64th Annual Technical Conference Proceedings
Virtual Event: May 3 – 7, 2021
https://doi.org/10.14332/svc21.proc.0016

 ISSN 0737-5921
ISBN 978-1-878068-41-5

Deposition Temperature Dependence of Optical and Structural Properties of Glancing Angle Deposited CdTe

Niva K. Jayswal, Dipendra Adhikari, Indra Subedi, Corey R. Grice, and Nikolas J. Podraza
Wright Center for Photovoltaics Innovation and Commercialization & Department of Physics and Astronomy, University of Toledo, Toledo, OH, 43606, USA

ABSTRACT

X-ray diffraction (XRD) patterns are compared for radio frequency (RF) sputtered glancing angle deposited (GLAD) CdTe films prepared on soda lime glass at 250°C and room temperature (RT) at different incident source flux angles (Φ) with respect to the substrate normal ranging from Φ = 0° - 80°. A smaller distribution of diffraction peaks are observed in high temperature deposited CdTe films at all glancing angles indicating more preferential crystallite orientation. Only the cubic (C) and mixed cubic + hexagonal (C + H) phases are observed in the XRD patterns for 250°C-deposited CdTe, while the hexagonal (H) phase has been observed at high Φ in RT CdTe. Crystallite size of polycrystalline CdTe films corresponding to the C(111)/H(002) diffraction peak located at 23.7° are calculated using Scherrer's equation showing that the high temperature films have larger crystallites. Complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, spectra are obtained from spectroscopic ellipsometry over the range of Φ and indicate sharper critical points with higher amplitudes compared to RT CdTe. In-plane compressive stress for high temperature and RT GLAD CdTe are observed through the shift of the lowest energy critical point relative to that of single crystal CdTe.

INTRODUCTION

Cadmium telluride (CdTe) is a very stable, cost effective, and high-performance absorber layer used in thin film photovoltaic (PV) devices [1]. CdTe has a bandgap of ~1.5 eV and when used as a PV absorber has achieved >22% efficiency [2]. However, in sputter deposited polycrystalline CdTe, recombination of photogenerated carriers in the absorber layer are efficient due to charge traps at grain boundaries, small crystallite size, and poor electronic quality of the film resulting in reduced electrical properties and reduced device performance [3]. Investigation of microstructural and optical properties of the CdTe absorbers are crucial to improve PV device efficiency. Polycrystalline CdTe thin films may exhibit both cubic zinc blende (C) and hexagonal wurtzite (H) phases which have been produced by pulsed laser deposition [4], physical vapor deposition [5], and RF magnetron sputtering [6]. Glancing angle deposition (GLAD) can be used to tailor both the phase structure and crystallite orientation by increasing the oblique source flux angle (Φ) between the substrate normal and the target normal [5,6]. In GLAD sputtering, the target material arrives to the substrate at an oblique angle relative to substrate normal. CdTe films deposited at room temperature (RT) at Φ > 40° exhibit mixed phase cubic + hexagonal (C + H) structures and some diffraction peaks corresponding only to the hexagonal phase, H(100), H(101), H(102), and H(103) [5,6].

The microstructural and optical properties are studied for radio frequency (RF) sputtered GLAD CdTe films prepared at a higher substrate temperature of 250°C to better correspond with high efficiency solar cells incorporating sputtered CdTe absorbers [6,7]. Here, we report the variation in microstructural properties in terms of crystallite orientation, phase structure, and crystallite size for films prepared at different Φ. Due to columnar structure formed during deposition at high Φ, different microstructures are formed due to atomic self-shadowing effects [5,6]. Optical properties of GLAD CdTe deposited at 250°C are determined in terms of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra by analyzing ellipsometric spectra and compared with that of GLAD CdTe films prepared at RT by Adhikari et al. [6].

EXPERIMENTAL DETAILS

GLAD polycrystalline CdTe thin films are prepared on soda lime glass substates at different Φ. GLAD sputtering involves an oblique angle between the normal extending from the centers of the sample and the sputtering target. CdTe films are fabricated at 250°C substrate temperature at Φ = 0°, 20°, 40°, 60°, and 80°. Glass substrates are cleaned ultrasonically for 90 mins in two 45 min steps with and without detergent in deionized water and then dried with nitrogen gas before deposition. To prepare CdTe at 250°C, glass substrates are heated for 70 mins in low argon flow of 5 SCCM at 15 mTorr pressure. High temperature CdTe films are prepared in argon flow of 23 SCCM at a pressure of 15 mTorr with a RF power of 100 W. X-ray diffraction (XRD) measurements (Raguku Ultima III diffractometer) are performed to study microstructural properties in terms of crystal phase structure, crystallite orientation,

https://doi.org/10.14332/svc21.proc.0016
 ISSN 0737-5921
ISBN 978-1-878068-41-5

and crystallite size of all the samples. Optical characterization of the films are performed using a single rotating compensator multichannel ellipsometer (M-2000, J. A. Woollam Co.) [8,9]. Ellipsometric spectra are collected in spectral range 0.73 - 5.89 eV at 70° angle of incidence.

RESULTS AND DISCUSSION

XRD patterns of CdTe films deposited at 250°C at different Φ are shown in Figure 1. Diffraction peaks indexed to C(111) and C(311) planes of the cubic zinc blende crystal structure have been observed for all GLAD CdTe films. The C(220), C(400), and C(331) orientation peaks also exist for the film deposited at Φ = 0°. The C(222) peak is observed for Φ ≠ 0°. No peaks attributed to only the hexagonal phase are found in this series of films, although the H(002) and C(111), H(110) and C(220), and H(112) and C(311) overlap. The H(002)/C(111) and H(112)/C(311) peaks are observed for all Φ. These overlapping peaks imply that a mixed phase C+H structure is possible, however it is unlikely as peaks unique to solely the hexagonal phase are not observed in these films. Figure 2 compares XRD patterns for individual Φ GLAD CdTe prepared at RT and at 250°C. Room temperature XRD patterns have been previously reported in Adhikari et al. [6]. As shown in Figure 2, the crystallite orientations of 250°C-deposited films are different from RT deposited films for all Φ. Diffraction peaks corresponding to only the hexagonal phase are not observed for 250°C GLAD CdTe films whereas these peaks are observed for the films deposited at RT for Φ ≥ 40°. As shown in Figure 1, a wider distribution of crystallite orientations are observed for Φ = 0° whereas it is least for Φ = 40°. This implies that crystallites are randomly orientated at Φ = 0° and more preferentially oriented for Φ = 40° and other values of Φ resulting in increased crystallite size corresponding to certain orientations. Crystallite size is determined from XRD using Scherrer's equation,

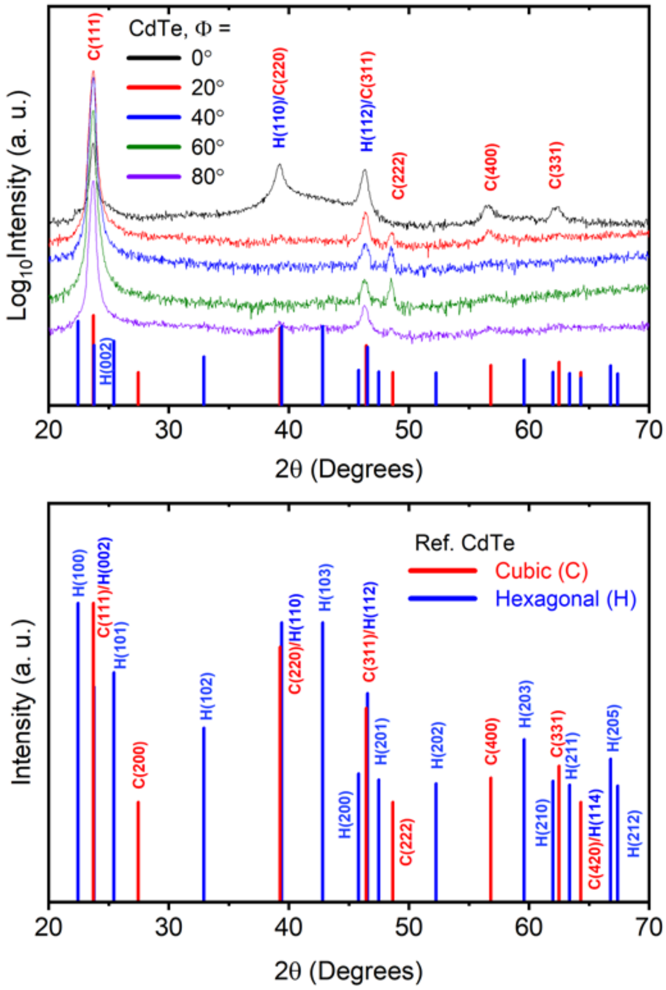
$$d = \frac{k\lambda}{\beta\cos\theta}$$

where k = 0.9 is shape factor (dimensionless), λ is wavelength of x-ray, β is the full width half maxima of diffraction peak, and θ is the Bragg's angle or the diffraction angle. Diffraction peaks at 2θ = 23.7° corresponding to C(111)/H(002) orientation crystallites are used to calculate crystallite size. Average crystallite sizes found in 250°C and RT deposited GLAD CdTe are compared in Figure 3. For 250°C-deposited CdTe, crystallite size is highest for the Φ = 40° film and lowest for the Φ = 0° due to lowest and highest distribution of crystallite orientations at Φ = 40 and 0°, respectively. Crystallite size of high temperature CdTe is larger than RT deposited CdTe due to more preferential orientation of crystallites at 250°C. At higher temperature, extra thermal energy facilitates the growth of the stable cubic phase as opposed to the metastable hexagonal phase. Also, the effect of atomic shelf-shadowing effect at higher Φ is decreased at high temperature due to extra thermal energy hindering formation of the tilt columnar structure and leading to larger crystallite sizes due to thermally enhanced diffusion of precursors on the surface [10].

Spectra in ε for polycrystalline CdTe films deposited on soda lime glass are obtained by applying a structural and parametric model to the measured ellipsometric spectra. The structural model consists of soda lime glass / bulk CdTe thin film / surface roughness, and the parametric model describing ε for polycrystalline CdTe consists of the sum of critical point (CP) parabolic band oscillators [11] and a Tauc-Lorentz oscillator [12]. All films are approximated as being isotropic. Surface roughness on top of the bulk CdTe is described by Bruggeman effective medium approximation [13] consisting of variable fractions of void (f_v) and bulk CdTe ($1-f_v$). Figure 4 compares spectra in ε for 250°C and RT GLAD CdTe prepared at Φ = 0° and 80°. The first three CPs represented as E_0, E_1, and $E_1+\Delta_1$ are found at 1.583 ± 0.009, 3.216 ± 0.127, and 4.126 ± 0.214 eV for Φ = 0° and 1.552 ± 0.007, 3.351 ± 0.120, and 4.315 ± 0.135 eV for Φ = 80° GLAD CdTe films prepared at high temperature. The CPs for crystalline CdTe are located at 1.49, 3.31, and 3.89 eV [14]. Film stress (X) is determined using a linear stress coefficient, $C_X(E_o)$ = 0.071 eV/GPa, relative to that of E_0 for single crystal CdTe [14]. In-plane compressive stress of 1.26 and 0.85 GPa are found in high temperature GLAD CdTe at Φ = 0° and 80°, respectively. RT GLAD CdTe have similar values with E_0 = 1.58 ± 0.01 and 1.54 ± 0.02 eV with corresponding compressive stress of 1.23 and 0.65 GPa for Φ = 0° and 80°, respectively. As shown in Figure 4, the CdTe films prepared at 250°C have sharper peaks with high amplitude compared to those prepared at RT due to the increased crystallite size of CdTe deposited at high temperature [15].

https://doi.org/10.14332/svc21.proc.0016

ISSN 0737-5921
ISBN 978-1-878068-41-5



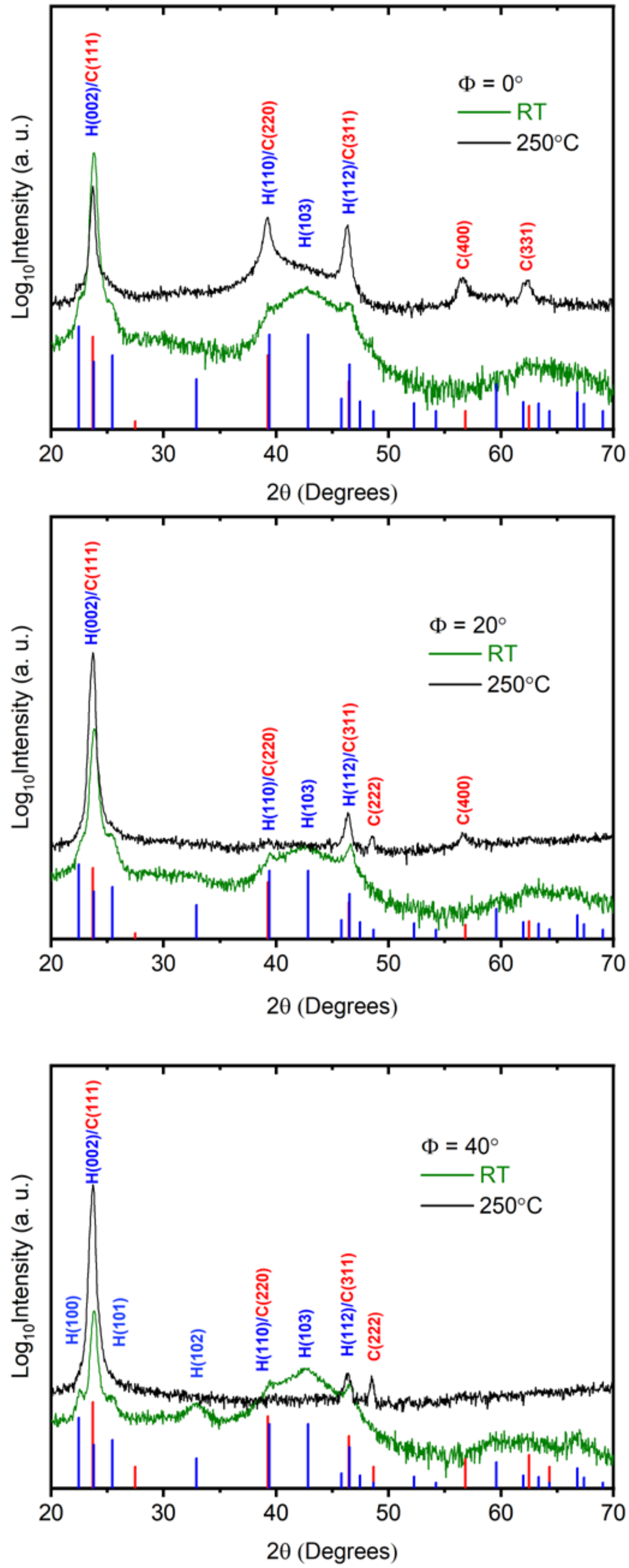


Figure 1. (top) X-ray diffraction (XRD) patterns of thin film CdTe deposited at different source flux angles (Φ) at 250°C substrate temperature. (bottom) Reference peaks for cubic zinc blend (C) CdTe (PDF# 97-010-8238) and hexagonal wurtzite (H) CdTe (PDF # 97-015-0941) are shown (MDI JADE software).

64th Annual Technical Conference Proceedings
Virtual Event: May 3 – 7, 2021
https://doi.org/10.14332/svc21.proc.0016
 ISSN 0737-5921
ISBN 978-1-878068-41-5

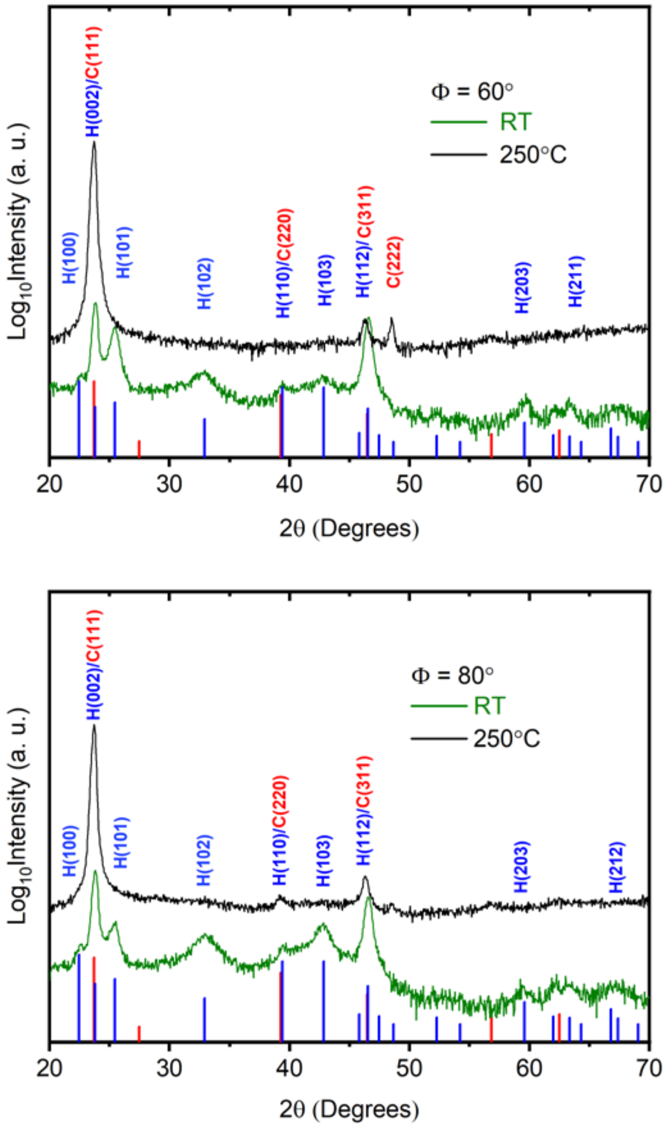


Figure 2. Comparison of XRD patterns of thin film CdTe deposited at different source flux angles (Φ = 0°, 20°, 40°, 60°, 80°) at RT and 250°C substrate temperatures.

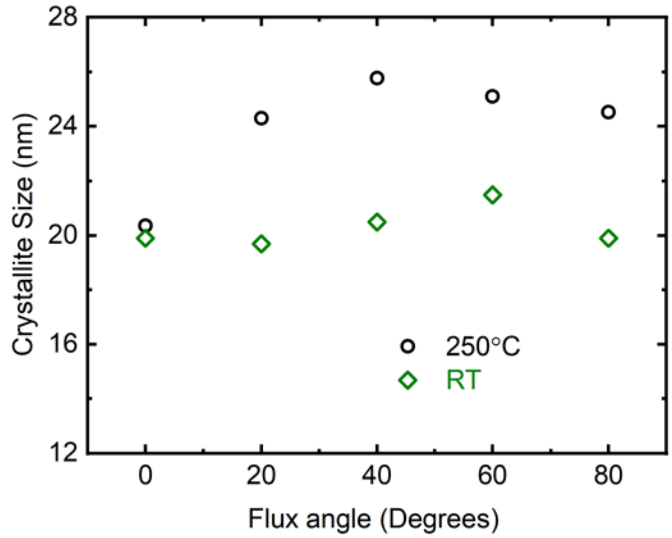


Figure 3. Crystallite size of CdTe deposited at different source flux angle and substrate temperature.

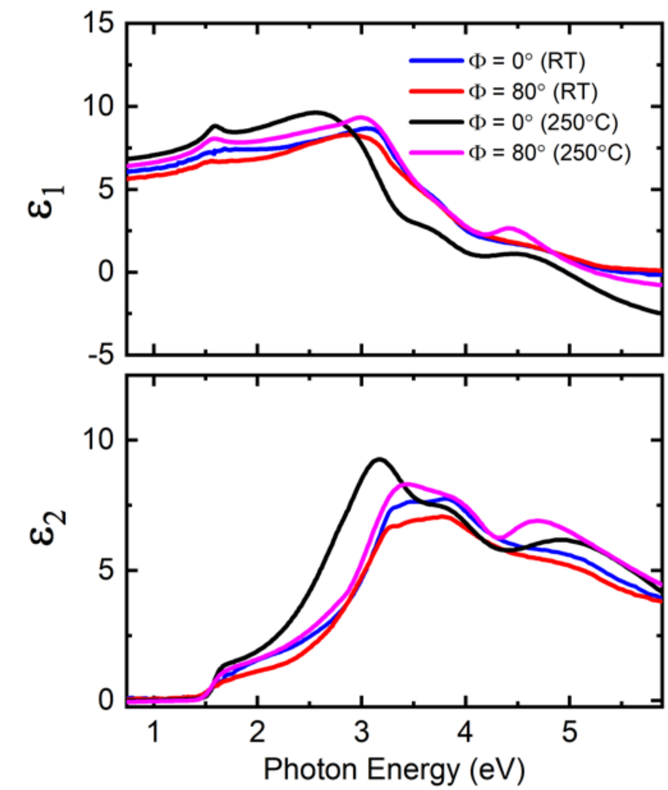


Figure 4. Comparison of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra of CdTe deposited at different flux angles at 250°C and RT.

https://doi.org/10.14332/svc21.proc.0016

ISSN 0737-5921
ISBN 978-1-878068-41-5

CONCLUSIONS

XRD studies of polycrystalline GLAD CdTe fabricated by RF sputtering at 250°C does not show diffraction corresponding to only the hexagonal crystal structure at any oblique source flux angle. High temperature CdTe films exhibits a lower number of diffraction peaks than RT CdTe and all peaks are either cubic or mixed phase (cubic + hexagonal). More preferential crystallite orientations, larger crystallite size, and the formation of the stable cubic phase over the metastable wurtzite phase occur at high temperature CdTe due to additional thermal energy increasing the diffusion length of precursors on the surface and facilitating a more thermodynamically stable crystal structure. The CP features in the complex optical response are sharper due to this increased crystallite size. Using high temperature GLAD CdTe as an interlayer in CdS/CdTe PV device is less likely to reduce lattice mismatch between the hexagonal wurtzite CdS n-type heterojunction partner and the cubic zinc blende CdTe p-type absorber as the hexagonal or mixed phase high Φ RT GLAD CdTe interlayer does [6]. Fabrication of the GLAD CdTe interlayer should be performed at lower temperatures and high Φ to promote the formation of the hexagonal phase while the remainder of the CdTe absorber may be deposited at higher temperature to promote larger crystallite size and improved electronic order.

ACKNOWLEDGEMENTS

This work is supported by National Science Foundation (NSF) Grant No. 1711534 and Air Force Research Laboratory under agreement number FA9453-18-2-0037 and FA9453-19-C-1002. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of Air Force Research Laboratory or the U.S. Government.

REFERENCES

1. M. Lingg, S. Buecheler, and A.N. Tiwari, "Review of $CdTe_{1-x}Se_x$ thin films in solar cell applications", *Coatings*, *9*(8), pp. 520, 2019. https://doi.org/10.3390/coatings9080520
2. M.A. Green, E.D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, and X. Hao, "Solar cell efficiency tables (version 56)", *Prog. Photovolt: Res. Appl.*, *28*(NREL/JA-5900-77544), 2020. https://doi.org/10.1002/pip.3303
3. M. Tuteja, P. Koirala, S. MacLaren, R. Collins, and A. Rockett, "Direct observation of electrical properties of grain boundaries in sputter-deposited CdTe using scan-probe microwave reflectivity based capacitance measurements", *Appl. Phys. Lett.*, *107*(14), pp. 142106, 2015. https://doi.org/10.1063/1.4932952
4. S.K. Pandey, U. Tiwari, R. Raman, C. Prakash, V. Krishna, V. Dutta, and K. Zimik, "Growth of cubic and hexagonal CdTe thin films by pulsed laser deposition", *Thin solid films*, *473*(1), pp. 54-57, 2005. https://doi.org/10.1016/j.tsf.2004.06.157
5. M.H. Ehsani, H.R. Dizaji, S. Azizi, S.G. Mirmahalle, and F.H. Siyanaki, "Optical and structural properties of cadmium telluride films grown by glancing angle deposition", *Phys. Scr.*, *88*(2), pp. 025602, 2013. https://doi.org/10.1088/0031-8949/88/02/025602
6. D. Adhikari, M.M. Junda, E. Bastola, P. Koirala, R.J. Ellingson, R.W. Collins, and N.J. Podraza, "Glancing angle deposited CdTe: Nanostructured films and impact on solar cell performance", *Surf. Coat. Technol.*, *381*, pp. 125127, 2020. https://doi.org/10.1016/j.surfcoat.2019.125127
7. V.V. Plotnikov, A.C. Vasko, A.D. Compaan, X. Liu, K.A. R.M. Wieland, Zeller, J. Li, and R.W. Collins, "Magnetron sputtering for II-VI solar cells: Thinning the CdTe", *Mater Res Soc Symp Proc*, *1165*, 2009. https://doi.org/10.1557/PROC-1165-M09-01
8. J. Lee, P.I. Rovira, I. An, and R.W. Collins, "Rotating-compensator multichannel ellipsometry: Applications for real time Stokes vector spectroscopy of thin film growth", *Rev. Sci. Instrum.*, *69*(4), pp. 1800-1810, 1998. https://doi.org/10.1063/1.1148844
9. B. Johs, J. A. Woollam, C. M. Herzinger, J. N. Hilfiker, R. A. Synowicki, & C. L. Bungay, "Overview of variable-angle spectroscopic ellipsometry (VASE): II. Advanced applications", *Proc. SPIE - Int. Soc. Opt. Eng.*, *10294*, 1029404, pp. 29-58, 1999. https://doi.org/10.1117/12.351667
10. C.M. Zhou, and D. Gall, "Competitive growth of Ta nanopillars during glancing angle deposition: Effect of surface diffusion", *J. Vac. Sci. Technol. A*, *25*(2), pp. 312-318, 2007. https://doi.org/10.1116/1.2539328
11. D. E. Aspnes, "Modulation spectroscopy/electric field effects on the dielectric function of semiconductors", *Handbook on Semiconductors, Optical Properties of Solids* 2, pp. 109-154, 1980.
12. G.E. Jellison Jr, and F.A. Modine, "Parameterization of the optical functions of amorphous materials in the interband region", *Appl. Phys. Lett.*, *69*(3), pp. 371-373, 1996. https://doi.org/10.1063/1.118064
13. H. Fujiwara, J. Koh, P.I. Rovira, and R.W. Collins, "Assessment of effective-medium theories in the analysis of nucleation and microscopic surface roughness evolution for semiconductor thin films", *Phys. Rev. B*, *61*(16), pp. 10832, 2000. https://doi.org/10.1103/PhysRevB.61.10832
14. J. Li, J. Chen, and R.W. Collins, "Optical transition energies as a probe of stress in polycrystalline CdTe thin films", *Appl. Phys. Lett.*, *99*(6), pp. 061905, 2011. https://doi.org/10.1063/1.3624536

https://doi.org/10.14332/svc21.proc.0016

ISSN 0737-5921
ISBN 978-1-878068-41-5

15. J. Chen, "Spectroscopic ellipsometry studies of II-VI semiconductor materials and solar cells", The University of Toledo, 2010.

FOR FURTHER INFORMATION

Prof. Nikolas J. Podraza
Department of Physics and Astronomy
University of Toledo
2801 W. Bancroft St.
Toledo, OH 43606 USA
419-530-4905
nikolas.podraza@utoledo.edu
www.weshinelightonstuff.com