Real time spectroscopic ellipsometry of Ag/ZnO and Al/ZnO interfaces for back-reflectors in thin film Si:H photovoltaics


Center for Photovoltaics Innovation and Commercialization, University of Toledo, Toledo OH 43606, USA

1. Introduction

A widely-used back-reflector (BR) for thin film hydrogenated silicon (Si:H) solar cells in the substrate/BR/Si:H(n-i-p) configuration consists of opaque Ag or Al, followed by a ~1500–3000 Å thick layer of ZnO, both sputtered onto a low-cost substrate such as stainless steel or polymer foil [1,2]. Quantum efficiency enhancement in the solar cell over the near-infrared range (1.2 to 1.8 eV; 650 to 1000 nm), where the thin film Si:H absorption is weak, arises due to reflection of near-infrared wavelengths back into the cell for possible absorption during additional passes. Additionally, the metal/ZnO interface is designed to be macroscopically rough, with protrusions on the order of the wavelength (~800 nm), so that the light rays are non-specularly scattered upon back-reflection which increases their optical path lengths. Such enhancement relies on a high reflectance of the metal/ZnO interface in the near-infrared spectral range; however, the incorporation of roughness at this interface can result in greater dissipative losses due to confined plasmons localized at the surfaces of roughness protrusions or due to propagating plasmons that require periodic roughness components for their excitation [3,4].

Using real time spectroscopic ellipsometry (RTSE) in this study, both the Ag/ZnO and Al/ZnO interfaces are characterized in detail as functions of the metal film surface roughness thickness on the microscopic scale, i.e., with protrusions on a scale much smaller than the wavelength. Although the microscopic interface roughness values studied here are smaller than those of optimized devices, trends observed as the roughness increases are of particular interest. This report focuses on the RTSE analysis and its outcome, whereas a previous paper has focused on the application of these RTSE results to improve BR performance in cells [2].

2. Experimental details

The Ag and Al films were deposited by rf magnetron sputtering onto smooth c-Si wafer substrates covered with thermal oxides (d oxide ~400 Å). The target surface area is 20 cm² and the target-to-substrate distance is 7 cm. The deposition process leading to the smoothest Ag yields a microscopic roughness thickness of d s = 4 Å, as deduced by an effective medium theory analysis of RTSE data after a final Ag bulk layer thickness of d b ~1500 Å. The deposition process for the smoothest Al yields a microscopic roughness thickness of d s = 15 Å after a final Al bulk layer thickness of d b ~1000 Å. Both such films were obtained at room temperature using a low Ar sputtering gas pressure of 4 mTorr, an Ar flow of 10 sccm, and a metal target power of 50 W. For Ag deposition, an increase in the substrate temperature to 190 °C yields an increase in the final microscopic surface roughness thickness as deduced by RTSE to d s ~105 Å, whereas for Al deposition, an increase to 85 °C yields an increase in this roughness to d s ~122 Å. The final roughness values from RTSE were compared with the root mean square (rms) values obtained from AFM measurements which probed 5 × 5 μm² areas of the metal films. Finally, ZnO was deposited on both Ag and Al surfaces at room temperature without a vacuum break using the same conditions under which the smoothest Ag and Al were prepared.

RTSE was performed using a rotating-compensator multichannel instrument (J.A. Woollam Co.) that can provide spectra in (ψ, Δ) from 0.75 to 5.0 eV. Rotating-compensator multichannel instrument designs are described in previous publications [5,6]. To improve
precision, pairs of \((\psi, \Delta)\) spectra were collected within a time of ~1 s, as averages over several optical cycle pairs. During the acquisition time for one set of \((\psi, \Delta)\) spectra, a bulk layer thickness of ~1 Å accumulates at the maximum deposition rate used here. Analyses of \((\psi, \Delta)\) spectra involve both numerical inversion and least-squares regression algorithms \cite{7}. As presented in the next section, the extracted information of interest reported here includes the dielectric functions of the metal and ZnO bulk layers, as well as the dielectric functions of the metal/ZnO interface layers, and the thickness evolution of the two layers. The angle of incidence for each deposition was fixed at a value within the range of \(65.0^\circ \pm 0.3^\circ\).

3. Results

The first key RTSE results in the study of the metal/ZnO interfaces entail the characterization of the final microscopic roughness on the metal surfaces as modeled by using the Bruggemann effective medium theory assuming a 0.5/0.5 volume fraction mixture of metal/void. This surface roughness appears as interface roughness when the metal/ZnO interface is formed. In Fig. 1 the roughness thicknesses on both Ag and Al films, as determined by RTSE at the end of the deposition, have been plotted against the root mean square (rms) roughness as measured by AFM. From the figure for Ag films, the near unity slope and small intercept indicate that RTSE is measuring a roughness value very close to the AFM rms value. In contrast for Al, the slope >1 indicates that RTSE returns a value of roughness larger than rms, and the negative intercept indicates that AFM detects a component of roughness that RTSE does not – possibly macroscopic roughness having an in-plane scale within an order of the wavelength \((\lambda \sim 800 \text{ nm})\). Because the relationships in Fig. 1 are closely linear, confidence in RTSE as a probe of microscopic roughness on a relative scale is strongly supported.

For the depositions of ZnO on these metal surfaces, the optical properties of the bulk metals were used, as shown in Fig. 2, and the optical properties of the ZnO bulk and metal/ZnO interface layers were deduced by numerical inversion without assuming a specific analytical form. In a first iteration of the overall analysis, the optical properties of the ZnO bulk layer were obtained from a separate deposition under identical conditions on smooth c-Si, and these were applied in the extraction of the thickness evolution of the metal/ZnO interface and ZnO bulk layers and the optical properties of the former (interface) layer. In a second iteration, fixed interface thickness and optical properties were used after interface stabilization in order to extract the optical properties of the ZnO bulk layer. A variable roughness layer on the ZnO surface was assumed and its thickness determined in all analyses.

Fig. 3(a) provides a comparison of the two sets of ZnO bulk layer optical properties – from the depositions on c-Si and on the smoothest Ag, under the same set of conditions. Fig. 3(b) shows the corresponding comparison of the ZnO optical properties for the two metal substrates, again for the smoothest metal surfaces. The data points were obtained by numerical inversion, and these results were subsequently fit using an analytical model assuming two Lorentzian-broadened critical point transitions between parabolic bands (lines) \cite{8}. The optical properties of ZnO deposited on the metals are sufficiently close to the results for the identical deposition on c-Si such that further iteration beyond the two steps does not affect the final outcome. As an example, the energies of the band gap associated with the lower energy critical point falls in the range of \(3.32 \pm 0.02 \text{ eV}\) for the three depositions.

Fig. 4 shows the time evolution of the ZnO bulk and metal/ZnO interface thicknesses for metal roughness layer thicknesses of 12 Å for Ag and 15 Å for Al. Here the inclusion of the interface layer is shown to improve significantly the quality of the fit to the full RTSE data set for both Ag/ZnO and Al/ZnO structures. In addition, the linearity of the bulk layer thickness with time improves by inclusion of the interface layer. The quality of fit in Fig. 4 is based on the squares of the differences between the real and imaginary parts of \(\rho = \tan \psi \exp (i\Delta)\), and is used as a relative measure versus time \cite{7}.

Fig. 5 shows the real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) parts of the dielectric functions of (a) the 78 Å thick Ag/ZnO interface layer obtained for an Ag film with a final surface roughness layer thickness of 28 Å and (b) the 83 Å thick Al/ZnO interface layer obtained for an Al film with a final surface roughness layer thickness of 33 Å. In both cases, the interface layer optical properties obtained from numerical inversion (circles) are fitted using Kramers–Kronig consistent models (lines). For Ag/ZnO, the interface layer model includes (i) a free electron component modeled using the Drude expression, (ii) a plasmon band modeled as a Lorentz oscillator, and (iii) a bound electron absorption feature due to the interband transitions for both Ag and ZnO, modeled assuming a single transition between parabolic bands near a critical point. In Al/ZnO the plasmon peak is better represented by a more general oscillator with an adjustable phase and exponent that can describe the asymmetric line shape \cite{8}. Also an additional weak oscillator must be incorporated into the Al/ZnO interface dielectric function. This oscillator represents the parallel band transition in Al near \(2U_{200} = 1.5 \text{ eV}\), where \(U_{200}\) is a Fourier coefficient of the crystal potential, and appears more clearly in the optical properties of bulk layer Al in Fig. 2(b).

Fig. 6 depicts the resonance energy of the localized plasmon (top) from the dielectric functions of Fig. 5 as well as the final interface layer thickness, both plotted as a function of the surface roughness thickness on the metal. For the Ag/ZnO interface, the plasmon energy
is 2.9 eV in the limit of a smooth Ag film and decreases to 2.4 eV for a Ag film with a final roughness layer thickness of 100 Å. In contrast, for the Al/ZnO interface, the resonance energy is relatively constant in the range of 3.3–3.4 eV. The lower panel of Fig. 6 shows that the thicknesses $d_i$ of the metal/ZnO interface layers increase at just under twice the rate of the final microscopic roughness thicknesses on

**Fig. 2.** Real (upper) and imaginary (lower) parts of the dielectric functions for bulk layer (a) Ag and (b) Al deposited under the smoothest surface (lines) and roughest surface (points) conditions.

**Fig. 3.** Real (upper) and imaginary (lower) parts of the dielectric function of the ZnO layer deposited on (a) the smoothest Ag (circles) and (b) the smoothest Al, both obtained after a ZnO bulk layer thickness of ~500 Å. These results were obtained by inversion of RTSE spectra (points); a fit using a Kramers–Kronig consistent model is shown (lines). The broken line in (a) is for ZnO on c-Si prepared under identical conditions whereas the broken line in (b) is for the ZnO on smoothest Ag, both after fitting with a Kramers–Kronig consistent model.
**Fig. 4.** ZnO thickness evolution on (a) Ag and (b) Al surfaces as modeled with and without an interface layer. In both cases the fit is improved by introducing the interface layer (vertical arrows).

**Fig. 5.** Real (upper) and imaginary (lower) parts of the dielectric function of (a) the Ag/ZnO interface layer with a thickness of 78 Å (circles) and (b) the Al/ZnO interface layer with a thickness of 83 Å. These results were obtained by inversion of RTSE spectra (points); fits using a Kramers-Kronig consistent model are shown (lines).
the corresponding bare metal film. This indicates that the influence of the plasmonic characteristics of the interface extends beyond the roughness region into the metal and ZnO layers. This is likely to be due to image dipole fields within the metal and screening by the ZnO. An $\approx 18 \text{ Å}$ intercept in Fig. 6 represents the interface thickness observed even in the absence of metal substrate roughness, attributed to a damaged layer that occurs in sputtering. In the analysis, the damaged layer is treated as an indistinguishable component of a single interface layer, whose optical properties are generated using the oscillators shown in Fig. 5.

4. Discussion

The features in the range of 2.4–2.9 eV for the Ag/ZnO interface in Fig. 5 can be identified definitively as localized plasmon excitations due to the lack of interband optical transitions in Ag or ZnO in this range. The observed Lorentz oscillator form can be reproduced by substituting the Drude equation into the Maxwell Garnett effective medium theory, yielding the following expression for the resonance energy: $E_0 = \left[\varepsilon_\infty + \varepsilon_a(k + f)/(1 - f)\right]^{-1/2} E_p$ [9]. Here $\varepsilon_\infty \approx 4$ accounts for the higher energy resonances in Ag, $\varepsilon_a \approx 4$ is the ambient dielectric function, $k = (1/L) - 1$, where $L$ is the depolarization factor, $f$ is the volume fraction of Ag, and $E_p = 8.8 \text{ eV}$ is the bulk plasmon frequency of Ag. The depolarization factor ranges from $L = 0$ for needle-like structures, through $L = 1/3$ for spheres in which case the dielectric function is isotropic, to $L = 1$ for sheet-like structures. Substituting $f = 0$ into the above expression yields the observed $E_0 = 2.9 \text{ eV}$ for a depolarization factor of $L = 0.43$, which corresponds to oblate surface structures. The reduction in $E_0$ with increasing roughness can then be attributed to an increase in volume fraction from near zero for widely separated protrusions to $f = 0.3$ for a greater fraction of large protrusions. The observed value for Al/ZnO of 3.3 eV in Fig. 4 is lower than the corresponding prediction with $E_p = 12.5 \text{ eV}$, in fact by more than $-0.5 \text{ eV}$. The discrepancy for the Al/ZnO structure may arise since the predicted energy lies within the interband region of the ZnO ambient. As a result only lower energy modes are possible, i.e., below the band gap of the ZnO where there is weak absorption. This may also account for the lack of a downward shift in energy, as well as the asymmetric lineshape. In fact, previous studies of Al nucleation have shown a very broad plasmon resonance, much broader than that for Ag, attributed to a short lifetime due to dissipation via interband excitations [10].

For both Ag/ZnO and Al/ZnO back-reflector structures, there are various mechanisms that can cause undesirable absorption in the near infrared. The primary source of absorption in Ag/ZnO is the localized plasmon band that appears in the imaginary part of the interface dielectric function and the weak interband absorption near the infrared region. On the other hand, in Al/ZnO structures, the (200) parallel band electronic transition with band gap $2|U_{200}| = 1.5 \text{ eV}$ in the bulk and interface Al components causes the most significant absorption in the near infrared. The absorption in Al/ZnO is also enhanced by the Drude free electron tail as seen in $\varepsilon_2$ in the near infrared region. From Fig. 2 one can observe that the intrinsic absorbance of the bulk metal increases as the substrate temperature and roughness increases, as noted from the decrease in amplitude of $\varepsilon_1$.

5. Conclusions

RTSE has been applied to investigate the optical properties of Ag/ZnO and Al/ZnO interfaces in back-reflectors (BRs) in the configuration used for substrate/BR/n-i-p thin film Si:H solar cells. The coupling of electromagnetic waves to localized plasmons associated with metal structure can be directly observed in the dielectric functions of the Ag/ZnO and Al/ZnO interface layers. No significant role of plasmons in dissipation is observed at 1.5 eV for Al/ZnO interfaces due to the higher bulk plasma energy in Al. In addition, the presence of Al interband transitions at low energy and ZnO interband transitions at high energy tends to place the allowable plasmon modes in the minimum absorption region of $\approx 3.3 \text{ eV}$. In spite of this, the dissipation in Al/ZnO at 1.5 eV is large primarily due to the combination of the interband and intraband transitions. The behavior for Ag/ZnO contrasts to that of Al/ZnO as the primary dissipation at $\approx 1.5 \text{ eV}$ in Ag/ZnO is through localized plasmons.
References


