Jennifer Wang received her B.S. in chemistry from Rice University in 2006. At NREL she participated in the Science Underground Laboratory Internships (SULI) program, working on the nanoscale manipulation of zinc oxide structures to improve their functionality in hybrid ZnO/organic nanocomposite photovoltaic devices. She presented this work with a poster at the 2006 AAAS Meeting in St. Louis. At Rice she performed additional undergraduate research on magnetic and semiconductor nanomaterials and the analysis of biodiesel by gas chromatography. Her interests outside the lab are in sustainable design and environmental advocacy, with the aim of integrating research and fieldwork with application and outreach. She is currently working in this field and will pursue a graduate degree in a related discipline.

David S. Ginley is currently a Group Manager in Process Development and Advanced Concepts at the National Renewable Energy Laboratory, leading activities in the applications of nanotechnology, organic electronics, transition metal oxides (ferroelectric materials, rechargeable Li batteries, and transparent conductors) and ink jet printing. He leads a team in the development of nanoparticle-based precursors to electronic materials, particularly as they apply to photovoltaic and optoelectronic technologies. Recent activities include a program on combinatorial approaches to electronic materials and a program on polymer-based photovoltaic cells and OLEDs. For more than 25 years, he has been active in developing a basic understanding of the relationships between structure and the optoelectronic properties in a variety of materials. Dr. Ginley graduated from the Colorado School of Mines with a B.S. in mineral engineering chemistry. He subsequently received a PhD from MIT in inorganic chemistry, where he worked in inorganic photochemistry and in the emerging area of photoelectrochemistry.

Sean Shaheen is a senior scientist at the National Renewable Energy Laboratory (NREL) in Golden, CO. He received his B.S. in physics from Carnegie Mellon in 1991 and his PhD in physics from the University of Arizona in 1999. His current research is focused on organic and nanostructured photovoltaic devices using novel polymers, dendrimers, and solution-grown organic/inorganic composite nanostructures. His research interests include studies of the complex interplay between molecular structure and bulk material properties and device behavior, with the goal of producing low cost solar cells from "smart" materials. He currently advises several graduate students and postdocs at NREL.

ORDERED NUCLEATION SITES FOR THE GROWTH OF ZINC OXIDE NANOFIBERS

JENNIFER WANG, DAVID S. GINLEY, AND SEAN SHAHEEN

ABSTRACT

Organic photovoltaics (OPVs) offer a promising route to low cost photovoltaic (PV) technology that can be inexpensively manufactured on a large scale for use in power generation and commercial products. Solar power conversion efficiencies of laboratory scale OPV devices have recently reached ~5%; however, projected efficiencies of at least 10% will be required for commercialization. An analogous approach that has arisen recently that can potentially increase efficiencies employs metal oxide semiconductors as the electron acceptor, creating a hybrid organic-inorganic device. This approach offers the advantage that the conduction band of the oxide can be tuned in a systematic way through doping, thus potentially achieving higher photovoltages in the device. Additionally, nanostructures of these materials can be easily grown from precursor solutions, providing a technique to precisely control the nanoscale geometry. This work focuses on using ZnO, which is known to have high electron mobility (>100 cm^2/Vs), as the electron acceptor. Nanofibers of ZnO can be grown from precursors such as zinc acetate or zinc nitrate to form arrays of nanofibers into which a conjugated polymer can be intercalated to form a composite PV device. The morphology of the nanofiber array is critical to the performance of the device, but current methods of nanofiber growth from a flat, polycrystalline nucleation layer allow for little morphological control. To overcome this limitation, we have created ordered arrays of ZnO nucleation sites with controllable size and spacing. Toluene solutions of diblock copolymer micelles with $ZnCl_2$ incorporated into the micellar cores were spin-coated onto glass substrates and etched with an O_2 plasma to yield hexagonally ordered arrays of ZnO nanoparticles that functioned as nucleation sites. Changing the concentration of $ZnCl_2$ and the molecular weight and ratio of the diblock copolymer resulted in systematic variation in the size and spacing of the nucleation sites. Thermal anneal treatment provided further modification of the nucleation layer, from which ZnO nanofibers were successfully grown from solution, although at present it is not known if the geometry of the as-grown ZnO nanofibers precisely reflects that of the underlying nucleation layer. This work provides a simple and useful method for potentially controlling the nucleation of ZnO nanofibers to be used in hybrid ZnO/organic nanocomposite PV devices.
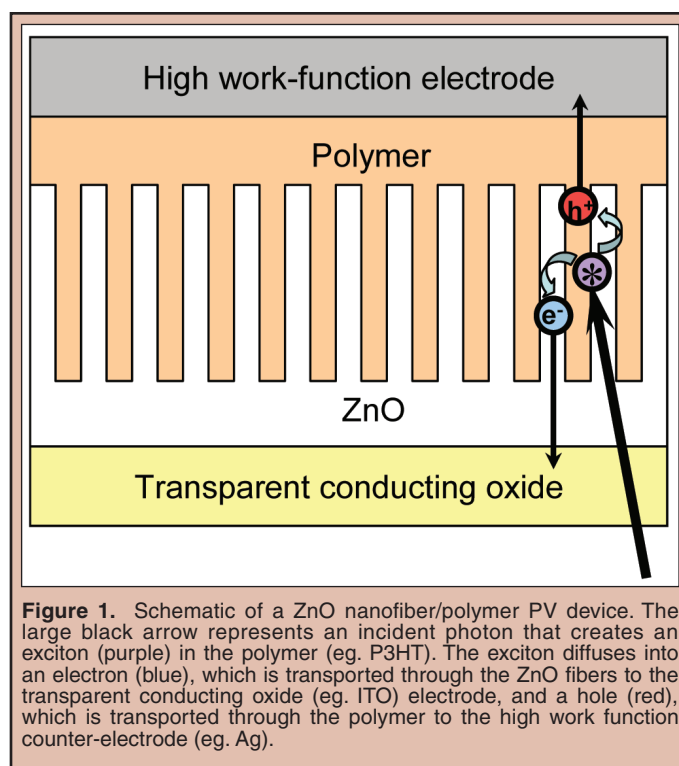
INTRODUCTION

Photovoltaic (PV) technology is regarded as an essential component in the future of global energy production. By harvesting energy directly from sunlight, PV systems are a renewable resource that can address growing global energy demands and reduce the consumption of fossil fuels with its detrimental effects on the environment. A PV device, or solar cell, converts absorbed photons directly into electrical charges, which then drive an external circuit. Current PV technologies utilize crystalline silicon and thin film inorganic materials, but the costs of these technologies limit their competitiveness in energy production. As such, the development of PV technologies with very high efficiencies or very low costs is a potentially lucrative endeavor.

Low-cost, moderate efficiency (15-20%) PV technologies require inexpensive materials for the active components and packaging, low-temperature atmospheric processing, and high fabrication throughput. All of these attributes can theoretically be realized in organic-based photovoltaics (OPVs). The use of organic materials provides great versatility in the alteration of key properties such as molecular weight, electronic properties, and surface and structural properties [1]. The ease and economy of production combined with a theoretical efficiency that matches that of conventional semiconductor PVs give OPVs a competitive edge in the overarching search for a PV technology that is both economically and technically viable for large-scale power production. Additionally, the flexibility of the materials allows for the incorporation of PV devices into myriad commercial products such as fabrics, plastics, and roofing.

Recent OPV devices fabricated in the research laboratory have exhibited solar power conversion efficiencies of ~5% [2]. Such devices are based on composite blends of a π-conjugated semiconducting polymer, such as poly(3-hexylthiophene) (P3HT), and a soluble fullerene derivative, such as [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM). The method of photoconversion in these composite blends is based on the ability of the polymer to absorb light and create excitons, which are dissociated through an ultra-fast photoinduced charge transfer between the polymer, the electron donor, and the fullerene, the electron acceptor.

An alternative to the polymer blend devices involves the use of metal oxide semiconductors such as SnO_2, TiO_2, or ZnO, all of which exhibit ultra-fast photoinduced charge transfer with conjugated polymers [3,4]. A major advantage to this approach is that the conduction band of the oxide can be tuned in a systematic way through doping, potentially resulting in increased photovoltages in the device. Additionally, nanostructures of these materials can be easily grown from precursor solutions, allowing for precise control over the nanoscale morphology. This work focuses on the use of ZnO, which is known to have high electron mobility (>100 cm²/Vs), as the electron acceptor.

A solution-based growth method employs precursors such as zinc acetate or zinc nitrate to form arrays of vertically aligned ZnO nanofibers into which a conjugated polymer can be intercalated to form a composite PV device [5]. The use of ZnO nanofiber arrays offers several advantages: a) increased donor-acceptor interfacial area leads to increased charge transfer, b) the electron transport pathways

Figure 1. Schematic of a ZnO nanofiber/polymer PV device. The large black arrow represents an incident photon that creates an exciton (purple) in the polymer (eg. P3HT). The exciton diffuses into an electron (blue), which is transported through the ZnO fibers to the transparent conducting oxide (eg. ITO) electrode, and a hole (red), which is transported through the polymer to the high work function counter-electrode (eg. Ag).

toward the negative electrode possesses very high electron mobility, c) the fixed morphology assures that the donor-acceptor interface does not change, potentially leading to better device lifetimes, d) material costs are reduced in device fabrication due to the lower cost of metal oxides compared to fullerenes, and e) the direction of current flow is inverted with respect to traditional blend devices, allowing for the use of more stable high work function counter electrodes [5]. Figure 1 is a schematic representation of the ZnO nanofiber/polymer PV device.

The morphology of the nanofiber array is critical to the performance of the device, as defects and disorder in the nanostructure and large nanofiber spacing lead to charge recombination. Increased efficiency may be achieved by reducing the nanofiber spacing to within the P3HT exciton diffusion length, which is presumed to be less than 10 nm. None of this necessary morphological control is provided by the current method of ZnO nanofiber growth from a continuous, polycrystalline nucleation layer.

To overcome this limitation, we have created ordered arrays of ZnO nucleation sites with controllable size and spacing. The method used was based on previously published work in which the nanoparticle arrays were self-assembled from monolayer films of diblock copolymer micelles [6]. The diblock copolymer used in this study, poly(styrene-*block*-poly4-vinylpyridine) (PS-P4VP), consists of a hydrophobic PS solvate block and a hydrophilic P4VP functional block. Because toluene is a selective solvent for the PS block, spherical micelles with a PS corona and a P4VP core form in dilute toluene solution [7]. $ZnCl_2$ is then added to the solution, whereupon it dissolves in the P4VP block [6]. We spin-coated the solution onto a glass substrate and exposed the resulting film to O_2 plasma, which served to both remove the PS-P4VP and oxidize the zinc salt to ZnO. The size and spacing of the ZnO nanoparticles were controlled through modification of the amount of $ZnCl_2$ and the

molecular weight and ratio of the copolymer blocks. Thermal anneal treatment of the nucleation layer allowed for successful growth of ZnO nanofibers using a chemical solution growth technique [8].

MATERIALS AND METHODS

Chemicals

All chemicals were used as received: $ZnCl_2$ (Aldrich), Toluene (Aldrich), Zinc acetate dihydrate (Aldrich), Zinc nitrate hexahydrate (Aldrich), NaOH (J. T. Baker), and PS-P4VP (Polymer Source). Three different PS-P4VP polymers were used: M_n^{PS} [kg mol^{-1}]/M_n^{PVP} [kg mol^{-1}]/polydispersity index = 47.6/20.9/1.14, 31.9/13.2/1.08, and 32.9/8.0/1.06, which will be referred to in this paper as PS-P4VP-1, PS-P4VP-2, and PS-P4VP-3, respectively.

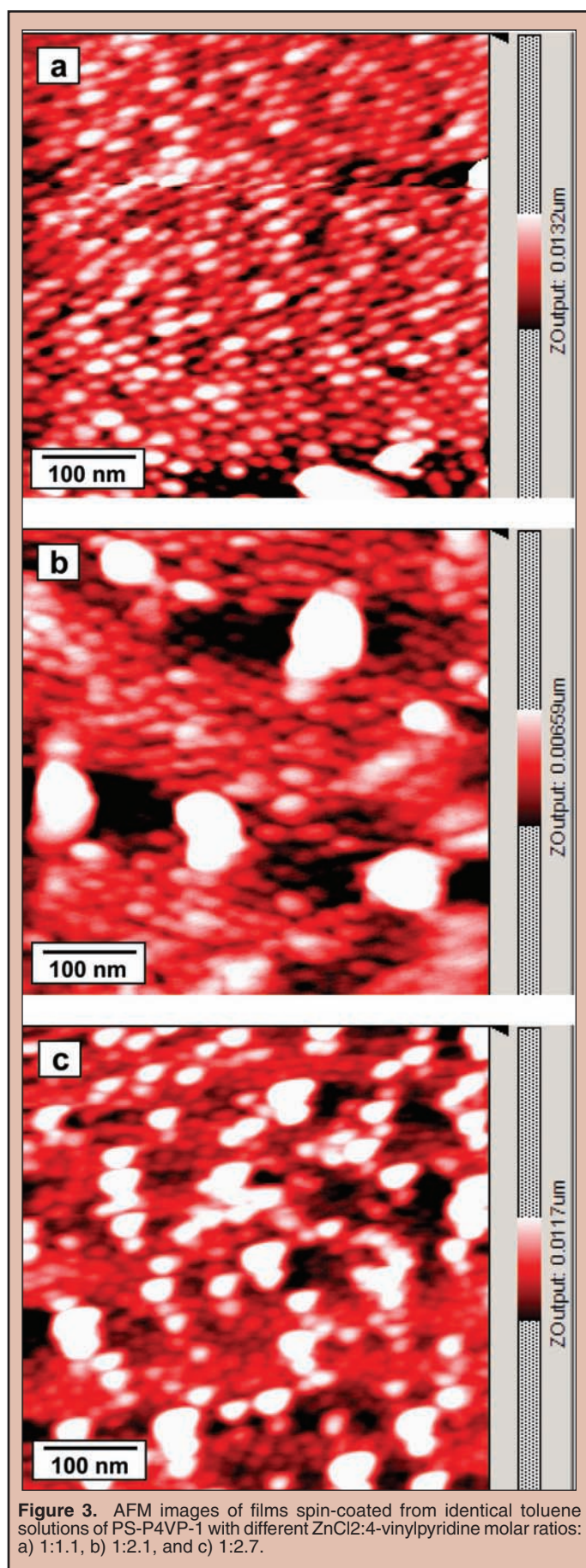### *Formation and Characterization of Ordered Nucleation Sites*

0.5 wt% toluene solutions of PS-P4VP were stirred at 70 °C for 2 h. $ZnCl_2$ was added to the micelle solutions and stirred at

Figure 2. Schematic of the formation of ordered ZnO nucleation sites from diblock copolymer micelles.
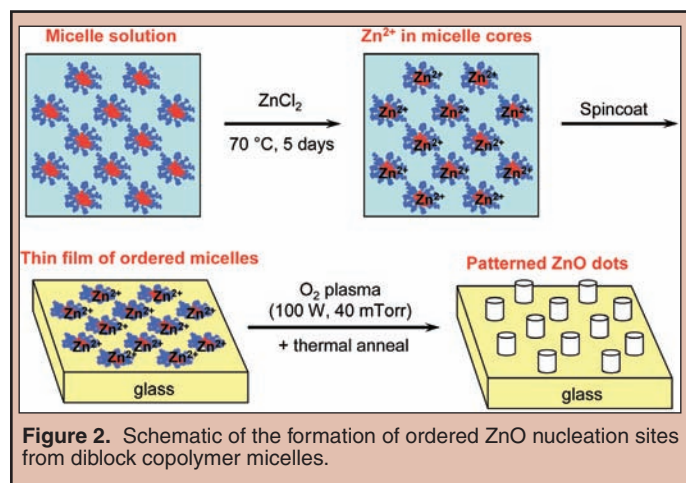
70°C for 3-5 days to maximize loading of $ZnCl_2$ into the P4VP core. Glass microscope slides (Fisher) were cut into 1 inch squares and cleaned by ultrasonic agitation in isopropanol for 10 minutes, followed by oxygen plasma cleaning (150 W, 500 mTorr) for 5 min. The $ZnCl_2$/PS-P4VP solution was spin-coated onto the glass at 2000 rpm for 1 min with an initial ramp speed of 2000 rpm/s. The films were then exposed to oxygen plasma (100 W, 40 mTorr) for 10 min, resulting in an array of ZnO nanoparticles. The films were subsequently annealed in air on a hot plate. A schematic of this entire process is given in Figure 2. The nucleation layers were characterized by atomic force microscopy (AFM) in tapping mode on a nanoSurf DFM and by scanning electron microscopy (SEM) on a FEI Quanta 400 FEG ESEM and a JEOL 6320 FE-SEM.

Hydrothermal Growth and Characterization of Nanofibers

The films of ZnO nanoparticles were rinsed with deionized water and ethanol and submerged in a stirring solution of 1 mM zinc nitrate hexahydrate and 80-90 mM NaOH at 70°C for 20 min [3,8].

Figure 3. AFM images of films spin-coated from identical toluene solutions of PS-P4VP-1 with different ZnCl2:4-vinylpyridine molar ratios: a) 1:1.1, b) 1:2.1, and c) 1:2.7.

The samples were rinsed again and dried in air at room temperature. The nanofiber arrays were characterized by SEM.

RESULTS

Nucleation Layer

Zinc Ion Concentration: Different amounts of $ZnCl_2$ were added to identical solutions of PS-P4VP-1 in toluene. The molar ratios of $ZnCl_2$:4-vinylpyridine were: a) 1:1.1, b) 1:2.1, and c) 1:2.7. After spin-coating the solutions onto glass and treating with O_2 plasma, the films were annealed for 2 h at 300°C to reduce noise and streaking effects in AFM imaging, the results of which are presented in

M_{PS}:M_{P4VP} (x 10³)	47.6:20.9 (PS-P4VP-1)	32.9:8.0 (PS-P4VP-2)	32.9:8.0 (PS-P4VP-2)
% P4VP	31	29	20
Diameter	37 nm	13 nm	15-20 nm
Edge-to-edge spacing	22 nm	9 nm	Variable
Height	4.0-5.5 nm	2.7-3.5 nm	1.5-4.2 nm
% Coverage	67	61	Unknown

Table 1. Effect of PS-P4VP molecular weight and ratio on nucleation layer morphology. Numbers are based on visual estimation.

Figure 3. Qualitatively, reduction of zinc ion concentration resulted in a decrease in the size of the nanoparticles, but it also resulted in the formation of several large nanoparticles randomly scattered across the substrate.

PS-P4VP molecular weight and ratio: The three different PS-P4VP polymers were used to make 0.5 wt % toluene solutions, followed by addition of $ZnCl_2$ at a constant molar ratio to 4-vinylpyridine of 1:2. After spin-coating the solutions onto glass and treating with O_2 plasma, the films were annealed for 30 min at 300°C. AFM images of the resulting nucleation layers are shown in Figure 4. Morphological changes are tabulated numerically in Table 1. Keeping a constant molecular weight ratio of approximately

M_{PS}:M_{P4VP} (x 10³)	47.6:20.9 (PS-P4VP-1)	32.9:8.0 (PS-P4VP-2)	32.9:8.0 (PS-P4VP-2)
% P4VP	31	29	20
Diameter	37 nm	13 nm	15-20 nm
Edge-to-edge spacing	22 nm	9 nm	Variable
Height	4.0-5.5 nm	2.7-3.5 nm	1.5-4.2 nm
% Coverage	67	61	Unknown

Table 2. Effect of thermal anneal on nucleation layer morphology. Image analysis was performed using Igor Pro by fitting to a model assuming a perfect hexagonal lattice.

30% P4VP and reducing the molecular weights of both copolymer blocks resulted in a significant decrease in the size, edge-to-edge spacing, height, and % coverage of the nanoparticle array, which maintained its hexagonal ordering. The hexagonal ordering was lost upon changing the molecular weight ratio to 20% P4VP while keeping a nearly constant M_{PS}.

Thermal anneal: Figure 5 shows SEM images of two nucleation layers spin-coated from the same PS-P4VP-1 toluene solution with 1:1.3 $ZnCl_2$:4-vinylpyridine and treated with O_2 plasma. One of the films received no anneal treatment and the other was
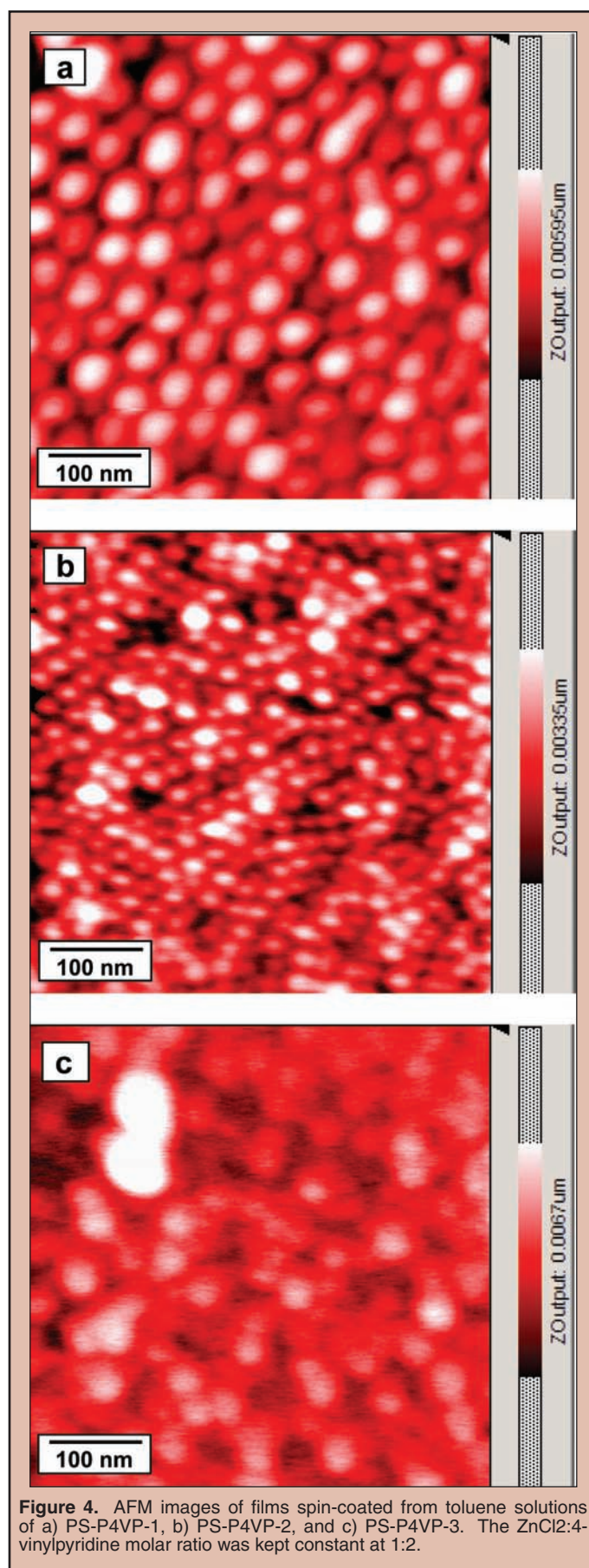

Figure 4. AFM images of films spin-coated from toluene solutions of a) PS-P4VP-1, b) PS-P4VP-2, and c) PS-P4VP-3. The ZnCl2:4-vinylpyridine molar ratio was kept constant at 1:2.
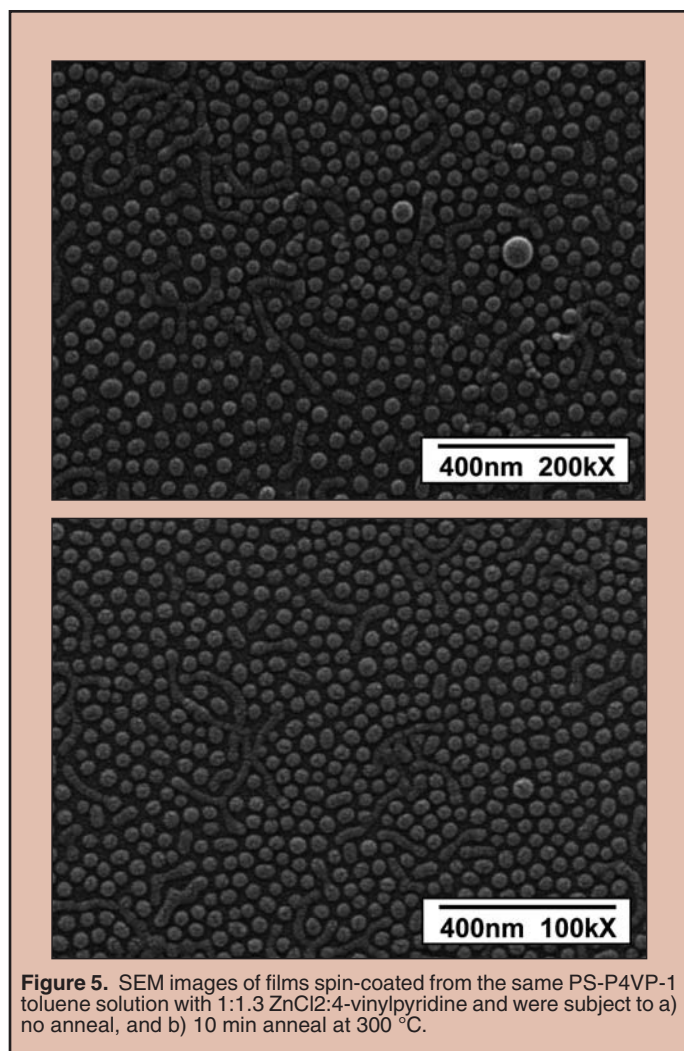
Figure 5. SEM images of films spin-coated from the same PS-P4VP-1 toluene solution with 1:1.3 ZnCl2:4-vinylpyridine and were subject to a) no anneal, and b) 10 min anneal at 300 °C.

annealed for 10 min at 300°C. Morphological changes are tabulated numerically in Table 2. Anneal treatment did not change the size of the nanoparticles, but it did result in better monodispersity, larger % coverage, and decreased edge-to-edge spacing.

Nanofibers

ZnO nanofibers were grown from solution on nucleation layers spin-coated from the same solution (PS-P4VP-1, $ZnCl_2$:4-vinylpyridine = 1:1.3) and had received different anneal treatments. SEM images of the results are presented in Figure 6. No anneal treatment caused the nucleation sites to be etched away during growth, and the resulting nanofibers appeared randomly on the substrate in isolation or arranged in small clusters (Figure 6a). Annealing at 300°C for 10, 30, and 60 min, and at 400°C for 20 min all resulted in the formation of "egg" structures, dense regions of vertically aligned nanofibers strewn about the substrate (Figure 6b). Each "egg" consisted of an outer circle full of nanofibers and an inner "yolk" of nanofibers that seemed to form an additional layer (Figure 6c). Only with a 2 h anneal at 300°C did a dense film of nanofibers form across the substrate (Figure 6d). With a 2 h anneal at 500°C, the isolated nanoparticles on the nucleation layer aggregated (Figure 6e), and the resulting nanofibers were randomly

arranged on the substrate in small clusters similar to the result of no anneal, but the fiber diameter increased (Figure 6f).

DISCUSSION AND CONCLUSIONS

Morphological Control of ZnO Nucleation Sites

We have examined three approaches to changing the size and spacing of ZnO nucleation sites formed from diblock copolymer micelles incorporated with a zinc salt. One route was to change the concentration of the zinc salt while keeping the size of the diblock copolymer micelles constant. With less precursor available to infiltrate into the micellar cores, the total precursor amount should be distributed evenly among the micelles. After spin-coating and O_2 plasma treatment, the film should exhibit smaller ZnO nanoparticles, while the center-to-center spacing should have remained constant (edge-to-edge spacing should have increased). Close examination of the Z-scales in Figure 3 reveals that decreased $ZnCl_2$ concentration does result in shorter nanoparticles. Due to the AFM tip resolution, however, this result is strictly qualitative, and it is unclear whether there was any change in the nanoparticle diameter. Decreasing the $ZnCl_2$ concentration caused the film to exhibit larger, aggregated nanoparticles scattered randomly across the surface. This suggests that the ratio of the zinc salt to the P4VP cores can be optimized so that the zinc-loaded micelles can achieve optimal monodispersity. Our experience showed that larger amounts of $ZnCl_2$ ($ZnCl_2$:4-vinylpyridine = 1:1.1 -1:1.3) led to greater monodispersity in the resulting nanoparticle array.

Another route to morphological control over the nucleation sites was to change the molecular weight and ratio of the diblock copolymer as purchased. As seen in Figure 4a and 4b, decreasing the molecular weight of each block while keeping their ratio constant to be a highly effective way of decreasing the size and spacing of the nanoparticles. Table 1 shows that by switching from PS-P4VP-1 to PS-P4VP-2, the estimated diameter decreased from 37 nm to 13 nm, and the estimated spacing decreased from 22 nm to 9 nm. The estimated height and % coverage also decreased. Further decreasing only M_{P4VP} seemed to hinder the formation of ordered micelles, and the resulting nanoparticles had variable size, spacing, and ordering (Figure 4c). Changing the PS-P4VP ratio, therefore, may be a more challenging approach that will require further investigation.

Lastly, thermal anneal treatment of the nucleation layer provided morphological control in that the nanoparticles became more monodisperse in size and exhibited closer spacing. Since the amount of ZnO remains constant during anneal, this result suggests that the nanoparticles became flatter and possibly more crystalline during the anneal process. Future work will examine changes in the crystallinity of the nanoparticles using X-ray diffraction.

Nucleation and Growth of ZnO Nanofibers

Thermal anneal of the ZnO nucleation layer was a critical factor affecting the morphology of the nanofibers that were subsequently grown. Figure 6 shows that a uniform film of vertically oriented ZnO nanofibers grew only from the nucleation layer that was annealed for 2 h at 300°C (Figure 6d). At the same temperature, shorter anneal
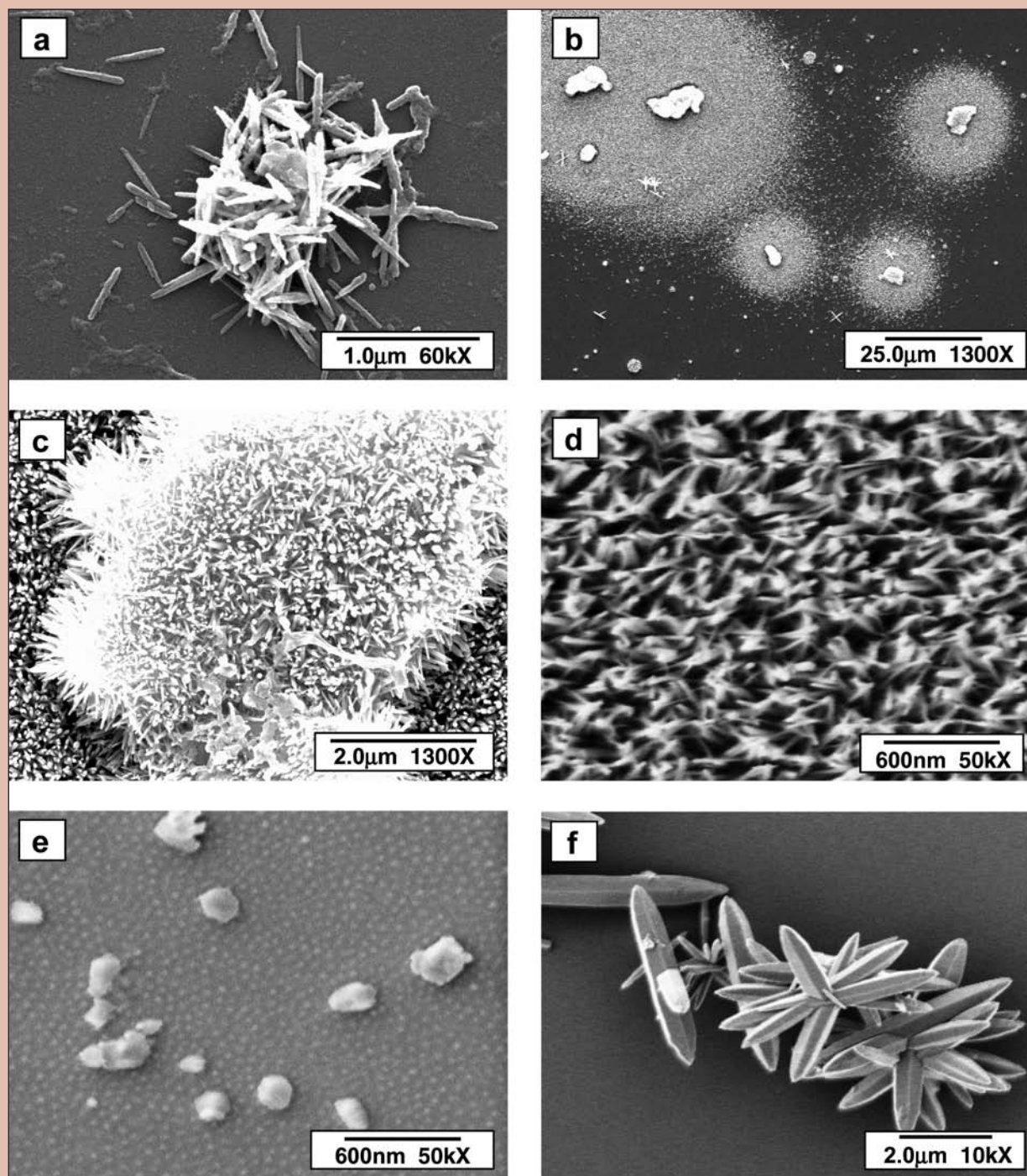
Figure 6. SEM images of ZnO nanofibers grown from nucleation layers that were annealed for: a) no anneal, b) and c) 10 min at 300 °C, d) 2 h at 300 °C, and f) 2h at 500 °C. The nucleation layer from which f) was grown is shown in e).

times ranging from 10 min to 1 hr resulted in the "egg" structure seen in Figures 6b and 6c. No anneal and anneal for 2 h at 500°C yielded isolated clusters of nanofibers, as seen in Figures 6a and 6f, respectively. These results suggest that adhesion of the nucleation sites is a possible factor contributing to successful nanofiber growth. Annealing for a long period of time (2 h) at a moderate temperature (300°C) may have provided the ideal rate and amount of interaction between the nanoparticles and the substrate, allowing for proper adhesion to nucleate the growth of nanofibers.

The vertical alignment of the nanofibers must also be addressed, as poorly aligned nanofibers can lead to incomplete intercalation of the polymer [5]. Figure 6d shows an array of nanofibers whose vertical orientation is fair at best, which presents another reason to further examine the anneal treatment. Previous work has shown

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that improved ZnO nanofiber alignment can be achieved through adjustment of the anneal time and temperature of the nucleation layer [5]. As mentioned in the previous subsection, thermal anneal may have an effect on the crystallinity and lattice orientation of the nucleation sites. Such properties affect the surface free energy of the nucleation layer, which in turn determines the epitaxial growth of ZnO nanofibers [8].

Another route to improving the crystallinity and orientation of the nucleation sites is to use a different zinc precursor in the diblock copolymer micelles. Zinc acetate is one potential candidate, as it is unique in its tendency to form textured ZnO surfaces upon decomposition, with the (0001) planes parallel to the substrate [9]. Lastly, the use of structure-directing agents in the growth solution may also provide control over the morphology of the nanofibers grown.

This report has presented a simple method for controlling the morphology of ZnO nucleation sites for the growth of ZnO nanofibers. The use of diblock copolymers with adjustable molecular weights provides valuable flexibility in the size and spacing of ZnO nanoparticle arrays formed from micelle solutions. These arrays functioned adequately as nucleation sites for the growth of a uniform film of ZnO nanofibers. Further investigations into the effect of thermal anneal and chemical precursors on the nucleation sites and resulting nanofiber morphology may result in the development of well-aligned ZnO nanofibers of optimal diameter and spacing for use in composite PV devices.

ACKNOWLEDGEMENTS

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