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DENSITY PROFILES IN SPUTTERED MOLYBDENUM THIN FILMS AND THEIR EFFECTS ON SODIUM DIFFUSION IN $Cu(In_xGa_{1-x})Se_2$ PHOTOVOLTAICS

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ABSTRACT

Molybdenum (Mo) thin films were sputtered onto soda lime glass (SLG) substrates. The main variable in the deposition parameters, the argon (Ar) pressure p_{Ar}, was varied in the range of 6 – 20 mTorr. *Ex situ* spectroscopic ellipsometry (SE) was performed to find out that the dielectric functions ε of the Mo films were strongly dependent on p_{Ar}, indicating a consistent and significant decrease in the Mo film density ρ_{Mo} with increasing p_{Ar}. This trend was confirmed by high-angle-annular-dark-field scanning transmission electron microscopy. ε of Mo was then found to be correlated with secondary ion mass spectroscopy profiles of Sodium (Na) in the $Cu(In_xGa_{1-x})Se_2$ (CIGS) layer grown on top of Mo/SLG. Therefore, *in situ* optical diagnostics can be applied for process monitoring and optimization in the deposition of Mo for CIGS solar cells. Such capability is demonstrated with simulated optical transmission and reflectance of variously polarized incident light, using ε deduced from SE.

INTRODUCTION

Thin film photovoltaics (PV) based on the CIGS technology is a promising candidate for low-cost, high-efficiency solar cell applications as it has demonstrated the highest energy conversion efficiency among all thin film PV technologies [1 - 3]. For CIGS cells, the most commonly used substrate is SLG coated with sputter-deposited Mo thin films as the metal contact [1 - 3]. An important process associated with this substrate is the Na diffusion from SLG through the Mo layer into the absorber layer. A proper amount of Na diffusion is known to be important for optimized cell performance [1]. For such diffusion, the Mo layer acts as the barrier, and hence may provide a mechanism to control the diffusion process by varying the Mo properties.

Some physical properties, such as conductivity, intrinsic stress, and morphology, of sputtered Mo films were studied extensively and were found to vary significantly with deposition parameters [4, 5]. However, the variation of Mo film density ρ_{Mo} was only studied briefly, even though it is expected to be closely related to the Na diffusion. Moreover, most of the previous studies were based on *ex situ* characterization methods, such as X-ray diffraction and scanning electron microscopy, that either provide only qualitative information or are incompatible with *in situ* high-throughput measurements. On the other hand, optical probing methods, such as ellipsometry, reflectance, and transmission, have the advantages of being able to be implemented *in situ*, in-line with real-time quantitative responses, and being sensitive to depth profiles, and thus are uniquely useful for studying thin film materials. [6]. If an optical diagnostic can be established that measures Mo film properties and correlates them with Na diffusion, it will greatly facilitate the research as well as manufacturing of CIGS solar cells.

EXPERIMENTAL DETAILS

A series of Mo thin films were sputtered onto SLG substrates with a DC power of 650 Watt and an Ar flow rate of 50 sccm. The total film thicknesses are in the range of 0.40 – 0.55 μm. The 6”x6” substrates were scanned in front of the 2”x10” target in order to cover the whole substrate area. Each Mo film was deposited with two substrate scans with the same scan speed. There was no external heating to the substrate. The key process variable, p_{Ar}, was varied in the range of 6 – 20 mTorr.

After deposition, the Mo/SLG samples were characterized by SE in the photon energy range of 0.75 – 3.6 eV where SLG is transparent. Since SE is very sensitive to surface non-idealities, such as oxide layer or surface roughness, it has been discussed before that improper treatments of the surface layer usually result in large errors in the deduced optical properties of the underlying film [7]. On the other

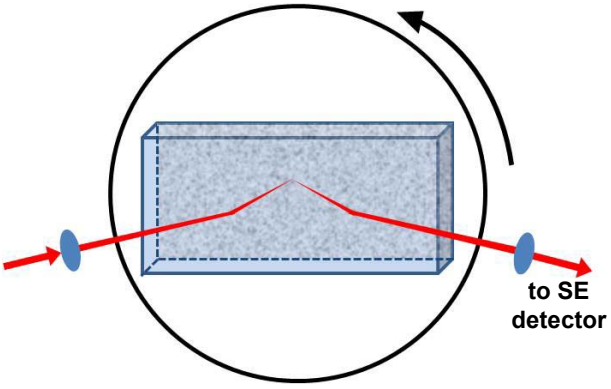

Figure 1 Through-the-glass configuration was used for SE measurements in this study with a rotatable sample holder. The Mo film side is indicated with texture.

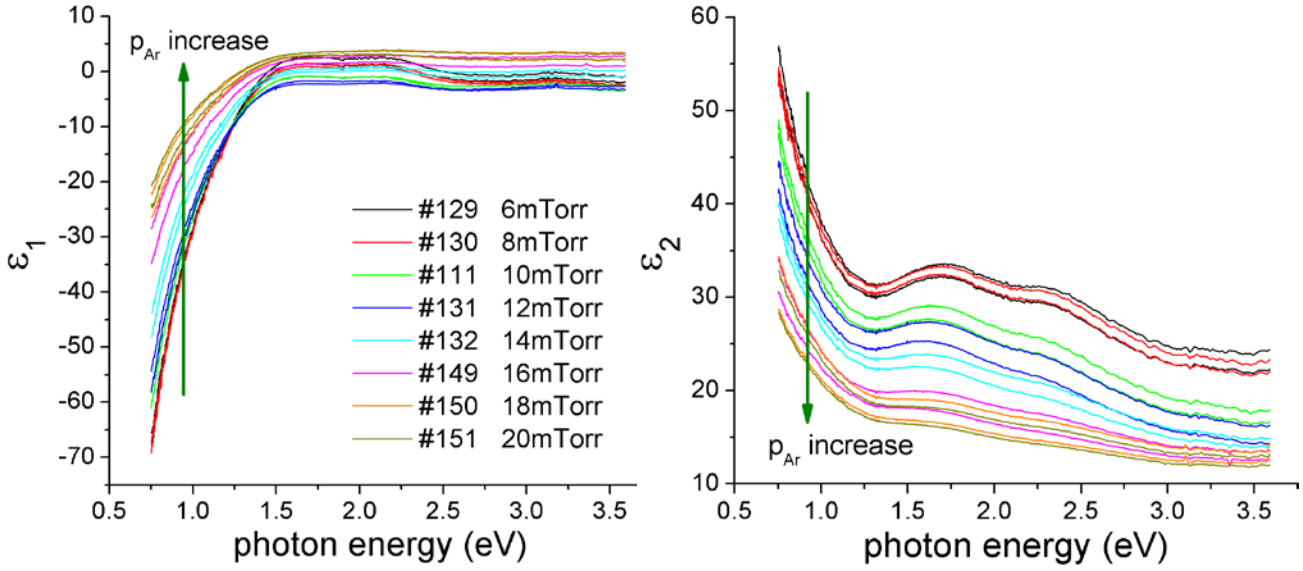

Figure 2 Real (left) and imaginary (right) part of the complex dielectric functions of the near substrate part of the Mo films as functions of p_{Ar}. ε_e and ε_o of a specific film are marked with the same color coding.

hand, the film/glass interface was found to be almost free of these non-idealities. Therefore, through-the-glass geometry was selected for the SE measurements as shown in Fig. 1. The Mo films in this study were found to be optically anisotropic, so SE measurements at multiple orientations were needed in order to obtain both the ordinary and extraordinary dielectric functions. This was accomplished by fixing the sample on a rotatable holder. At each orientation, anisotropic SE data were taken at angles of incidence (AOI) from 45 to 70°. Focusing optics were used to eliminate the beam reflected at the SLG/air interface from the probing beam reflected at the SLG/Mo interface, as these two beams are optically incoherent.

RESULTS AND DISCUSSIONS

In SE analyses, it was found that uni-axial anisotropy was sufficient to model the Mo films in this study, that exhibit clear in-plane optical anisotropy. Therefore, two sets of complex dielectric functions, the ordinary one ε_o and the extraordinary one ε_e, were needed to describe each Mo film. The anisotropic SE data taken at multiple orientations and AOIs for each sample were analyzed together in order to extract its ε_o and ε_e simultaneously with good confidence limits or error bars. The resulting optical properties are plotted in Fig. 2.

It can be seen that both ε_o and ε_e vary significantly with p_{Ar}. In general, high p_{Ar} Mo films are optically less anisotropic, indicated by smaller difference between their ε_o and ε_e compared to low p_{Ar} films. The most important difference between various p_{Ar} Mo films, however, exists in the amplitudes of their dielectric functions. This is more clearly observed in ε_2 in the right panel of Fig. 2.

In the classical theory of materials optical properties, ε can be expressed as a sum of a series of Lorentzian oscillators:

$$\varepsilon(E) = \varepsilon_1^{\infty} + \sum_n \frac{A_n}{(E_n^2 - E^2) - i\Gamma_n E} \qquad (1)$$

where E is photon energy; $\varepsilon_1\infty$ is the contribution to ε_1 from the oscillators located at photon energies much higher than the studied spectral range; A_n, E_n, and Γ_n are the amplitude, resonance energy, and the broadening of the n^{th} oscillator [6]. A similar expression exists as deduced from modern quantum theory of materials optical properties. It should be noted that E_n and Γ_n have different physical meanings in these two theories, but in either case, A_n is always proportional to the number of atoms per unit volume, or the density of the material [6].

As is for typical metals, the dominant feature in Fig. 2 is the free electron absorption (< 1.2 eV), corresponding to a Lorentzian oscillator in Eq. (1) with E_n=0, or the Drude oscillator [6]. In this case, neglecting $\varepsilon_1\infty$ as it is usually much smaller than the Drude oscillator, the negative amplitude in ε_1 or the positive amplitude in ε_2 is proportional to A_n as well as the Mo film density ρ_{Mo} [6]. Above 1.2 eV, two critical point (CP) structures [6], with resonance energies located at ~1.7 and 2.4 eV respectively, are observed. In these two cases, A_n cannot be estimated from ε_1 because of the non-negligible contribution of $\varepsilon_1\infty$, but can be estimated from the amplitude of ε_2. It is observed that in all the main structures in ε described above, the amplitudes in both ε_o

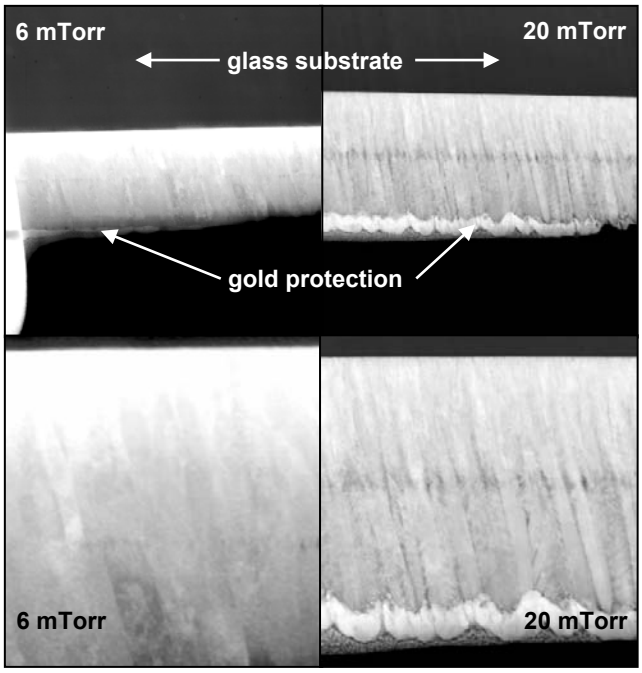

Figure 3 Cross-sectional HAADF STEM images of the Mo film deposited at an Ar pressure of 6 mTorr (left two panels) and 20 mTorr (right two panels).

and ε_e decrease significantly, indicating a consistent and significant decrease in ρ_{Mo}, with increasing p_{Ar}. It should also be noted that all the Mo films in Fig. 2 are highly absorbing, with the calculated penetration depth in this photon energy range no more than 27 nm. Therefore, the optical properties and the associated indication in ρ_{Mo} only apply to the near substrate part (~ 50 nm) of the Mo films.

To confirm the SE indication in ρ_{Mo} above, the microstructure and morphology of selected Mo films were examined by high-angle-annular-dark-field scanning transmission electron microscopy (HAADF STEM). An FEI Tecnai F20-UT microscope operating at 200kV was used for imaging. Cross sectional TEM samples were prepared by focused ion beam technique (FIB) using a FEI Nova200 dual beam FIB system. The intensity of a HAADF STEM image is proportional to the atomic number and the thickness of the film [8]. Because the only element probed here is Mo, there is only one atomic number for all the samples; and the TEM sample prepared by FIB have rather uniform thickness, the intensity of HAADF STEM images can then be related to the local density of Mo in the films – lower intensity indicates lower density. It can be seen from the HAADF STEM images shown in Fig. 3 that the near substrate ρ_{Mo} of the p_{Ar}=6 mTorr Mo film is significantly higher than that of the p_{Ar}=20 mTorr Mo film, consistent with the SE results described above. It is also noticeable that within a specific Mo film, local ρ_{Mo} decreases with distance from the SLG substrate.

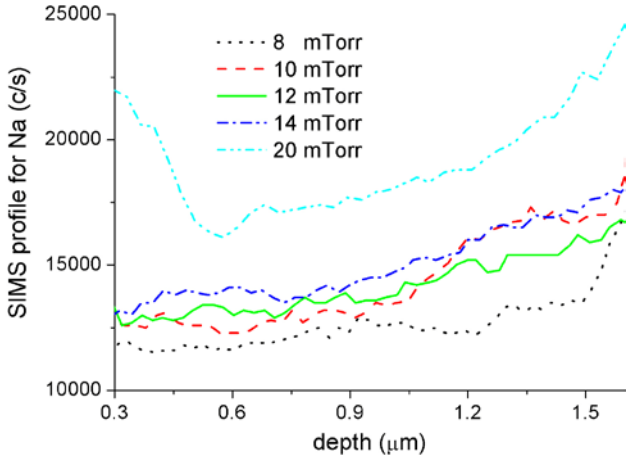

Figure 4 SIMS depth profile for Na in the CIGS layer grown on Mo/SLG with indicated p_{Ar} for Mo deposition.

In the fabrication of CIGS solar cells, the Mo layer acts as a barrier to Na diffusion from SLG into the absorber layer grown on top of Mo/SLG. The diffusion coefficient should be inversely dependent on ρ_{Mo}. Even though, as stated earlier, the SE indication in ρ_{Mo} only applies to the near substrate part of the Mo films, it may be used to estimate the average density of the entire Mo film. Additionally, as seen in Fig. 3, the near substrate part is the densest in a specific Mo film, and thus should be essentially the bottle neck for the Na diffusion. Therefore, the near substrate ρ_{Mo}, which the optical property is sensitive to, as shown in Fig. 2, is expected to have a strong effect in determining the Na diffusion.

To verify this hypothesis, standard CIGS layers were grown by the three-stage method with identical deposition parameters [9] on selected Mo/SLG samples from the set in Fig. 2. The resulting CIGS films were depth profiled using secondary ion mass spectroscopy (SIMS) to determine the Na distribution. The SIMS results plotted in Fig. 4 not only show an expected trend of increasing Na concentration with increasing p_{Ar}, and hence decreasing ρ_{Mo}, but also vary on a relative quantitative scale similar to that in Fig. 2. This demonstrates a close correlation between the optical properties in Fig. 2 and the Na distribution in Fig. 4.

A proper amount of Na diffusion is known to be important for the fabrication of high efficiency CIGS solar cells [1]. The observations above present an opportunity of setting up an optical diagnostic for the optimization and control of Na diffusion. To demonstrate such capabilities, the normal incidence (AOI=0°) transmission from the Mo side, the AOI=45° reflectance from the Mo side for p-polarized light, and the AOI=45° reflectance from the back side of the SLG substrate for s-polarized light are simulated in Fig. 5, assuming a sample structure of 20 nm Mo layer deposited on SLG and using the optical properties in Fig. 2. It can be seen that in all the cases of Fig. 5, the difference between

the two samples is significant and hence detectable by the optical diagnostics based on intensity measurements. For the optical diagnostics based on polarization measurements, such as SE with two measured quantities, or for thicker Mo films on SLG, the sensitivity is expected to be higher.

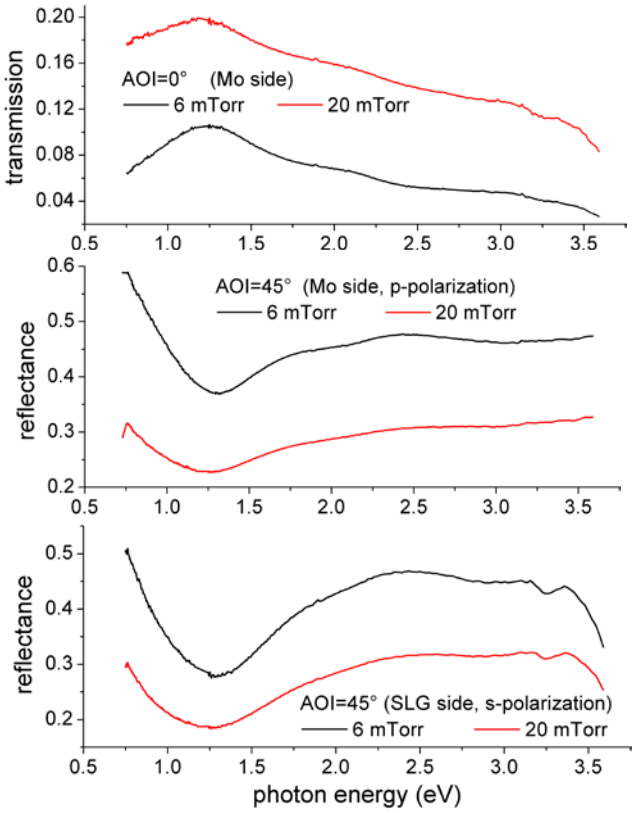

Figure 5 Simulated normal incidence transmission and AOI=45° reflectance from both the Mo film side and the back side of SLG for a 20 nm Mo layer deposited on SLG substrate, using the optical properties in Fig. 2.

SUMMARY

A series of Mo thin films were deposited on soda lime glass by sputtering at different Ar pressures. The Mo films were characterized by through-the-glass spectroscopic ellipsometry. The optical properties of the near substrate part of the Mo film were found to vary significantly, indicating a consistent and significant decrease in the near-substrate Mo density with increasing Ar pressure. This trend was confirmed by cross-sectional HAADF STEM images. It was also found that the near substrate part is the densest in a specific Mo film. Therefore, this part is expected to play an important role in determining Na diffusion. The effect of Mo density profiles on Na diffusion was confirmed by SIMS profiles of Na in the CIGS layers grown on top of different Mo/SLG samples. Finally, the capability of an *in situ* optical diagnostic for the control of Na diffusion for CIGS solar cells was demonstrated through simulations.

ACKNOWLEDGEMENT

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REFERENCES

[1] Luque, A., and Hegedus, S. (Eds.), *Handbook of Photovoltaic Science and Engineering*, Chichester, UK, John Wiley & Sons Ltd., 2003.

[2] Ingrid Repins, Miguel A. Contreras, Brian Egaas, Clay DeHart, John Scharf, Craig L. Perkins, Bobby To, and Rommel Noufi, "19.9%-efficient ZnO/CdS/CuInGaSe$_2$ Solar Cell with 81.2% Fill Factor", *Prog. Photovolt: Res. Appl.* **16** 235 (2008).

[3] Philip Jackson, Dimitrios Hariskos, Erwin Lotter, Stefan Paetel, Roland Wuerz, Richard Menner, Wiltraud Wischmann, and Michael Powalla, "New world record efficiency for Cu(In,Ga)Se$_2$ thin-film solar cells beyond 20%", *Prog. Photovolt: Res. Appl.* **19** (4) (2011).

[4] John H. Scofield, A. Duda, D. Albin, B. L. Ballardb, and P. K. Predeckib, "Sputtered molybdenum bilayer back contact for copper indium diselenide-based polycrystalline thin-film solar cells", *Thin Solid Films* **260** 26 (1995).

[5] H. A. Al-Thani, D. L. Williamson, F. S. Hasoon, M. Young, S. Asher, J. L. Alleman, and M. M. Al-Jassim, "The Effect of Mo Back Contact on Na Out-Diffusion and Device Performance of Mo/Cu(In,Ga)Se$_2$/CdS/ZnO Solar Cells", *conference publication of the 29th IEEE Photovoltaics Specialists Conference*, pp. 720-723, New Orleans, LA USA, May 2002.

[6] Tompkins, H. G., and Irene, E. A. (Eds.), *Handbook of Ellipsometry*. Norwich, NY, William Andrew Pub., 2005.

[7] Jian Li, Ingrid Repins, Bobby To, Lorelle Mansfield, Sukgeun Choi, Miguel Contreras, Fred Lewis Terry Jr., and Dean Levi, "Effects of substrate temperature on the optical properties of polycrystalline CuInSe$_2$ thin films", *conference publication of the 35th IEEE Photovoltaics Specialists Conference*, pp. 3450-3455, Honolulu, HI USA, June, 2010.

[8] Pennycook, S. J. and D. E. Jesson, "High-resolution incoherent imaging of crystals", *Phys. Rev. Lett.* **64** 938 (1990).

[9] Contreras, M. A., *et al.*, "Progress toward 20% efficiency in Cu(In,Ga)Se$_2$ polycrystalline thin-film solar cells", *Progress in Photovoltaics: Research and Applications*, **7**(4) p. 311-316 (1999).