CHARACTERIZATION OF EXPERIMENTAL TEXTURED ZnO:Al FILMS FOR THIN FILM SOLAR CELL APPLICATIONS AND COMPARISON WITH COMMERCIAL AND PLASMONIC ALTERNATIVES

David N. R. Payne[1], Stuart A. Boden[1], Owain D. Clark[1], Alan E. Delahoy[2] and Darren M. Bagnall[1]
[1]Nano Research Group, Electronics and Computer Science, University of Southampton, SO17 1BJ, UK
[2]EPV Solar, Inc., 8 Marlen Dr., Robbinsville, NJ 08691, USA

ABSTRACT

We present the comprehensive characterization of several experimental ZnO:Al films for thin film solar cell applications. The morphological and optical properties of these films are determined using traditional and new, experimental measurement techniques and results are compared to those of the commercial Asahi U-type TCO as well as samples of planar TCOs coated in silver nanoparticles. Results show that the textured ZnO:Al films provide far superior scattering to the commercial alternatives studied. Nanoparticle coated planar TCOs also show scattering enhancement with results suggesting that nanoparticle layers could be tuned to predominantly scatter light within a chosen wavelength range.

INTRODUCTION

Thin film amorphous silicon (a-Si) solar cells are one of the most important photovoltaic technologies; they are cheap and lightweight, they can be deposited at low temperature on flexible substrates and silicon is abundant within the Earth's crust. However, short diffusion lengths necessitate thin active regions and this, combined with low absorption ensures an absolute requirement for effective light-trapping, otherwise a significant amount of light reflected from the back of the cell escapes through the front of the device.

One proven method for improving total absorption in a thin a-Si solar cell is by texturing the top transparent conducting oxide (TCO). This works by scattering light into the plane of the semiconductor and increasing the effective optical path length for light within the silicon layer. To enable optimal scattering within low cost cells a suitable TCO must be used which exhibits excellent electrical and optical properties and can be fabricated and textured economically. Most successful commercial TCOs are based on tin oxides, with Asahi U type being one of the most successful as it is highly optimized for a-Si solar cells [1]. However, in recent years it has become apparent that ZnO:Al films are capable of providing improved transparency with superior haze characteristics in comparison to tin oxides [2].

Although heavily textured TCOs can demonstrate very high scattering, growing thin film solar cells on an extremely rough superstrate can be exceptionally troublesome and a compromise between scattering and device quality must be sought. A promising alternative to complete reliance on texturing is the use of metal nanoparticles. These nanoparticles are relatively smooth and are therefore likely to cause fewer fabrication issues whilst their plasmonic properties could significantly enhance scattering [3].

In this work, we present the extensive characterization of a series of experimental ZnO:Al films, each with uniquely textured surfaces created by varying fabrication parameters. These films are an extension of previous efforts in this area [2, 4]. The morphological and optical properties of these films are compared to the popular commercial TCO, Asahi U-type, as well as experimental samples of planar TCOs coated in silver nanoparticles.

EXPERIMENTAL TECHNIQUES

Sample Fabrication

Textured ZnO:Al films were prepared on soda-lime glass substrates by reactive hollow cathode sputtering using metallic Zn targets [4]. The deposition pressure was 260 mTorr and the substrate temperature was approximately 230°C. Both static and dynamic depositions were performed and films of different thickness were prepared in order to vary the feature size.

Metal nanoparticle coated planar TCOs were fabricated using the metal island film approach. Each sample consists of a thin (~40 nm) layer of planar ITO on glass, the ITO layer is then coated with nanoparticles by using electron beam evaporation to deposit Ag films of specific thicknesses and annealing for 2 hours at 200°C. Several different film thicknesses were used in order to vary the shape and size of the resulting metal nanoparticles.

Characterization

We have employed various methods to characterize the physical and optical properties of all samples as well as the electrical properties of each of the TCO samples. Surface topography was determined from a combination of scanning electron microscopy (SEM) and atomic force microscopy (AFM). AFM analysis was used to accurately determine the surface profile and extract roughness parameters. SEM was used to image the sample surface at various magnifications. A Focused Ion Beam (FIB) system was also employed to prepare cross-sections through the samples, allowing measurement of layer thicknesses. Initial electrical characterization has been carried out via standard four point probe measurements used to determine sheet resistance. The four point probe system used was a Jandel RM3-AR capable of measuring sheet resistance to an accuracy of ~0.3%.

The basic optical transmission properties of all samples have been determined using standard haze measurements. These measurements have been carried out using a Fianium white light laser source along with a integrating sphere (IS) and BWTEK spectrometer with a wavelength range of 450 to 900 nm. The IS was set up in double beam mode in order to obtain high accuracy results [5]. Haze measurements provide a relatively rapid and simple means of quantifying the overall scattering caused by a surface, however, in the case of photovoltaic devices, the angle of scatter is crucial to device performance and therefore more sophisticated measurements are also required in addition to haze.

To determine the angular distribution of scattered light, angle resolved scattering measurements are typically used. We have enhanced this measurement technique to include wavelength dependent detail, resulting in wavelength and angle resolved scattering measurements (WARS). These measurements are carried out using a Fianium white light laser source together with a custom built motorized goniometer system and BWTEK spectrometer (wavelength range of 450 nm to 900 nm). The goniometer system consists of 7 highly accurate computer controlled motorized stages, allowing for extremely precise sample alignment. Once a sample has been mounted and aligned within the system the white light laser is directed through the sample and detected by a spectrometer through a fiber initially positioned at 0° (detecting specular transmission). The sample and laser are then kept stationary as the fiber is rotated around the angle θ. Spectrometer measurements are taken between the angles of 0° and 80° at 1° intervals. An annotated 3D rendering of the custom built WARS measurement system is shown in Figure 1.

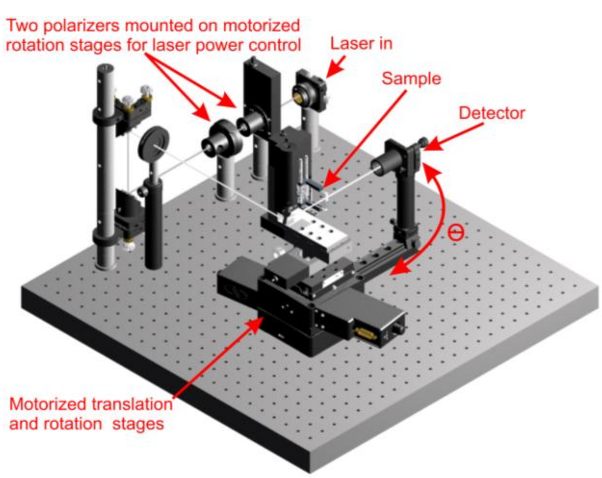

Figure 1. 3D rendering of WARS setup

The WARS measurement process has been fully automated and is controlled by a LabVIEW™ software interface which has been developed in house. The measurement data is then automatically processed by a custom built Matlab® program which normalizes all measurements of scattered light with respect to the specular transmission and then outputs various 2D and 3D graphical representations of the results. For an accurate representation of the total scattering at an angle θ, the distribution of the scattered light around the azimuthal angle φ must also be considered. This is important because light scattered at larger angles of θ is distributed over a wider area and therefore the in plane measurement must be scaled accordingly to give approximate results for the solid angle θ revolved around φ, see Figure 2. The Matlab® post processing code carries out this conversion using a sin(θ) based relationship which can be calculated using simple geometry with the assumption that the scattering is isotropic around φ.

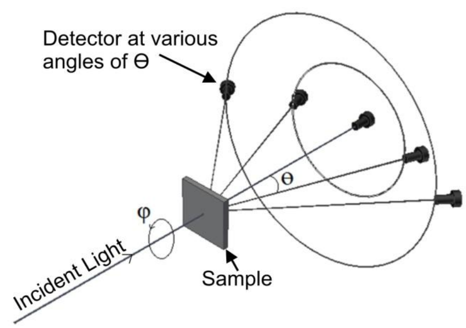

Figure 2. 3D illustration of the distribution of scattered light

RESULTS AND DISCUSSION

Textured TCO Samples

AFM and SEM analysis of the surface topography of the experimental ZnO:Al samples shows vast differences between samples in terms of feature size, shape and overall surface RMS roughness, with the majority of films having a highly faceted surface structure. SEM images of the commercial Asahi U-type TCO and two of the ZnO:Al samples are shown in Figure 3. Some of the experimental ZnO:Al samples appear to have very similar shaped surface features to the Asahi U-type although In general the features of the experimental ZnO:Al films are considerably larger than those of the commercial TCO alternative. Many of the ZnO:Al films consist of very high aspect ratio surface features, therefore it was necessary to use special purpose high aspect ratio AFM probes in order to accurately determine the surface topography and roughness parameters. The specific probe used was a TESP-HAR probe from Veeco. Asahi U-type was found to have an RMS roughness of around 40 nm; this value agrees well with literature [6]. The ZnO:Al samples range in RMS roughness from ~80 nm to around ~130 nm, considerably rougher than Asahi U-type.

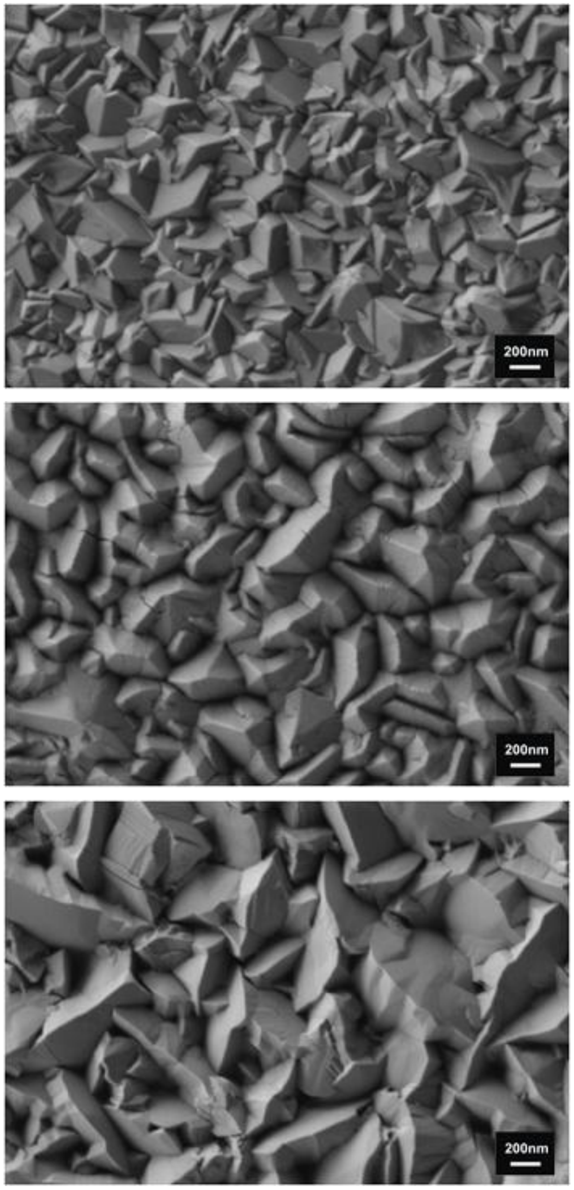

Figure 3. SEM images of Asahi U-type (top), ZnO:Al #751 (middle) and ZnO:Al #757 (bottom)

To determine an approximate value for the film thickness of a TCO, it is conventional to use ellipsometry measurements which are capable of providing highly accurate results. However, in the case of some of the very rough ZnO:Al samples analysed here, fitting ellipsometry data proved to be extremely troublesome. Therefore a focused ion beam (FIB) was used to create cross sections within the samples, enabling approximate values for film thickness to be measured from SEM images. An example SEM image of a cross section in the ZnO film #751 is shown in Figure 4. Asahi U-type was found to be around 970 nm thick, the ZnO:Al films were found to range between 642 nm and 3.1 µm in thickness.

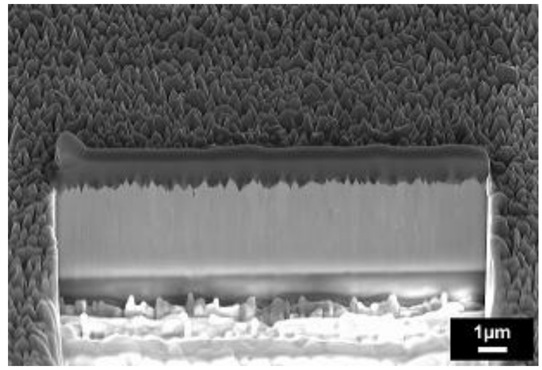

Figure 4 Cross section of Zno:Al #751

Four point probe measurements show that all of the ZnO:Al samples have a low sheet resistance of between 2 and 7 Ω/☐; this is significantly lower than the commercial Asahi U-type at 11 Ω/☐. The measured sheet resistance for several of the TCO samples is shown in Table 1 along with calculated resistivity values. For photovoltaic device applications a sheet resistance of around 10 Ω/☐ or less is considered to be good. Thus the ZnO:Al samples exhibit excellent resistance values.

Sample	Sheet Resistance (Ω/☐)	Resistivity ($\times 10^{-4}$ Ω cm)
Asahi U-type	11.00	10.67
ZnO:Al #386	6.57	4.22
ZnO:Al #751	2.81	6.41
ZnO:Al #757	2.01	6.26

Table 1. Sheet resistance values for all textured TCOs

Haze measurements show that the ZnO:Al films provide extremely high haze, far superior to that of Asahi U-type, see Figure 5. As expected, results show a reduction in haze at longer wavelengths for all samples. Corresponding total transmittance measurements show that on average over the wavelength range, the majority of the ZnO:Al samples transmit around ~75% of the light, slightly less than Asahi U-type transmission at ~80%.

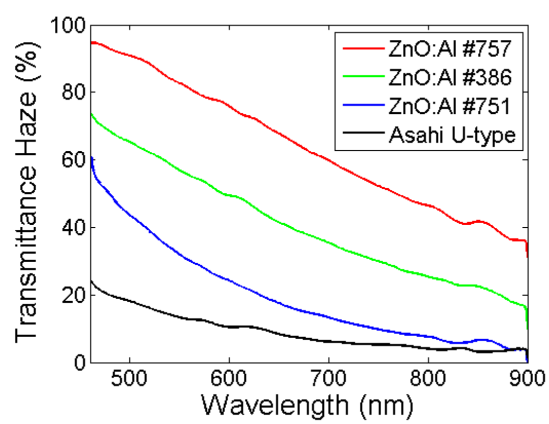

Figure 5. Haze measurements for textured TCOs

Results from WARS measurements show very clear differences between the angles and wavelengths of scattering for the commercial and experimental TCO samples. A sample of the WARS results for Asahi U-type and ZnO:Al films #751 and #757 is shown in Figure 6.

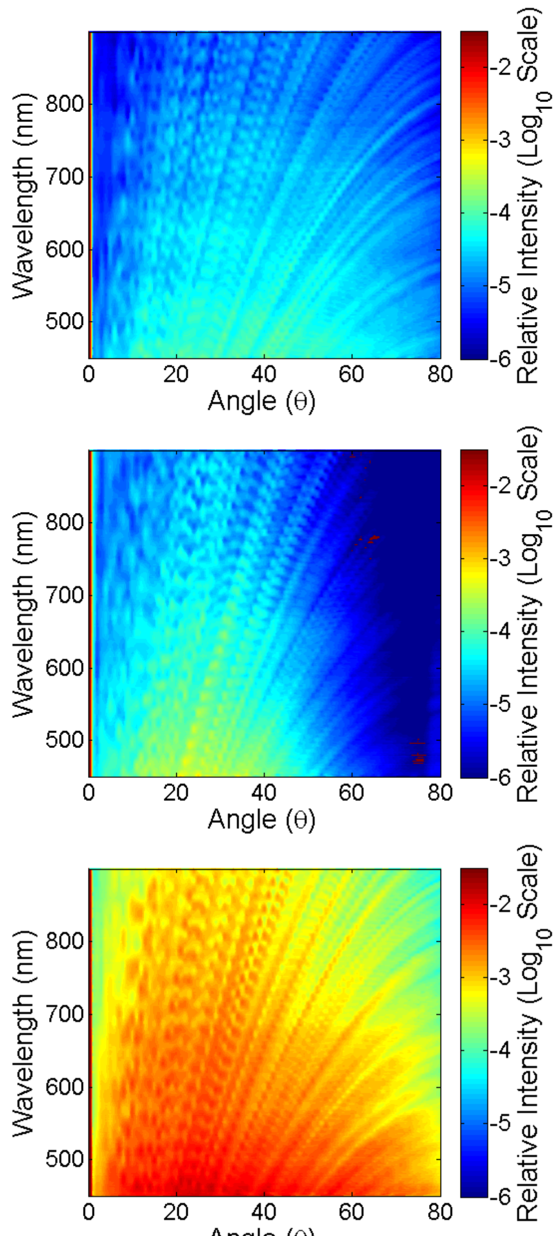

Figure 6. WARS results for Asahi U- type (top), Zno:Al #751 (middle) and ZnO:Al #757 (bottom)

The WARS results clearly show that the ZnO:Al films exhibit superior high angle scattering when compared to the commercial Asahi U-type. As expected, Asahi U-type appears to provide a reasonably high scattering intensity over a broad distribution of angles at shorter wavelengths (600 nm). The rougher ZnO:Al films generally show an even higher intensity of scattering and the angular distribution of scattered light varies significantly per sample, with the best sample being ZnO:Al #757 which shows intense scattering over a broad angular range up to wavelengths of ~800 nm.

Metal Nanoparticle Coated Samples

The surface topography of the metal nanoparticle coated samples has been determined using SEM images. Various initial silver layer thicknesses ranging between 2.5 nm to 20 nm were deposited, resulting in a range of samples with different sizes, shapes and distributions of nanoparticles. Example SEM images of the 7.5 nm and the 20 nm annealed samples are shown in Figure 7.

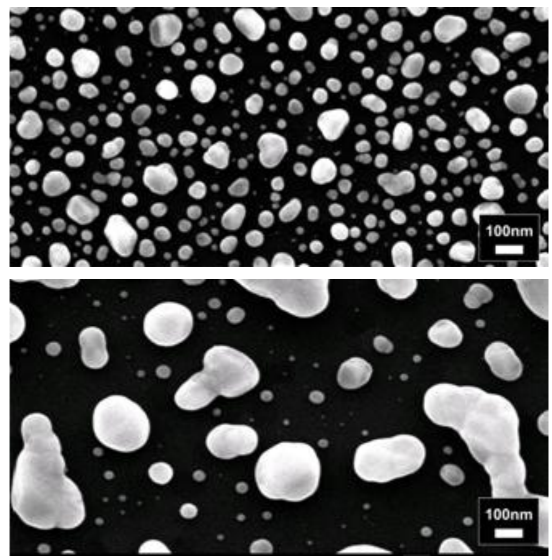

Figure 7. SEM images of 7.5 nm annealed Ag layer (top) and 20 nm annealed Ag layer (bottom).

Haze measurements for the nanoparticle coated samples are shown in Figure 8. These results show a dramatic increase in haze as particle size increases; however, increases in absorption and reflection were also present causing the arrays of larger nanoparticles to have an average overall transmission of only around 45%.

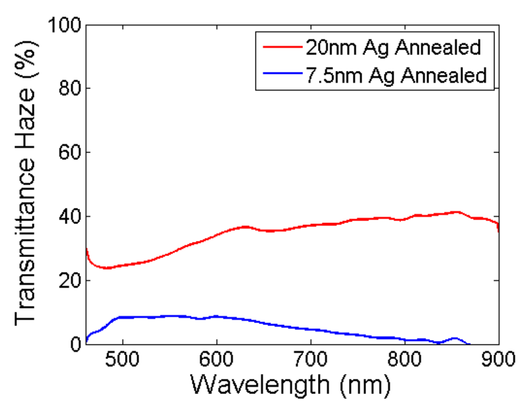

Figure 8. Haze measurements for two MNP coated samples

Finally, WARS results for two of the nanoparticle coated planar TCO samples are shown in Figure 9. As with the textured TCO WARS measurements, these results are for the scattering in transmission. Thus they provide information on scattering enhancement for nanoparticles used at the front interface of a thin film device structure.

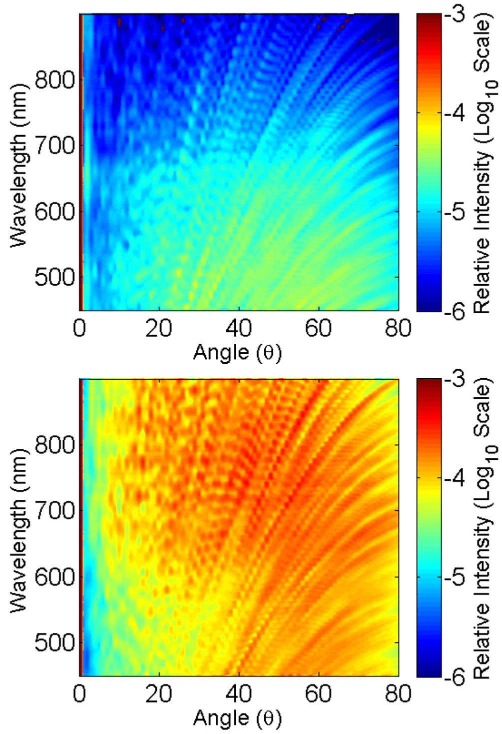

Figure 9. WARS results for 7.5 nm annealed Ag layer (top) and 20 nm annealed Ag layer (bottom)

The WARS results show a significant increase in scattering in comparison to a standard planar TCO. Interestingly, it can be observed that by varying the size and distribution of the Ag nanoparticles, the scattering peak can be tuned to particular wavelengths. This may be partially due to the change in surface texture but it is likely that plasmonic effects are also involved, and this trend agrees well with plasmonic theory [3]. In general, annealing thicker layers of Ag leads to larger nanoparticles which form more ellipsoidal shapes as opposed to smaller spherical nanoparticles. These larger, ellipsoidal nanoparticles have a red-shifted resonant frequency [3], therefore the peak wavelength of scattering also red-shifts.

CONCLUSIONS

Experimental textured ZnO:Al films have been physically, electrically and optically characterized and it is clear from the results that these TCOs are superior to the commercial Asahi U-type in several ways. Experimental ZnO:Al samples exhibit sheet resistances that are typically ~60% lower than Asahi U-type, whilst optically they provide excellent haze. However, whilst the haze of the ZnO:Al films is very good, the overall transmission of the films is generally lower than that of Asahi U-type and this is a crucial property for front contact TCOs in photovoltaic devices. WARS results for the ZnO:Al samples show that some of the samples scatter intensely over an excellent angular distribution and often scattering is still high at wavelengths of above 800 nm. This indicates that some of the ZnO:Al films could be particularly suitable for lower band gap µc-Si or micromorph solar cells. However, in general the best ZnO:Al films were also the roughest and the high aspect ratio of the surface features of these samples is likely to be extremely problematic for silicon deposition.

The metal nanoparticle coated TCO samples do not exhibit scattering intensities as high as the textured ZnO:Al samples but they do generally scatter to higher angles and the peak wavelength of scattering varies with nanoparticle size and distribution. This suggests that nanoparticle layers could be tuned to provide optimal scattering for a particular semiconductor absorber layer. However, the application of nanoparticles also has an effect on the reflection and absorption of light. It is therefore likely that nanoparticle layers such as these will be more beneficial when incorporated into the back reflector of the device, where the increased reflection becomes a useful property.

Future work includes further optimization of the experimental textured ZnO:Al films, followed by their use as superstrates for the growth of a-Si and µc-Si solar cells. Further analysis of the effects of Ag nanoparticles should also be carried out, particularly for the application of long wavelength scattering within µc-Si solar cells.

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