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Solar Energy Materials & Solar Cells 82 (2004) 279–290
Solar Energy Materials & Solar Cells
www.elsevier.com/locate/solmat

Spectroscopic ellipsometry investigation of optical and interface properties of CdTe films deposited on metal foils

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Abstract

Optical and interface properties of the CdTe films electrodeposited on Molybdenum and Stainless Steel substrates were investigated using variable angle spectroscopic ellipsometer measurement and multilayer optical analysis. The refractive index of CdTe film obtained from the multilayer optical modeling is found to be lower than single crystal data. The Bruggeman effective medium analysis shows that the films consist of nearly 11% void due to poor crystallinity resulting in the lower refractive index. The multilayer optical model also indicates the presence of a Te rich interface between CdTe and substrate, which can be associated to the kinetics of CdTe electrodeposition that starts from nucleating Te on substrate surface followed by the formation of CdTe.

Keywords: CdTe; Ellipsometry; Electrodeposition; Flexible substrate

1. Introduction

CdTe is an ideal semiconductor material suitable for the photovoltaic device manufacturing. Conventionally CdTe devices are fabricated in superstrate configurations on transparent substrate [1]. This requires the device to be fabricated on glass substrate resulting in significant increase in the module weight, breakage during processing and higher cost. The manufacturing of these devices on flexible substrate offers processing, manufacturing cost and operational advantage over modules

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0927-0248/$ - see front matter
doi:10.1016/j.solmat.2004.01.025

fabricated on glass substrate. Because of the low substrate weight, thin film devices fabricated on flexible substrate can achieve higher specific power compared to single crystal modules making them suitable for space application. The greater radiation resistance of polycrystalline materials is also an added advantage for space application of these devices [2].

The growing interest of depositing CdTe films on flexible substrate resulted in research on various flexible substrate and feasible deposition methods [3]. Conducting (stainless steel, Molybdenum etc.) [3–5] as well as insulating (polyimide) [6] substrates are investigated for the device fabrication. Monolithic integration of the devices require the devices to be fabricated on an insulating substrate with conductive layer or a conducting substrate with an insulator layer and the latter seems to have a process advantage over the first. Close spaced sublimation (CSS) and electrodeposition techniques are the most popular among the several feasible deposition methods available to deposit photovoltaic quality CdTe films.

Good optical quality CdTe films are essential for the fabrication of the high efficiency devices. Also the CdTe/substrate interface properties are important for formation of ohmic contact. The surface of CdTe films in device configuration deposited on metal substrate is not accessible for surface treatments and hence forming an ohmic contact is difficult. Generally a layer of p-dopant is placed between CdTe and the metal. The CdTe film deposition conditions are critical in forming suitable interface between CdTe and Metal. The interface and optical studies reported in the previous work required the removal of the films from the metal substrate [5]. On the other hand, Ellipsometry being a nondestructive technique does not require the films to be removed from the opaque substrate for the optical studies. Ellipsometer measures the dielectric response of the materials in either bulk or multilayer structure. Dielectric responses of thin films are strongly influenced by the structural and compositional properties of the films and these properties can be extracted using multilayer optical modeling. However, no paper has been reported so far that employs spectroscopic ellipsometry (SE) technique for studying optical and interface properties of CdTe films on opaque substrate. In this paper we investigated the optical and interface properties of photovoltaic quality CdTe films electrodeposited on stainless steel (SS) and molybdenum (Mo) substrates using SE.

2. Experiment

2.1. Deposition

The CdTe thin films were electro deposited on flexible stainless steel and molybdenum substrates from a bath containing 1 M $CdSO_4$ and 100–200 ppm TeO_2. Prior to the addition of TeO_2 the solution was electro purified at a potential more positive than the deposition potential of cadmium. The films were prepared by potentiostatic technique with potentials in the range of -1050 to -1070 mV between the substrate and an Hg/Hg_2SO_4 (0.5 M H_2SO_4) reference electrode. The solution was maintained at 80°C and was continuously stirred with a magnetic stirrer. The concentration of the tellurium ions was maintained by adding proper amount of TeO_2 to the solution at regular intervals such that the average concentration of the tellurium ions remains constant during the electro deposition. The deposition kinetics of CdTe from acidic solutions can be found elsewhere [3–5].

2.2. Variable angle spectroscopic ellipsometry

SE measurements were carried out using J.A. Woollam variable angle spectroscopic ellipsometer (VASE). VASE is a rotating analyzer Ellipsometer equipped with an auto-retarder, which is useful in measuring the depolarization caused by the surface roughness and thickness uniformity. Measurements were carried out at energies from 0.725 to 4.6 eV with a step of 0.0125 eV with samples positioned at three incident angles near to the Brewster angle. Samples are rinsed in Br-methanol solution (1–2 s rinse in 0.2 vol% Br-methanol solution) to clean the surface. VASE measurements are carried out on CdTe films under Ar flowing to reduce the surface degradation during the measurements.

Fig. 1 shows the basic ellipsometry configuration used for multilayer thin film structure analysis. Monochromator splits white light from the light source into different components. The polarizer sets the polarization of the monochromatic light, the output of which is the plane-polarized light. The plane-polarized light has two orthogonal components, p-plane wave parallel to the plane of incidence and the s-plane wave perpendicular to the plane of incidence. For a plane polarized light, both p-wave and s-wave are in same phase but different in amplitude. After reflection from the sample, both phase and amplitude of the s- and p-plane waves changes and the light becomes elliptically polarized. The analyzer and detector combination determine the phase and amplitude information of the reflected light. Ellipsometer measures the ratio of p- and s-complex reflectance of the sample. The relation between these complex reflection coefficients and the ellipsometry parameters Ψ and Δ are given by $\tan\Psi e^{i\Delta} = R^{\mathrm{P}}/R^{\mathrm{s}}$, where R^{p} and R^{s} are the total complex reflection coefficients for p- and s-waves respectively. The ellipsometry parameter Ψ corresponds to the ratio of the magnitude of the total reflection

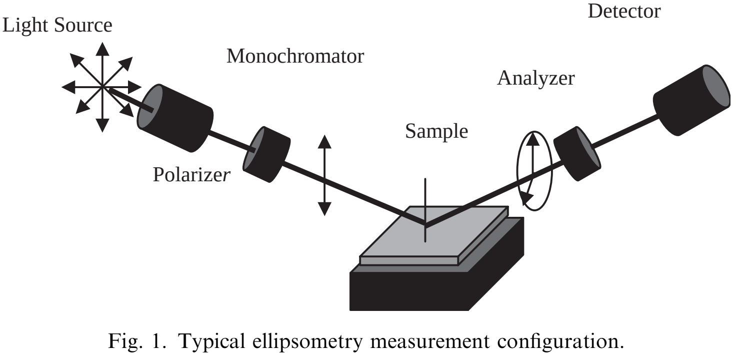


Fig. 1. Typical ellipsometry measurement configuration.

coefficient and Δ is the phase shift in p-and s-waves due to the reflection. In general, ellipsometry analysis consists of (a) measurement of ellipsometry parameters Δ and Ψ, (b) optical modeling using oscillator models to functionally describe the optical properties of the sample, (c) generation of data using the optical model, (d) fit model generated data to minimize the error.

By definition dielectric response is the measure of dipole moment per unit volume of the material. This suggests that precise knowledge of the dielectric response of a polycrystalline material can be used to determine the volume fraction of the materials in a mixed phase. This is possible by combining the individual dielectric response of the constituent phases using effective medium models to obtain the effective dielectric response. For example a random mixture of two phases is shown in Fig. 2. The dielectric response of this heterogeneous system can be described by a Bruggeman effective medium (BEM) approximation given by the relation [7]

$$0 = f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon}, \tag{1}$$

where ε_a and ε_b are respectively the dielectric function of the two phases a and b, and ε is the effective dielectric function of the heterogeneous medium. In the present work, the optical constants of the CdTe films are obtained from the multilayer optical modeling consisting of oscillator models. Sensitive CdTe/metal interface properties are investigated using BEM models that use the Te and CdTe single crystal data from the literature.

2.3. Multilayer optical modeling

The optical model consists of metal substrate, interface layer, CdTe layer and surface roughness layer. Both surface roughness and interface layers are modeled

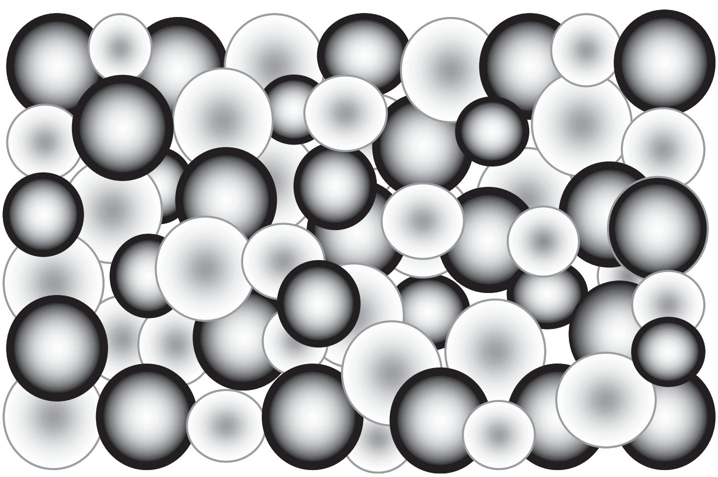


Fig. 2. Schematics of a heterogeneous system consists of random mixture of two (black and white) phases.

using BEM layer consisting of 50% void + 50% CdTe and 50%Mo/SS + 50%CdTe respectively. The surface roughness model assumes that the CdTe surface features are uniformly distributed hemispheres. The CdTe layer optical properties are simulated with oscillator models. The thickness of the CdTe film was obtained from fitting the data in the transparent region of the spectrum using a Cauchy dispersion relation. The refractive index in the transparent region and the thickness obtained from Cauchy dispersion relation were used to perform a point-by-point fit starting from the transparent region, to extract approximate values of the CdTe optical functions. The error in the point-by-point fit, measured by a 90% confidence limit, and was determined to check the quality of the n and k data. The optical functions thus obtained are called initial spectra and are close to the bulk dielectric response of the bulk CdTe film, free of substrate, interface, and surface roughness effects.

The initial spectrum was fit with a General Oscillator model, which uses a linear summation of Kramers–Kronig (KK) consistent oscillators to describe the various optical transitions. The fundamental transitions $E_0(A)$ in the spectra was modeled with a parametric Gaussian broadened polynomial superposition (GBPS) semiconductor oscillators [8]. The electronic transitions at higher energies are modeled using Lorentzean and Gaussian oscillators. The strength, broadening and positions for these oscillators were adjusted to match the initial spectrum. In the next procedure, the expected ellipsometric parameters ψ and Δ of the multilayer structure were generated using this parametric dispersion layer in the optical model. The generated data are compared with the experimental data and fit to reduce the error using the Marquardt–Levenberg algorithm [9]. In this procedure, the thickness and refractive index of the film are slightly adjusted. Also, non-ideal features like thickness non-uniformity are introduced into the model to fit the depolarization measured using the autoretarder. The root mean square error (MSE) is used to quantify the difference between the experimental and predicted data. The MSE is calculated by

$$\mathrm{MSE} = \left\{ \frac{1}{2N - M} \sum_{i=1}^{N} \left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\mathrm{exp}}}{\sigma_{\Psi j}^{\mathrm{exp}}} \right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta j}^{\mathrm{exp}}} \right)^2 \right] \right\}^{1/2}, \tag{2}$$

where $\sigma_{\Psi j,\Delta j}^{\mathrm{exp}}$ is the standard deviation in the measured ellipsometry parameters Ψ and Δ, Ψ_i^{mod} and $\Delta_i^{\mathrm{mod}}$are the model generated ellipsometry parameters, Ψ_i^{exp} and Δ_i^{exp} are the measured ellipsometry parameters, N is the number of measured parameters, and M is the number of fitted parameters. By using the experimental standard deviation as the weighing parameter in the fit, the contribution due to noise in the MSE is reduced significantly. The sequence of obtaining the point-by-point fit, adjusting the oscillator strength and then fitting to reduce the MSE was repeated several times until a minimum value of MSE was obtained without significant parameter correlation. A good fit is obtained when MSE is close to unity. A detailed description of measurement and data modeling strategies can be found elsewhere [10].

3. Results

3.1. Optical constants

VASE measurement on as-deposited films exhibits poor optical (pseudo-dielectric constants $\langle \varepsilon_2 \rangle$) response, which may be a result of either surface roughness and/or the presence of less polarizable species on the surface. Since the electrodeposited films are nearly specular, the poor response could be due to the presence of the less polarizable species like oxides or some residual layer from the electrodeposition bath. In order to remove the less polarizable species, the CdTe films are rinsed in 0.2 vol% Br-Methanol solution several time and VASE measurements are carried out after every rinse to monitor the cleaning process. Fig. 3 shows the effect of dielectric response for the CdTe films after sequential Br rinses. ED-as is the dielectric spectrum for the as-deposited film and ED-1st, ED-2nd, ED-3rd and ED-4th are the dielectric spectra obtained after 1st, 2nd, 3rd and 4th Br-Methanol rinses respectively. During the first three rinses, the dielectric response of the film improved significantly indicating systematical removal of the residual layer. Fourth rinse onwards the dielectric response did not improve, instead started to decrease. This decrease in response could be due to the formation of a-Te on the surface and its subsequent oxidation in the ambient air.

Multilayer optical analysis using oscillator models was carried out to extract the optical constants of CdTe films. Figs. 4 and 5 shows the best-fit and experimental data for ellipsometry parameters Ψ and Δ. Also shown in the inset is the multilayer optical model used for extracting optical constants of the CdTe films. The

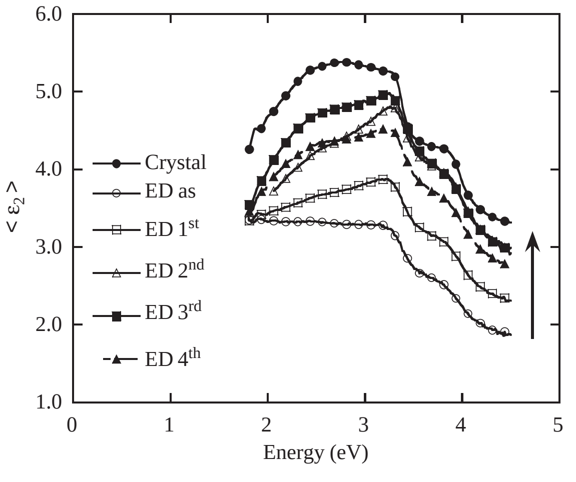
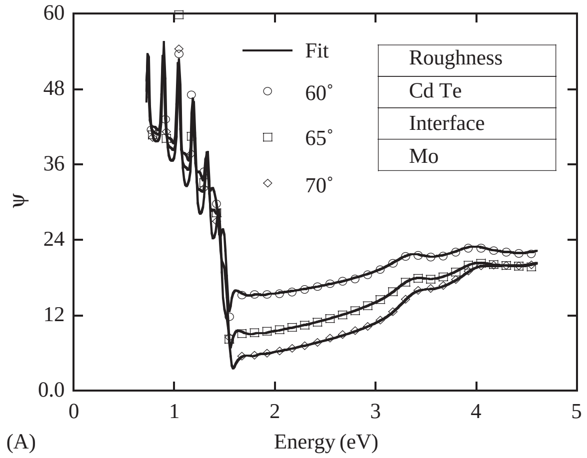


Fig. 3. Measured dielectric spectra of the CdTe/Mo sample obtained after each Br rinses. ED-as is the dielectric spectrum from the as-deposited film and ED-1st, ED-2nd, ED-3rd and ED-4th are the dielectric spectra obtained 1st, 2nd, 3rd and 4th Br-methanol rinse respectively. Crystal is the dielectric spectrum for CdTe single crystal with similar amount of surface roughness.



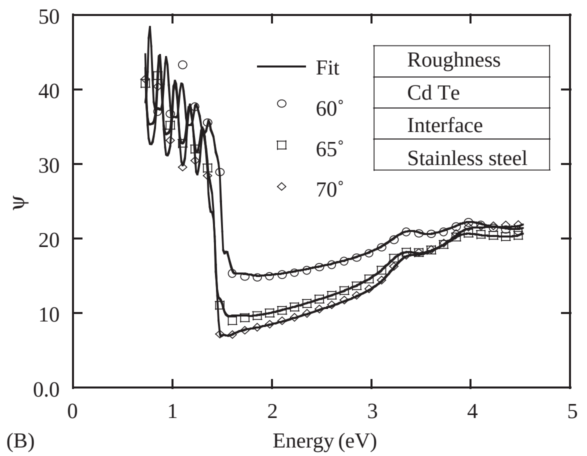


Fig. 4. (A and B) Measured and best-fit data for Ψ at three different incident angles (60°, 65° and 70°) for CdTe films deposited on (A) Mo and (B) stainless steel substrates. The inset shows the multilayer optical model used for this analysis.

measurement and fit was carried out at three incident angles to improve the confidence in the data fitting. Not all data points are shown to improve the clarity of the figure. The fit is excellent in both transparent and absorbing regions of the spectra. The thickness of interface layer, CdTe and surface roughness layer obtained from the best fit are listed in Table 1.

The optical constants obtained from this best fit are shown in Fig. 6A and B along with the CdTe single crystal data for comparison [11]. Electronic transitions E_0, $E_0 + \Delta_0$, $E1$ and $E_1 + \Delta_1$are marked in the figure. The optical constants of CdTe films deposited on Mo and SS substrates are very similar. However, the refractive indexes of the electrodeposited films are less than that of a single crystal. This lower refractive index is consistent with the values reported for as-deposited films in Ref.

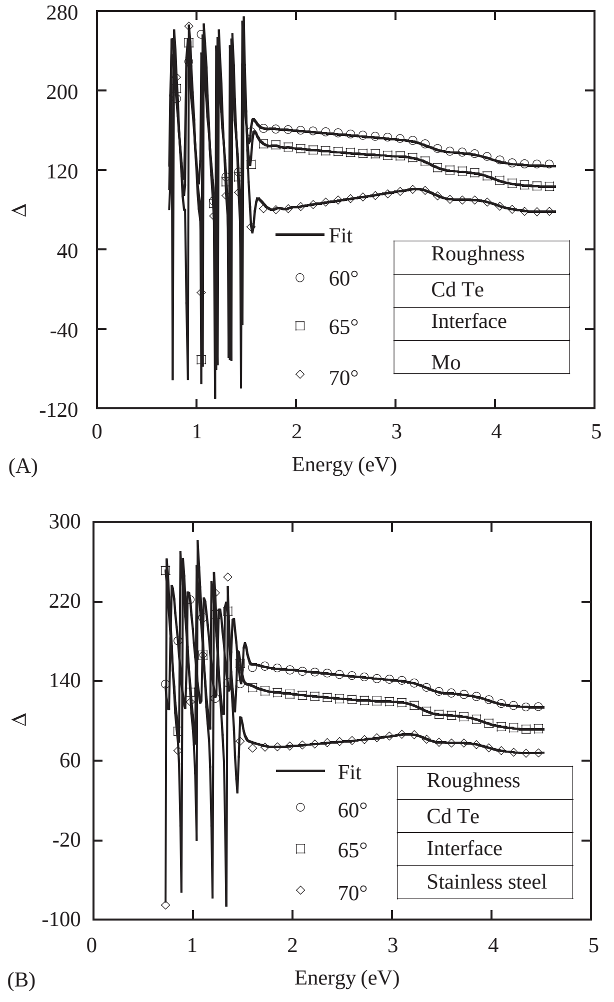


Fig. 5. (A and B) Measured and best-fit data for Δ at three different incident angles (60°, 65° and 70°) for CdTe films deposited on (A) Mo and (B) Stainless Steel substrates. The inset shows the multilayer optical model used for this analysis.

[12]. The low refractive index can be due to the smaller grain in these films resulting in significant amount of voids.

3.2. BEM analysis

The optical model used for the Bruggeman effective medium analysis is shown in Fig. 7. Surface layer is modeled using BEM similar to the oscillator model, but the void fraction is allowed to vary. This variable void fraction is to take care of the deviation of the CdTe surface features from an ideal uniform distribution of

Table 1
Best-fit values obtained from the oscillator and BEM analysis

Substrate	Surface roughness			CdTe			Interface layer			
	Thickness (nm)	CdTe (%)	Voids (%)	Thickness (nm)	CdTe (%)	Voids (%)	Thickness (nm)	Mo/SS (%)	CdTe (%)	Te (%)
Oscillator models										
SS	16.6 ± 0.1	50	50	1491 ± 0.3	—	—	6.2 ± 0.4	50	50	—
Mo	10.3 ± 0.1	50	50	1569 ± 0.2	—	—	2.2 ± 0.5	50	50	—
BEM analysis										
SS	22.6 ± 0.3	61	39 ± 0.05	1433 ± 5	89	11 ± 0.05	13.5 ± 5	72	0 ± 0.5	26 ± 0.9
Mo	19.2 ± 0.3	68	32 ± 0.03	1516 ± 1	89	11 ± 0.02	7.2 ± 2	60	0 ± 0.5	40 ± 1.4

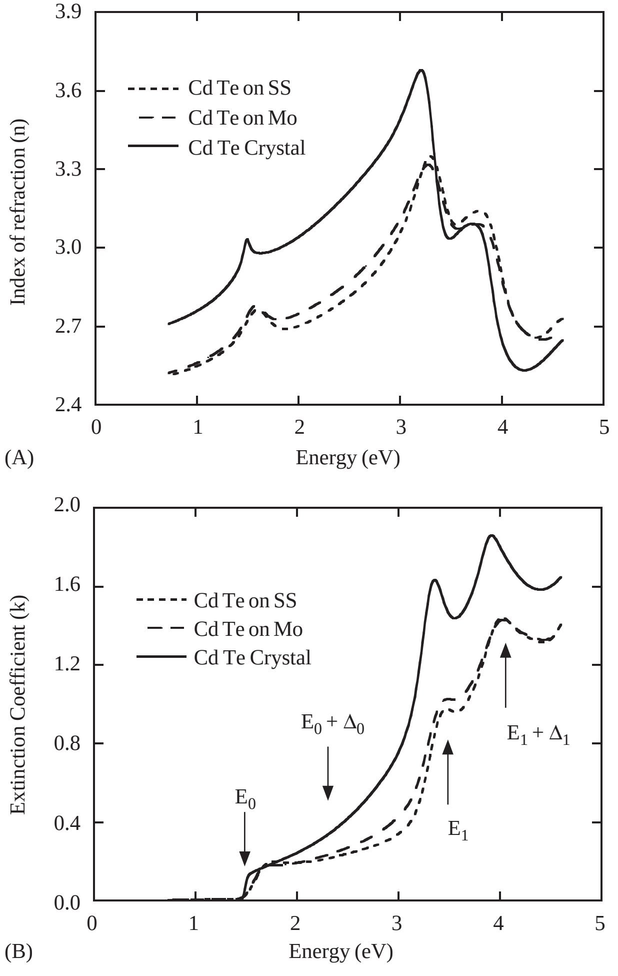


Fig. 6. Refractive index (A) and extinction coefficient (B) of CdTe film obtained from the multilayer optical model best fit. Also shown is the refractive index of CdTe single crystal for comparison.

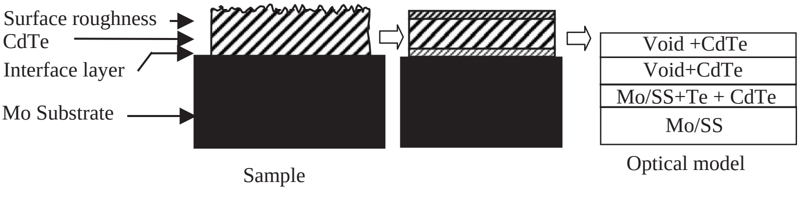


Fig. 7. Schematics of CdTe sample and optical model used for the BEM analysis.

hemispheres. The CdTe lower index refraction resulted from the polycrystalline nature of the films is modeled by another BEM layer consisting of single crystal data with variable amount of voids. In order to use BEM models successfully, the CdTe grain size has to be less than 0.1λ, where λ is the wavelength of the probing light. Since the grain size is very small in Electrodeposited CdTe films, BEM model can be successfully employed over a large spectral range. The CdTe/metal interface properties are investigated for the presence of Te. This study was carried out by using a 3-element BEM interface layer consisting of CdTe, metal and Te. The results of the BEM analysis are shown in Table 1. The quality of the data obtained from the multilayer optical model can be judged from the confidence limit, the measure of uniqueness of the data. The confidence limits shown for the fit variables are excellent except for the interface layer thickness. The roughness and interface layer thickness are different from the oscillator model due to the change in the void and Mo/SS fraction in these layers. There is a certain amount of uncertainty in determining the correct thickness of this interface layer. At the same time the interface layer consists of Te and the excellent confidence limit in the Te void fraction suggests that the interface layer is real. It also suggests that interface between the CdTe and the metal substrate is rich in Te. This higher amount of Te can be associated to the kinetics of CdTe electrodeposition that start from nucleating Te on Mo surface followed by the formation of CdTe. BEM analysis also shows that the electrodeposited film consists of nearly 11% void compared to the single crystal, which is the reason, the electrodeposited films shows a low refractive index. The CdTe film thickness is consistent with the values obtained from the oscillator models.

4. Conclusion

Photovoltaic quality CdTe films are deposited by electrodeposition on Mo and SS substrates. Strategy for VASE measurement and optical modeling to obtain true optical constants of these films are described. Index of refraction of CdTe films is lesser than the single crystals due to the smaller grains. BEM analysis shows that electrodeposited films consist of nearly 11% voids compared to single crystal resulted from the polycrystalline nature of the films. The interface between the CdTe and metal substrate analyzed using the BEM model shows that the interface is rich in Te.

Acknowledgements

The CdTe program at CIE-UNAM was supported by PAPIIT-UNAM (IN115102) and CONACYT, Mexico (38542-U).

References

[1] R.W. Birkmire, Annu. Reve. Mater. Sci. 27 (1997) 625–653.

[2] D.J. Flood, I. Weinberg, Advanced solar cells for satellite power systems, NASA Technical Memorandum 106777, November 1994.
[3] X. Mathew, G.W. Thomson, V.P. Singh, J.C. McClure, S. Velumani, N.R. Mathews, P.J. Sebastian, Sol. Energy Mater. Sol. Cells 76 (2003) 293–303.
[4] G.P. Hernandez, X. Mathew, J.P. Enriquez, N.R. Mathews, P.J. Sebastian, Sol. Energy Mater. Sol. Cells 70 (2001) 269.
[5] X. Mathew, P.J. Sebastian, A. Sanchez, J. Campos, Sol. Energy Mater. Sol. Cells 59 (1999) 99.
[6] A.N. Tiwari, A. Romeo, D. Baetzner, H. Zogg, Prog. Photovolt. 9 (2001) 211.
[7] D.E. Aspnes, Thin Solid Films 89 (1982) 249–262.
[8] C.M. Herzinger, B. Johs, US Patent No. 5,796, 983, issued August 18, 1998, Dielectric Function Parametric Model and Method of Use.
[9] D.W. Marquardt, J. Soc. Ind. Appl. Math. 11 (1963) 431.
[10] P.D. Paulson, R.W. Birkmire, W.N. Shafarman, J. Appl. Phys. 94 (2003) 879–888.
[11] D.E. Aspnes, H. Arwin, J. Vac. Sci. Technol. A2 (1984) 1309–1315.
[12] A.E. Rakhshani, J. Appl. Phys. 81 (12) (1997) 7988.