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Nanostructured Transparent Conductive Oxides for Photovoltaic Applications

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ABSTRACT

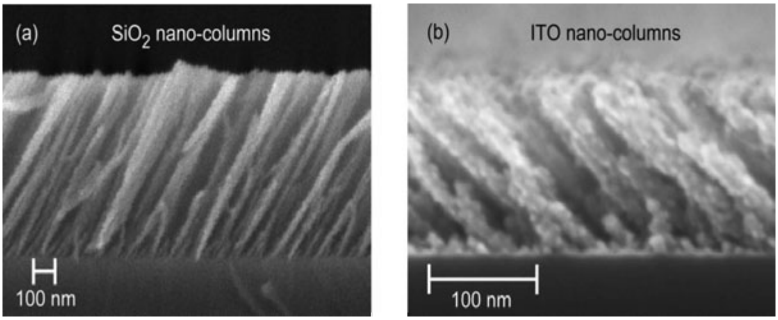
Oblique-angle deposition is used to fabricate indium tin oxide (ITO) optical coatings with a porous, columnar nanostructure. Nanostructured ITO layers with a reduced refractive index are then incorporated into antireflection coating (ARC) structures with a step-graded refractive index design, enabling increased transmittance into an underlying semiconductor over a wide range of wavelengths of interest for photovoltaic applications. Low-refractive index nanostructured ITO coatings can also be combined with metal films to form an omnidirectional reflector (ODR) structure capable of achieving high internal reflectivity over a broad spectrum of wavelengths and a wide range of angles. Such conductive high-performance ODR structures on the back surface of a thin-film solar cell can potentially increase both the current and voltage output by scattering unabsorbed and emitted photons back into the active region of the device.

INTRODUCTION

Transparent conductive oxides such as ITO are commonly used for a wide variety of applications, including liquid crystal displays (LCDs), light emitting diodes (LEDs), and thin-film solar cells. Conventional ITO is a dense material with fixed refractive index characteristics that limit its performance as an optical coating. However, lower index ITO films have recently been demonstrated by employing an oblique angle deposition technique to form porous films with a columnar nanostructure [1-4]. In this work, we review the formation of nanostructured ITO films, and demonstrate the use of low index ITO layers in both ARC and ODR structures that can enhance photovoltaic (PV) device performance.

OBLIQUE ANGLE DEPOSITION OF NANOSTRUCTURED ITO

Oblique angle deposition is a technique that uses a physical-vapor deposition process, such as electron-beam evaporation, to deposit a material layer with a columnar nanostructure. In oblique angle deposition, the substrate is mounted inside the evaporation chamber at a non-normal angle relative to the vapor flux. Initially, islands of evaporated material form on the substrate in random locations. Because the flux of evaporated material in a high-vacuum chamber flows from the source in only a straight line, and because the substrate is mounted at a non-normal angle to the direction of the flux, a shadow region forms behind each self-assembled island that newly arriving flux cannot reach [4]. Thus, the substrate is not uniformly coated, but instead columns begin to form on top of the islands. This nano-columnar layer can be described



(a) **(b)**

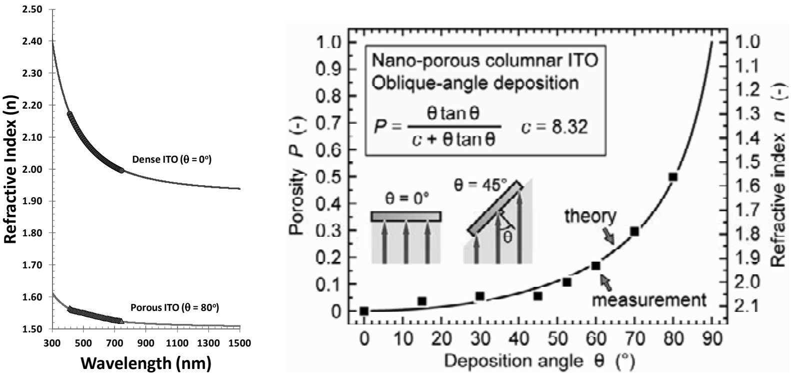
Figure 1: Cross-sectional scanning electron micrographs of nanostructured optical thin-films deposited by oblique angle deposition using **(a)** silicon dioxide and **(b)** indium tin oxide materials.

as having a certain volume porosity, defined as the volume of air within the layer divided by the total volume of the layer. At a larger deposition angle (farther from normal), the nano-columns will be spaced farther apart, and thus the porosity will be greater. In addition, the refractive index of the layer will decrease as the porosity increases, and can be modeled by a linear-volume approximation.

Oblique angle deposition is a self-organized process that can be applied to many different materials [2]. Figure 1, for example, depicts cross-sectional scanning electron micrographs of two nanostructured thin films: one employing silicon dioxide material (SiO_2) and the other indium tin oxide. Both films were deposited at highly oblique angles (~ 80^o), resulting in the formation of well-defined nanorod structures.

Because the gaps between the nanorods can be much smaller than the wavelength of visible and infrared light, the nanostructured layers typically act as a single homogenous film with a refractive index intermediate in value between the ambient air and the nanorod material, decreasing in refractive index with increasing porosity. Figure 2 (a) compares the measured refractive index dispersion curve from a conventional, dense ITO film to the refractive index characteristics of a layer of nanostructured ITO deposited at a highly oblique angle. Both the conventional dense ITO film and the low-index nanostructured ITO film were deposited on silicon substrates and measured by ellipsometry. A Cauchy model was then employed to extrapolate the refractive index dispersion curves over a wider range of wavelengths of interest for photovoltaic applications.

Nanostructured ITO coatings can be fabricated over a range of deposition angles, enabling the porosity and the refractive index to become a tunable parameter [4]. The experimentally measured relationship between the ITO refractive index and the deposition angle is shown in Figure 2 (b). The calculated porosity is included in the same graph as a second ordinate. The experimental results summarized in Figure 2 (b) highlight that as the deposition angle increases, the refractive index decreases and the porosity increases. Poxson *et al.* have developed a theoretical model for the relationship between the porosity and the deposition angle



(a) **(b)**

Figure 2: **(a)** Experimentally derived variation in refractive index as a function of wavelength for dense and porous ITO; and **(b)** Porosity calculated from the measured refractive index (at λ = 462 nm) as compared with a theoretical curve from Poxson *et al.* [2] using model parameter c = 8.32, both plotted as a function of deposition angle [4].

for films fabricated by the oblique-angle deposition method, independent of the material type [2]. This theoretical model closely fits the experimental data from nanostructured ITO layers, and both the theoretical curve and experimental data suggest that oblique angle deposition can be used to engineer the optical properties of ARC and ODR structures employing ITO.

CONDUCTIVE ANTIREFLECTION STRUCTURES

Theoretically, Fresnel reflection losses at the top surface of a thin-film solar cell can be minimized by employing a graded index ARC structure. However, the unavailability of materials with the desired refractive indices, particularly materials with very low refractive indices, has traditionally prevented the implementation of graded and step-graded refractive index designs. For the first time, oblique angle deposition of nanostructured ITO enables the formation of conductive, step-graded ARC structures.

Antireflection coatings with specular surfaces have been fabricated using multiple layers of ITO materials with different refractive indices to reduce reflectance and improve transmittance into photovoltaic devices. Figure 3 compares the measured transmittance of an uncoated SiC substrate to a SiC substrate coated on one side with a two-layered ITO coating. A semi-insulating SiC substrate was employed as an optical window in this experiment to characterize the antireflective properties of nanostructured ITO because SiC is a wide energy gap semiconductor (E_g ~ 3.23 eV for 4H-SiC) that combines a relatively high refractive index (n ~ 2.6) with low absorption over a wide spectral range of interest for photovoltaic applications. Beyond the band edge cutoff (λ ~ 385 nm), transmittance through the semi-insulating 4H-SiC substrate is almost entirely limited by Fresnel reflection losses, which can exceed 20% at each (top and bottom) SiC-air interface.

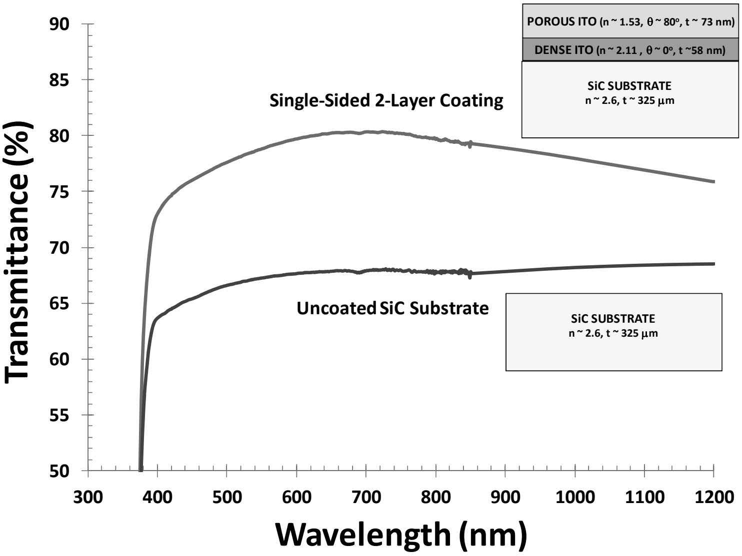


Figure 3: Measured transmittance through both an uncoated and an ITO-coated SiC substrate as a function of wavelength at normal incidence. Structure schematics are shown inset.

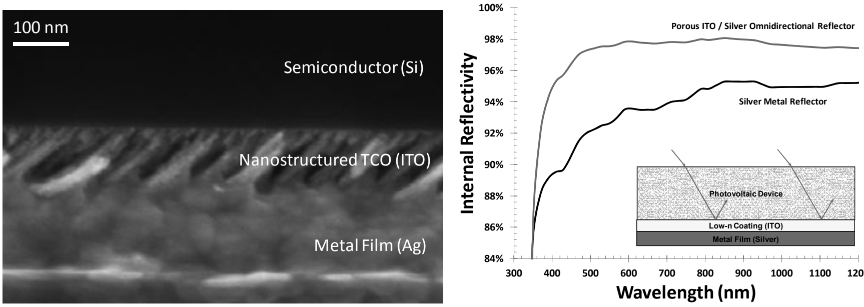
The ITO-coated SiC sample was prepared in an electron-beam evaporator using two different deposition angles ($\theta \sim 0^o$ and 80^o). In order to quantify the thickness and refractive index of each individual layer, a sacrificial silicon substrate was placed alongside the SiC samples during each deposition step. The thickness (t) and refractive index (n) of the single-layer films on silicon were measured with an ellipsometry-based characterization system and the extracted parameters at 462 nm are shown inset in the top right hand corner of Figure 3. The transmittance of the coated and uncoated SiC substrates was then measured as a function of wavelength at normal incidence using a JASCO V-570 spectrophotometer. As seen in Figure 3, the transmittance through a SiC substrate is significantly improved over a broad spectrum (~ 400 nm to 1200 nm) by the application of a step-graded antireflection coating. At a wavelength of 700 nm, the transmittance through the SiC substrate has been increased from less than 68% to over 80%. At a wavelength of 1000 nm, the transmittance through the SiC substrate has been increased from 68.2% to nearly 78%. The measured transmittance spectrum of the ITO-coated structure has been well fit using generalized Airy formulas [5], suggesting that absorption in the step-graded ITO coating is minimal over the measured wavelength range.

CONDUCTIVE OMNIDIRECTIONAL REFLECTORS

Internal reflectors on the underside of a semiconductor structure can improve the performance of a variety of photovoltaic and optoelectronic devices, including LEDs, photodiode detectors, and thin-film solar cells. By incorporating a high-performance back reflector, unabsorbed photons can be recycled and scattered back into the active region of a PV device. Since unabsorbed and emitted photons can strike the rear surface at a wide range of different angles, these back reflector structures should be omnidirectional in nature. Simple metal films can function as omnidirectional reflector structures, but are limited to 90-95% reflectivity in the best cases, and many common metals have much lower internal reflectivity performance.

A two-layer structure consisting of a metal film and a low refractive index dielectric on a semiconductor provide a means of increasing the internal reflectivity over a broad spectrum of wavelengths and a wide range of angles. For example, Xi *et al.* have reviewed the theoretical performance of such a bi-layer reflector structure and compared theoretical and measured results for the specific case of a low-n SiO_2 / silver (Ag) ODR structure on GaP [6]. In a second example, Kim *et al.* have demonstrated a conductive ODR structure consisting of a low-n ITO / Ag bi-layer on a GaN-based LED [1]. In this work, we have fabricated a conductive ODR structure on a higher refractive index silicon substrate.

Figure 4 (a) depicts a cross-sectional scanning electron micrograph of an omnidirectional reflector structure comprised of a layer of nanostructured ITO and a metal film on the back side of a silicon semiconductor substrate. The sample was fabricated by first depositing approximately 100 nm of nanostructured ITO via e-beam evaporation at an oblique angle of ~80°. A 500 nm thick layer of Ag metal film was then deposited over the nanostructured ITO to form an ODR structure. The projected normal incidence performance of such a porous ITO / silver ODR structure as an internal reflector is summarized in Figure 4 (b). The internal reflectivity of the ODR structure as a function of wavelength is calculated as in Reference [6], using the measured refractive index properties of porous ITO (e.g. Figure 2) and literature-based estimates of the optical properties of Si and Ag. Compared with a silver-only metal back reflector, the addition of low-n ITO increases the internal reflectivity over a broadband of wavelengths of interest for photovoltaic devices. Moreover, a porous ITO / silver ODR structure



(a) **(b)**

Figure 4: **(a)** Cross-sectional scanning electron micrograph of an omnidirectional reflector (ODR) structure consisting of a layer of nanostructured ITO and a metal film on the back side of a silicon substrate; and **(b)** Comparison of the calculated internal reflectivity of a porous ITO / silver ODR structure on silicon as a function of wavelength to a silver metal only reflector. Application of an ODR structure to the back side of a photovoltaic device is illustrated with the inset cross-sectional schematic.

is projected to have a peak internal reflectivity in excess of 98%. High performance back reflectors can enhance the optical path length inside any thin-film solar cell, and can lower the dark current of photovoltaic devices operating in the radiative limit [7-8].

CONCLUSIONS

Nanostructured ITO coatings have been fabricated over a range of deposition angles, enabling the porosity and the refractive index to be tuned. These nanostructured ITO layers have then been incorporated into advanced optical structures relevant for photovoltaic applications. The current output from thin-film solar cells, for example, can be increased by including nanostructured ITO layers in ARC structures on the front surface to minimize reflection losses. Nanostructured ITO layers with a reduced refractive index can also be incorporated into an ODR structure capable of achieving high internal reflectivity over a broad spectrum of wavelengths and a wide range of angles. Such conductive, high-performance ODR structures on the back surface of a thin-film solar cell can potentially increase both the current and voltage output by scattering unabsorbed and emitted photons back into the active region of the device.

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