substrate.

As we mentioned earlier there are many advantages for gas phase processing. Similar to Chapter 3 and Chapter 4, we synthesized SiNCs using a low-pressure non-thermal plasma. The deposition of nanocrystals occurs directly out of the described reactor into thin-film layers using inertial impaction through a slit-shaped orifice onto a substrate placed beneath[68, 124]. This reactor enables us to control thickness of the film, pressure, sample-orifice distance and forwarded RF power to the glass tube.

As we discussed in Chapter 3 there is a stand off distance between orifice outlet and the top surface of PDMS substrate which is around 4-5 mm. This distance plays a significant role on the thickness and porosity of the thin film during deposition via back and forth rastering motion of the substrate. For instance, decreasing the distance would result in a thin film with lower porosity (higher density) and increasing the distance on the other hand, would result in higher porosity (lower density) [5, 68]. This is a consequence of the dynamics of SiNCs exiting the reactor from orifice outlet.

Since we fixed the value for stand off distance and the frequency of rastering motion for substrate (3 sec for each back and forth motion), the only parameter which impacts the thickness of the thin film is the number of rastering cyclces. In other words, changing the time of rastering from 20 mins as discussed in Chapter 3 to 10 mins and 5 mins results in a thinner and thinnest film in our results, respectively. We also produced samples with higher rastering time, 30 mins, as well. We used SEM analysis to evaluate the thickness of the layers depending on rastering time.

As we discussed the surface functionalization of the SiNCs will improve their PL properties, but changing the surfaces may also influence the mechanical behavior of the layer as a whole. We used a facile method to surface functionalize the SiNCs in the gas phase during the plasma process as previously studied by *Anthony et al.* [4]. Here, we used 1-dodecene for surface functionalization. We also measured the PL and QY for the produced film and results presented in Fig 5.10. We also used SEM to compare the surface morphology of non-surface functionalized and surface functionalized thin films under similar conditions.

In a summary of our experiments, Figure 5.6 presents a work flow of this parametric study.



Figure 5.6: Schematic diagram for investigating the impact of film thickness, surface functionality of SiNCs via gas phase plasma and shear modulus of the PDMS substrate on mechanical properties of SiNC thin film

5.2.3 Results

Film Thickness: We used a mechanical diamond glass cutter pen to mark our samples for thickness measurements. Figure 5.7 depicts the cross sectioning of samples produced via non-thermal plasma with various rastering deposition times. Regarding the the SEM image, which consisted from samples with 5 mins , 10 mins and 30 mins rastering time, the thickness of the film increased linearly with respect to the time of rastering deposition in plasma reactor. We performed a linear

regression and the R^2 value was 0.9918. We also attempted a exponential fit, for which the R^2 value was 0.9602. We expect that the deposition rate is linear, but it is possible that at low thicknesses there is a deviation from this behavior. Future work will investigate the sub-micron film thicknesses to evaluate if the rate remains constant even very close to the substrate, where packing effects may influence the porosity of the SiNC layer. In Figure 5.7 sample in red represented the results from Chapter 3 for comparison.



Figure 5.7: SEM images for PDMS with 3:1 slenderness ratio as defined in chapter 3 with rastering deposition time of 5 mins (Sample 1), 10 mins (Sample 2) and 30 mins (Sample 3) and averaged measured thickness of the film with corresponding standard deviation in comparison with the sample discussed with same slenderness ratio and 20 mins (in red)of rastering deposition time from previous chapter

Modulus of SiNC Layers (Estimated Values): We used the same methodology employing the onset of bifurcation to estimate the neo-Hookean coefficient for the SiNC layers subject to the parametric variation as noted above. The results are plotted in Figure 5.8. The asterisks on the bars indicate samples which had a statistically significant deviation from the value we obtained for the samples originally examined and reported in Chapter 3.



Ratio of neo-Hookean coefficients $\mu_{\rm ratio}$

Figure 5.8: The methodology introduced in Chapter 3, employed to estimate neo-Hookean coefficient for SiNC layars corresponds to parametric variation. The asterisks indicate samples with significant deviation from value we abrtained in Chapter 3

The first observation is that the thickness of the SiNC layers does influence the neo-Hookean coefficient, with thinner layers exhibiting increased μ as compared to the thicker layers. However, increasing the thickness beyond the 4-5 μ m, which was our standard, does not appear to alter the μ of the SiNC layers. From this, our hypothesis is that the soft PDMS substrate creates microstructural changes or densifications of the SiNCs, altering their mechanical behavior close to the substrate - yet once the layer reaches a certain critical thickness, the effect diminishes as the subsequent layers are deposited and they are less able to respond to the substrate's mechanical properties during deposition. Figure 5.9 presents the calculated mechanical property (neo-Hookean coefficient)of the SiNC thin film deposited on PDMS. The asterisks show the samples with neo-Hookian value significantly deviate from samples reported in Chapter 3.

Next, we can observe that the modulus of the PDMS also changes the resulting SiNC modulus,



Figure 5.9: Neo-Hookean coefficient of all sample introduced in this section. The samples with asterisks, present the data with significant deviation from samples reported in Chapter 3

with decreasing PDMS modulus creating a decreased μ for the SiNCs. Our hypothesis to this regard is still very nascent and this research is ongoing, but we can draw some ideas from what we observed during the thickness measurements. The thinnest layers of SiNCs on substrates made with the standard PDMS recipe (10:1 prepolymer:curing agent) have a higher modulus (are stiffer) as compared to the thicker layers. From this it is reasonable to expect that near the substrate there are effects from the impact of the NCs onto the PDMS, but as the layer becomes thicker these substrate effects are diminished. When we decrease the modulus of the PDMS by altering the recipe, we possibly alter the damping effect of the SiNCs impacting upon the substrate. We know that the thickness of the SiNC layer does not vary with changing PDMS modulus, but it's possible that the propagation of the substrate effect is reduced for the substrates with lower modulus. Our ongoing experiments will check this possibility by studying very thin layers of SiNCs (rastered for ≤ 5 mins) to test the limits of the substrate effect in terms of how far into the SiNC film is plays a role in the mechanical behavior.

Notable is that the surface functionalization plays no statistically significant role in the modulus of the SiNC layers (see Figure5.9). This is especially important regarding the fact that the SiNCs with in-flight surface functionalization display much higher PL quantum yields as compared to those made without surface functionalization (See Figure. 5.10). We can conclude that, for brightly emissive layers of SiNCs on PDMS, one can perform surface functionalization without disrupting the layer's mechanical behavior.



Figure 5.10: The surface functionalization applied in gas phase during plasma processing and sythesis of SiNCs. The PL and QY measured. This results coupled with mechanical property estimation of corresponding samples presented in this Figure. The results here, confirm that improving the oprical properties and QY do not interfere with mechanical property of the SiNC thin film.

5.2.4 Conclusions

This study is nearly complete. In summary, we have investigated some of the parameters of SiNC layer properties and PDMS properties. We discovered that reducing the thickness of the SiNC layer increases the modulus of the layer, and that in-flight surface modification greatly improves

the PLQY but does not appear to significantly alter the modulus of the SiNCs. However, reducing the PDMS modulus by altering the recipe for fabrication causes a significant reduction in the SiNC layer modulus. Our ongoing experiments and modeling will seek to explain these parametric effects and recommend future experiments.

5.3 Unbending- Another Finite Bending Condition for Mechanical Property Estimation

5.3.1 Introduction

Prior experiments involved the deformation of SiNC layers deposited on PDMS in a relaxed condition, and the bifurcations we observed upon bending the system as a whole. Here, instead we focus on experimental observations and physical circumstances which result in surface instabilities (wrinkling) of SiNCs layers deposited onto PDMS substrates in a prestretched condition, with future applications in tunable gratings and new manifestations of LEDs and other devices. Prior work has shown the emergence of wrinkling patterns in these systems [104], but here we have performed experiments to understand the conditions of the SiNC layers and the PDMS under which these wrinkling patterns are formed.

5.3.1.1 SiNC deposition

In this section, we discuss the various deposition schemes for placing the SiNCs layers onto the PDMS. The goal is to deposit a uniform layer of SiNC onto the PDMS as thin film, under varying pre-stretched conditions. We are interested in studying how the optical and physical properties of the SiNCs are altered when various degrees of pre-strain are applied to the PDMS.

We prepared a stage (Figure 5.11) which can be used to obtain any stretching ratio between 0-100%, and which is compatible with holes in both ends to be mounted onto a pushrod in the plasma reactor. This apparatus helps us to use PDMS as a substrate since we apply coaxial stress-strain to substrate. One end is fixed, and the other end is moving with a corresponding twisting screw. We achieve uniform deposition by rastering the substrate as mounted on the stage underneath the orifice. The rastering is a back and forward movement which helps to keep the thickness uniform throughout the substrate. While this allows for easy control over the applied pre-strain in the long direction and uniform deposition, it also leads to a pronounced bi-axial deformation due to the Poisson's effect of the PDMS, meaning that during the applied linear pre-strain there is also a compression across the perpendicular edge of the PDMS. This compression is measured to be \sim 10 percent at the waist of compression in the middle section (Figure 5.12).



Figure 5.11: Sample holder for various stretching ratios (left), sample holder for finite bending around pushing rod (right)

	A1	A2	A3	A4	A5			
Fixed	B1	B2	B3	B4	B5	1	Moving	Fixed
	C1	C2	C3	C4	C5			

Figure 5.12: Above view of sample, relaxed after deposition

5.3.2 Results

As we discussed in previous section about loading the substrate in the reactor, here, we present the results for both methods. In the first method, the PDMS sample was loaded on the sample holder and pre-stretched between 5% to 40% beyond the initial length (relaxed). After the SiNCs were deposited uniformly onto the PDMS in the reactor via inertial impaction, we used the screw on the stage to return the substrate to its original length steadily. During this process, SiNCs (which were experiencing no tensile force or compression on the pre-stretched PDMS) start to experience compression and this makes surface instabilities on SiNC layers. These wrinkles are observed by mounting the stage-sample setup in a vacuum chamber of SEM. The corresponding wrinkles for 20% applied pre-strain are depicted in Figure 5.13. Their axis can be categorized based on the area in which they formed, depending on the tensile or compressive forces that they experience during relaxation of the PDMS. Again, we see this combination of forces due to the Poisson's ratio of

the PDMS, leading to the SiNC layer experiencing compression near the clamps and tension near the waist of the pre-stretched PDMS. We categorized these responses to pre-stretched forces into 3 regimes based on position on the pre-stretched substrate: pure compression, pure tension, and a combination. In order to study the whole deposited area, we divided each deposited area of sample to 15 cells, including 3 rows (A-B-C) and 5 columns (1to5). The corresponding deposited area with cells shown in Figure 5.14 and Figure 5.12. Since the PDMS applied pre-strain was 20%, the



Figure 5.13: SEM image of deposited area with 20 percent pre-stretching condition, Column A3-B3-C3 (left), Columns A2-B2-C2 and A4-B4-C4 (middle), Columns A1-B1-C1 and A5-B5-C5 (right)



Figure 5.14: SEM image of deposited area with 20 percent pre-stretching condition, Column A3-B3-C3 (left), Columns A2-B2-C2 and A4-B4-C4 (middle), Columns A1-B1-C1 and A5-B5-C5 (right)

shape of the substrate during the SiNC deposition is not rectangular. Moreover, this new geometry will result in an interesting force response that include wrinkles on the surface of the SiNCs. The SEM images from different regions are shown in Figure 5.13. We can categorize the corresponding surface instabilities into 3 distinctive types: each occurs in specific cell areas depicted in Figure 5.14. As we can see, in the area near clamps of both side, where the deposited area changes

its thickness to some sufficient amount we observe vertical Lines. These areas include columns A1-B1-C1 and A5-B5-C5. However, in the column A2-B2-C2 and A4-B4-C4 we observe transient or inclined directions with respect to the X-Y Cartesian coordinate introduced in Figure 5.12. In the center, including middle column (A3-B3-C3) we observe horizontal wrinkles. Since these mechanical instabilities are different in terms of direction they appear throughout the deposited area, we justify the observation from mechanical point of view.

Figure 5.15 shows a diagram of the forces on the PDMS during stretching and corresponding tension/compression experienced by the PDMS during stretching. In order to understand the force distribution (tensile vs. compressive), we represented the PDMS in a top view schematic before deposition (in pre-stretch condition) and after deposition (in relaxed condition). The stage is set to move in one direction and it designed to stretch the PDMS from 100% (Zero sterteched) to 200% (double stretched), depending on the experiment design and initial PDMS dimensions. The Poisson Ratio for PDMS is ~ 0.5 [138]. This means that the strain in longitudinal direction is twice the strain in compression along the middle section of the sample. So, the PDMS area near the clamps



Figure 5.15: pre-stretched before deposition or during deposition

experience tension, however, one clamp is fixed in position. During deposition SiNCs these areas are deposited on a stretched surface but experience zero force while the SiNC layers are formed. After deposition, when the PDMS is relaxed back to its original length, SiNCs will experience compression near the edges (columns 1 and 5 in our areal mapping scheme) and they start to form surface instabilities as shown in the Figure 5.13 (right). However, the middle section of PDMS (column 3) is under compression during the deposition. By returning to relaxed condition, the SiNC layer in the middle section would experience tension. Ultimately, in this middle section the

SiNC layers form instabilities perpendicular to the ones near edges. Between the edge regions and the middle region (columns 2 and 4), the SiNCs experience a hybrid of these responses.

In order to limit the scope of this study, we focused on to the formation of instabilities near edges, which result from the SiNC layers experiencing pure compression after the PDMS is relaxed. As a part of manufacturing design, we had to provide a design to able reproduce this (near edges) kind of surface instabilities which in order to categorize them in a similar formation direction since we apply one-dimension force to the substrate. Due to the nature of the PDMS, it is impossible to eliminate the tensile force experienced by the SiNCs when the PDMS is pre-stretched using the stretching stage we described hre so far. Thus, we have to provide a new experimental set up for loading the PDMS: our solution is to use finite bending of the PDMS. This approach will mostly eliminate the Poisson's ratio effects on the region in the middle of the PDMS. Since the PDMS wraps around the pushrod, the upper surface (SiNC-coated surface) experiences a strain in the circumferential direction and there would be no dimensional change corresponding Poisson's effect for substrate.

We explored finite-bending as a way to minimize the bi-axial effect as observed for the stretching stage described above. To achieve this, we cast the PDMS into aluminum molds of calculated size, attached handles to the PDMS during the process with a commercial painting foam (Foam Board), and wrapped it around the pushrod, gripping the handles together at the base using a staple. Then, SiNCs are deposited onto the PDMS (which is deformed via this finite bending), and when the handles are released, the PDMS returns to its relaxed state. Figure 5.11 shows both setups. Figure 5.16 shows a picture of a prospective sample going under finite bending elastic deformation. We wrapped PDMS around the pushing rod and deposited SiNCs on the wrapped substrate. In order to guarantee an evenly deposited film on substrate we have to clamp the PDMS (Figure 5.16). The microscope picture shown in right side of the Figure 5.16, is captured by Optical-Electrical Microscope (Keyennce) under aforementioned conditions. This picture confirms the formation of wrinkles with the new design for substrate. However, since we applied some force to clamp the PDMS all around the push-rod, there would be extra force we applied for wrapping around the rod.

As the next step, we had to find exact substrate dimensions that allow the substrate to wrap around the rod without the need of additional clamping or stretching.



Figure 5.16: Early design for finite bending surface instabilities by wrapping PDMS around the rod, the picture on right is the microscope image of the sample after unwrapped with the scale bar of 10 micrometer

To measure the exact size, we need the sample to be wrapped around the pushrod with no tension. We used a mathematical calculation to find the width to thickness (w/t) ratio for a corresponding pre-strain (here it is 20%). So then with that ratio, we are able to wrap the substrate around the pushrod with no extra force which makes it feasible to have surface instabilities based on pure finite bending. (Figure 5.17). Based on the Constitutive Laws and Neo-Hookean assumptions given in Figure 5.17, we are able to apply the corresponding w/t ratio to make an aluminum cast for fabricating PDMS with handles. Figure 5.17 shows the corresponding result for this set up, beside a picture of the setup, including the aluminum cast and flexible handles for sample to be wrapped around the push-rod and securely fixed in place during deposition. This helps us to make sure that during the deposition the rotation of substrate with the pushrod for uniform deposition will not change the position and distance of substrate from the orifice which is an important factor for formation of uniform and continuous SiNCs film on the substrate. The thickness and width of the PDMS sample, in the reference configuration, is taken in such a way that there are no tractions on the surface when it is rolled on a cylindrical rod of a given outer radius. When the system undergoes the unbending deformation the thin SiNC layer deposited on the outside surface of the PDMS experiences a compressive force. This is similar to the compressive force faced by the top surface of the SiNC in the method involving finite bending. Therefore, like in the finite bending experiments, we expect the formation of instabilities on the surface of thin film above a critical

compressive stress. This value of compressive stress depends upon the geometric configuration and mechanical properties of the system. We now able to produce surface instabilities based on pure



Figure 5.17: A new method for pure bending surface instabilities, the mathematical correlation and assumptions for incompressible, Neo-Hookean material (left)

bending, and the microscope image also confirms this result. Figure 5.18 shows a set of wrinkles produced by pure bending effect. These wrinkles spanned over different areas in the sample including rows A1-A2-A3-A4-A5 and C1-C2-C3-C4-C5. The surface instabilities will be studied



Figure 5.18: A new method for pure bending surface instabilities, the mathematical correlation and assumptions for incompressible, Neo-Hookean material (left)

by their amplitude and the size. Since the mechanical properties leading to instability formation are dependent on the bilayer system of PDMS and SiNCs, this study provides an opportunity to correlate the luminescence and mechanical properties of the SiNC layer based on the surface wrinkles. Our early calculation is based on images from an optical microscope which helps us measure the size of the wrinkles based on where the wrinkles are formed. Table 5.1 provides a list

Deposition	Time of Deposition	Pressure (Torr)	Forward RF-Power	
movement	(Seconds)		(Watt)	
Full round (360	30- 150	3.5-4.2	25-30	
degree)				
Segment by segment	60- 120	3.6-4.2	25	
rastering				

of operation conditions used for making surface instabilities in SiNC plasma reactor. The time of

Table 5.1: List of operation used for making surface instabilities in SiNC plasma reactor at PNL

deposition can turn into number of rotations of sample around the rod underneath the orifice. To calculate this number, we measured each rotation time under the orifice in the plasma deposition reactor which is \sim 3 seconds. This will help us to compare the thickness of the film quantitatively. The forward power is the power sent out to the plasma reactor and can be optimized with matching box. It is the operator's duty to check the appearance (shape, intensity and length) of the plasma for set of recorded parameters. The power range stated in the table is used to form SiNCs with high crystallinity. The crystallinity can be checked by XRD. To verify the crystallinity, we performed a brief power study using the same flowrates and pressure, however, the power received was 30 and 25 respectively. Figure 5.19 shows the XRD patterns from these samples, indicating a higher degree of crystallinity for 30 Watt power than 25 Watt. The clear peaks from the [111], [220] and [311] crystallographic planes at 28.460°, 47.510° and 55.910° observed respectively [130]. This can be further verified by Raman Spectral Analysis [74, 107, 128]. This has been proven with other studies made for SiNCs [3].



Figure 5.19: XRD for SiNCs deposited on PDMS, 30 Watt(Left), 25 Watt (right)

Figure 5.20 shows a peak-to-peak distance measurement for these surface instabilities as based on the optical microscopy. The microscope image shown in Figure 30 is one of the corresponding samples used for this measurement. Lamda (λ) is the length of peak to peak separation of two wrinkles next to each other. This λ changes from ~ 1 micron to more than 20 microns, corresponding to the different cell areas we defined for each PDMS sample (see Fig. 22). The aforementioned system includes 15 equal size cells and these wrinkles repeated with different size in various cells. Moreover, since each rotation under orifice takes ~ 3 seconds, then 10 rounds equal to 30 seconds (~ 100nm), 20 rounds equal to 60 seconds (~ 200nm) and 30 rounds equal to 90 seconds (~ 300nm). These thickness calculations are based on experimental image samples captured by SEM. Increasing the time or number of rotation (while we keep same speed for rotation) will result in thicker films on the substrates. Regarding the previous SEM thickness measurements Figure 5.20 includes average size with corresponding standard deviation. Since we have 3 samples with varying thicknesses we can measure the λ of the wrinkles for each sample. All calculations are based on optical microscope images.



Figure 5.20: Lambda (λ) measurement for surface instabilities, 10 round rotations in the reactor(upleft), 20 round rotations(up-right) and 30 round rotations (bottom), numbers are corresponding to the cells that measurement done with specified standard deviation for each averaged size letter corresponding to the cell which wrinkle instabilities observed



Figure 5.21: A sample of PDMS deposited with SiNCs under pre-stretched condition for 10 round rotation(left), definition of Lambda (λ) and thickness of the SiNCs film(right)

The λ measured based on the schematic diagram shown in Figure 5.21. As demonstrated in Figure 5.20, λ is not changing much for most of the samples, however, near the edges, including(A1-A5 and C1-C5) the standard deviation is bigger, which means the size of λ changing from few microns to 10 microns.

To able to track the surface instability regimes and their amplitude changes on the surface we have to observe the cross-section image of formed wrinkle patterns by microscopy. Cross-sectional

imaging for these soft substrates has been an issue for many instruments and techniques including surface and thickness measurement by spectroscopic ellipsometry and Focused Ion Beam (FIB) cross-sectioning with SEM. Atomic Force microscopy (AFM), however, is a physical and optical method which provides new information about surface morphology in micrometer scale. This method has its own limitation including the maximum scanned size per each cycle. This method has been used for the sample shown in the result section for 20 rounds and the image shown in Figure 5.22. In this figure, a 3D model is constructed based on surface topology data from the AFM tip over a 20x20 micrometer area. This 3D model is conjugated with a cross section estimation to help us evaluate the amplitude of these surface instabilities.

In future experiments, we will study the influence of SiNC size and the regime of wrinkles. Ultimately, we intend to study multilayer film composed from SiNCs with different sizes to study varied emission wavelengths.



Figure 5.22: Atomic Forced Microscopy (AFM), AFM scanned a line across a 20 by 20 micrometer area and provided a 3D model and a cross-sectional view for investigating the amplitude of these surface instabilities

5.3.3 Conclusion

In this section, we introduced another class of finite bending problem. Surface instabilities formed on thin film of SiNCs deposited on PDMS and their corresponding patterns categorized based on tenssion and compression deformation of the substrate. In order to control the formation of surface instabilities, we intorduced finite bending (unbending) for prestretched substrate (PDMS) undergoing plasma deposition process. In this configuration, final bilayer system unwrapped and compressed the thin film of SiNCs on top. Surface instabilities formed and their size and presence redorded for different thicknesses of the thin film. Our study showed these surface instabilities change to cracks and fractures on the thin film by increasing thickness of the thin film. The size of these instabilities will be correlated to the mechanical property ratio of the thin film to the one of the substrate. These results will be coupled by a theoretical moding to estimate mehanical properties of the SiNCs deposited on PDMS as thin film.

5.3.4 Future work

A theoretical model will be applied to the system introduced in this section for mechanical property estimation. This evaluation will be compared with results presented in Chapter 3 and parametric study introduced earlier in this chapter. This effeort will provide a new technique for estimating the mechanical property measurement of the thin films of SiNCs in an *in-situ* and non destructive fashion.

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