www.vbripress.com/aml, DOI: 10.5185/amlett.2016.5965 Published online by the VBRI Press in 2016

Effect of substrate on the structural and electrical properties of Mo thin films

M. K. Thakur, Om Pal Singh, Karuna Thakur, Rahul Parmar, Kuldeep Singh Gour, N. Muhunthan, Sandeep Singh, Dinesh Singh, N. Vijayan, H. K. Singh and V. N. Singh*

CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi 110012, India

*Corresponding author. Tel: (+91) 11-45608562; E-mail: singhvn@nplindia.org

Received: 26 April 2015, Revised: 27 November 2015 and Accepted: 20 May 2016

ABSTRACT

To be used as back contact for CZTS/CIGS thin film solar cell, good adhesion to the substrate and low resistivity of the Mo thin film is necessary. In this study, molybdenum thin film has been deposited on soda lime glass, sapphire, quartz, and a single crystal yttria-stabilized zirconia (YSZ) using DC magnetron sputtering at 400°C. The structural, electrical, surface morphology and adhesion test using scotch tape test were carried out. Films deposited on all the substrates passed the adhesion test. Lattice parameter of films deposited on various substrates was almost same, but the strain % was different. The size of grain in the film deposited on soda lime glass and YSZ single crystals were larger compared to films deposited on quartz and sapphire. In the case of SLG, Na helped in the grain growth and in the case of YSZ, the crystalline nature of YSZ helped in grain growth. Resistivity result indicated films having pure metallic behavior. The resistivity for sample deposited on YSZ single crystal was very low. AFM study showed that the film made on soda lime glass is having higher surface roughness than other substrates and it was lowest for samples deposited on YSZ single crystal. The cross-sectional TEM study of Mo thin film deposited on glass showed columnar structure of the film. Copyright © 2016 VBRI Press.

Keywords: Mo thin film; soda lime glass; YSZ; DC sputtering; cross-sectional SEM and TEM.

Introduction

With the advancement of technology, the demand for energy is increasing tremendously which is creating a pressure on non-renewable sources of energy. Scientists are working since a long time to search for renewable resources which can replace these conventional sources. As we know, solar energy is the ultimate source of energy; so converting this solar energy into usable form of energy which can be stored for later use is the best alternative. Solar cells are devices which convert light energy into electrical energy and hence are the best replacement for conventional sources to solve the upcoming energy crisis. Among all the present technologies; CZTS and CIGS based thin film solar cells are the most researched [**1-5**]. The highest reported efficiency for CZTSSe based solar cell is 12.6% [**6**] and for CIGS is 22.3% [**7**]. The theoretical conversion efficiency for single junction solar cell is nearly 32% [**8**]. Besides CIGS, CZTS and its selenide compounds are more popular as an absorber layer for thin film solar cell application [**9-11**].

To ensure high efficiency of a CIGS/CZTS based solar cell device, an ideal ohmic back contact is needed for enhanced transport of majority charge carriers and low recombination for minority charge carriers [**12**]. According to researchers, molybdenum has been found to be the most suitable material for back contact among all other materials; like, W, Ta, Cr, V, Nb or Ti due to its inertness, high melting point, high thermal stability, high conductivity and mechanical hardness [**13-15**]. Thus, Mo has the capability to be used as a surface electron collector layer because of its high electronic conducting capabilities. Generally, the molybdenum film is deposited using DC magnetron sputtering. It is well known that sputtering parameters, such as; sputtering power, working gas pressure and working distance control the properties of sputter-deposited thin films. For example, films deposited at lower working gas pressures generally have poor adherence to the substrate, higher conductivity and are under compressive stress; whereas those deposited at higher gas pressures tend to have good adherence, high resistivity and are under tensile stress [**13**]. Therefore, deposition of molybdenum in two-layer sequence has also been suggested [**14, 17**]. It was experimentally observed that Mo films get peeled off from the substrate when the substrate was glass and stainless steel. Mo as its oxide, nitride, carbide, selenide and sulfide compounds have several applications in electronics [**18-25**]. The goal of our present work is to reduce the stress and increase the adhesion of the Mo film which affects the properties of CIGS/CZTS layer. Our aim in this work is to obtain Mo thin films with lower resistivity so that its contribution to the series resistance of the device is negligible. The motivation of this work is to find out the effect of substrate on the resistivity, adhesion & structural properties of the molybdenum thin film.

Experimental

Materials

Molybdenum target having 2 inch diameter, 3 mm thickness and 99.99% purity purchased from Vin Karola Instruments, USA was used for sputtering.

Sodalime glass, quartz, sapphire and YSZ substrates were purchased from Optochem International, Delhi, India and argon gas with purity 99.9999% was supplied by Linde Gas, Singapore.

Material synthesis

Mo thin films were deposited on soda lime glass, sapphire, quartz and a single crystal YSZ (Yattria stabilized zirconia). Before deposition, the substrates were cleaned by ultra-sonicating them in de-ionized water for 5 min, acetone for 10 min and finally in propanol for 5 min. The cleaned substrates were finally dried using a nitrogen blower. Deposition was carried out in DC magnetron sputtering system with the base pressure of 1×10^{-5} torr and Ar flow rate of 20 SCCM. Before sputtering, the target was pre-sputtered for 6 min in order to remove any impurity present. The substrate temperature was maintained at 400 ^{o}C and deposition was carried out for 15 min.

Characterizations

The structural characterization was performed using X-ray diffraction (XRD, θ-2θ) (Bruker D8 Advance). The crystallite size (D) was calculated using the Scherer equation, $D= 0.9\ \lambda/\ \beta\ \cos\theta$; where λ is the wavelength of the X-ray used (0.15406 nm); β, the full width at half maximum (FWHM) of the highest-intense peak; and θ, the Bragg angle. For resistivity measurements, a standard four probe setup was used and for surface morphology multimode AFM with Nano Scope V controller (Veeco Ltd., USA) was used. Cross-sectional TEM analysis of Mo deposited on soda lime glass substrate was carried out by making cross-sectional sample and studying it under transmission electron microscope (HRTEM, FEI G2, F-30, s-twin, The Netherlands) operating at an accelerating voltage of 300 kV. Cross sectional SEM studied were carried out using FESEM.

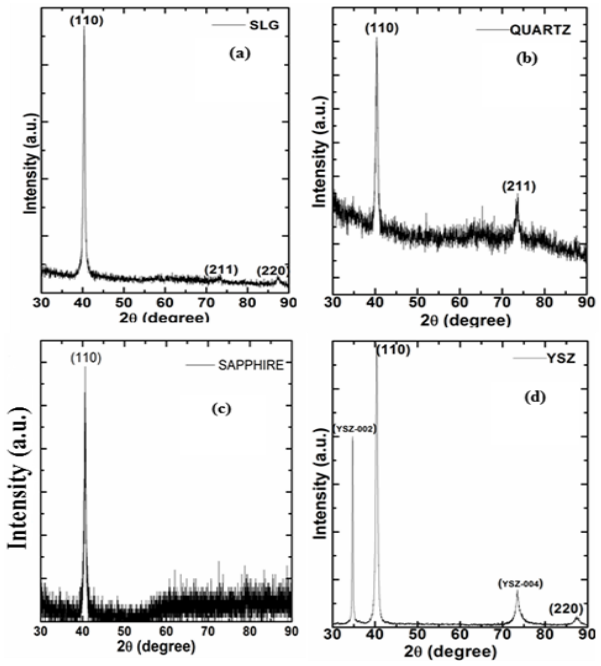

Fig. 1. XRD patterns of Mo thin films deposited on (a) soda lime glass, (b) quartz, (c) sapphire and (d) YSZ.

Results and discussion

Fig. 1(a-d) show the XRD patterns of Mo film deposited on SLG, quartz, sapphire and YSZ substrates, respectively. The characteristic XRD peak of Mo oriented along (110) plane is observed in all XRDs. Some other peaks corresponding to Mo were also observed which were similar to earlier reported liter dose [**26-28**]. The XRD data matched well with the JCPDS files. Very high intensity of (110) reflections in the XRD patterns clearly showed strong texturing and orientation. From the XRD data of films, lattice parameters, grain size, strain % and type of strain (using the strain formula; strain (%) = Δa/a × 100)) were estimated and the values are mentioned in **Table 1**.

Table 1. Effect of substrate on lattice parameter, strain %, grain size, and type of strain of the Mo thin films.

Substrate	Lattice parameter (Å)	Strain %	Grain size (Å)	Strain type
SLG	3.159	0.369	162.7	compressive
Quartz	3.160	0.416	91.3	compressive
Sapphire	3.159	0.369	97.4	compressive
YSZ	3.157	0.321	162.7	compressive

The above result indicates that the film made on single crystal (YSZ) is oriented due to crystalline nature of YSZ substrate. Lattice parameter for all the samples is almost same. Strain % is different for samples on different substrates and has very low value for samples deposited on single crystal (YSZ). The value of grain size is same for samples deposited on soda lime glass substrate and YSZ single crystal and is lower for samples deposited on two other substrates. It has been reported earlier that at higher temperature, sodium from the soda lime glass helps in grain growth of the Mo film [**11**].

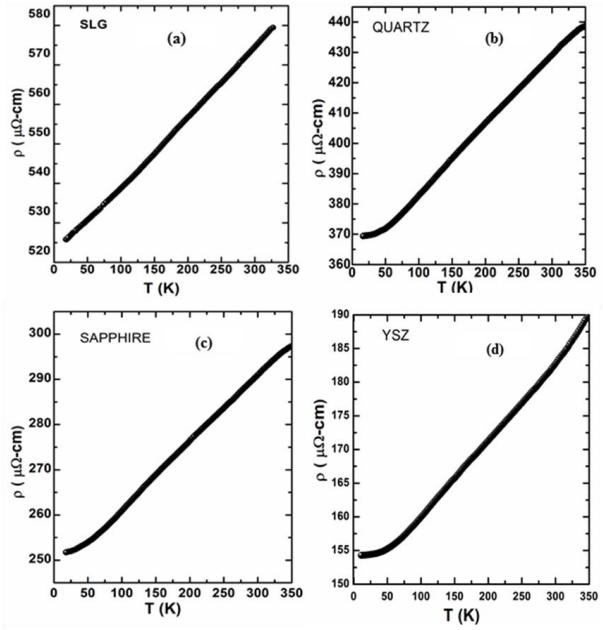

Fig. 2. Temperature vs. resistivity plot of Mo thin film deposited over various substrates.

Temperature vs resistivity was measured using a standard four probe measurement system and the results are shown in **Fig. 2 (a-d)**.

The resistivity of film was calculated using the standard resistivity formula.

$$\rho = (V/I)\ ((w \times t)/l) \quad (1)$$

where, V is the applied voltage, I is observed current, w is the width of the film, t is thickness of film, l is the distance between two inner probes.

From R-T data, one can observe that with increase in temperature the resistivity of samples is also increasing which shows that molybdenum film is having pure metallic nature. The value of resistivity changes with substrate and the value for Mo film deposited over YSZ single crystal was lowest and was highest for the samples deposited on soda lime glass substrate.

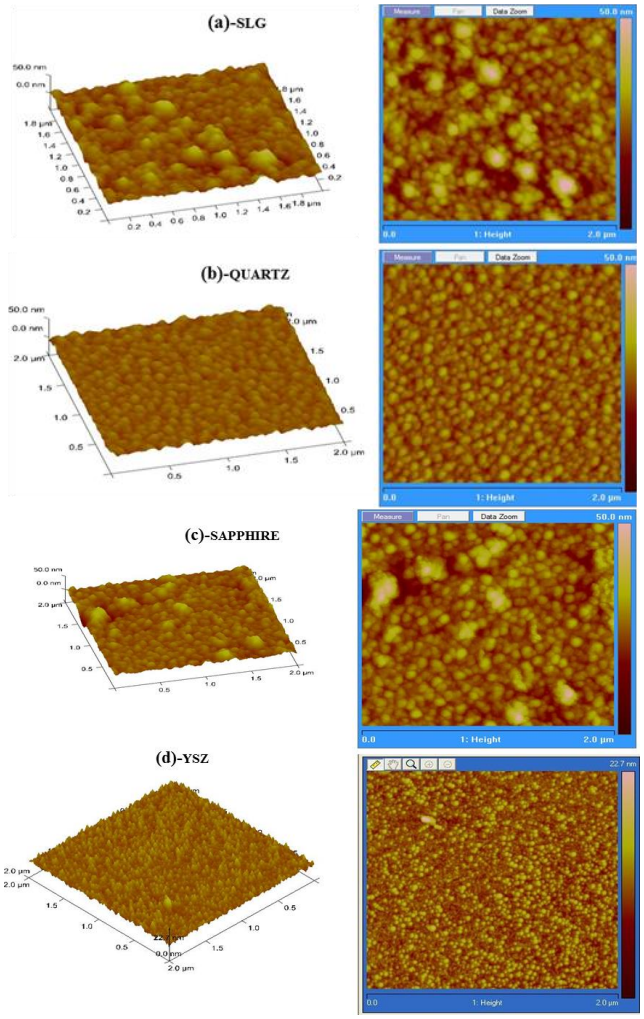

Fig. 3. AFM images (left 3D and right 2D) of Mo thin films deposited on (a) soda lime glass, (b) quartz (c) sapphire and (d) YSZ substrates.

Table 2. Average roughness of Mo films deposited on various substrates.

Substrate	Average roughness (nm)
SLG	5.53
Quartz	2.93
Sapphire	3.85
YSZ	1.75

AFM images of Mo thin films deposited on (a) SLG, (b) quartz, (c) sapphire and (d) YSZ (left 3D and right 2D) are shown in **Fig. 3** (**a-d**). The average roughness of all the films is calculated and is presented in **Table 2**. The average roughness value for Mo films deposited on soda lime glass is much higher compared to other substrates and is very low for YSZ single crystal.

Fig. 4(**a**) shows the lattice image of Mo deposited on SLG substrate. The observed lattice spacing of 2.22 Å corresponds to (110) plane of Mo. The columnar structure of Mo on soda lime glass can be seen in **Fig. 4**(**b**). The SAED pattern (**Fig. 4**(**c**)) of film shows that the film is polycrystalline with textured structures. The columnar growth of Mo thin film on SLG can be seen in cross-sectional SEM micrograph of **Fig. 4** (**d**). There were no voids or porosity in Mo thin films. Mo thin film is densely packed.

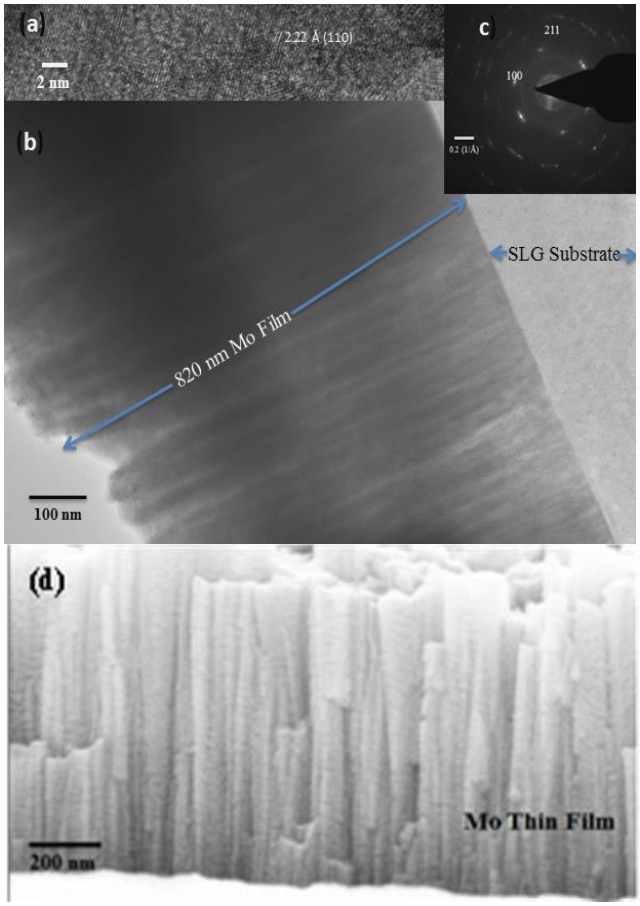

Fig. 4. (a) HRTEM image, (b) cross-sectional TEM showing the columnar growth of Mo, (c) SAED pattern of Mo and (d) Cross-sectional SEM micrograph of Mo thin film on soda lime glass substrate.

Conclusion

We have successfully grown molybdenum thin film on soda lime glass, quartz, sapphire, and YSZ single crystal by DC magnetron sputtering at 400°C. It was observed that lattice parameter for films are nearly same but the strain% was different due to different crystalline nature of substrates. Films on crystalline substrate (YSZ) grew epitaxial and therefore have minimum stress. The grain size for samples deposited on YSZ and SLG are same. Larger grain in films deposited on soda lime glass shows that sodium had influenced the grain growth at higher temperature. Cross-sectional SEM images showed columnar growth of Mo on

soda lime glass. Temperature dependent resistivity value indicated that the film grown on YSZ single crystal has lowest resistivity value. AFM data also indicated that film roughness was lesser for samples deposited on single crystal substrate. The present work can be a guideline for obtaining good quality Mo thin films for solar cell applications.

Acknowledgements

MK and VNS acknowledge Department of Science and Technology (DST) India for support through the fast track project for young scientist by sanction order no. SR/FTP/PS-124/2011dated February, 2012. We are thankful to CSIR-India and MNRE, Govt. of India (Sanction No. 31/ 29/2010-11/PVSE) for their financial support. The authors are grateful to CSIR-India for TAP-SUN program. OPS and NM are thankful to UGC for SRFships.

Reference

1. H. Katagiri, N. Sasaguchi, S. Hando, S. Hoshino, J. Ohashi, and T. Yokota, *Sol. Energy Mater. Sol. Cells*, **1997**, *49*, 407. **DOI:** 10.1016/S0927-0248(97)00119-0
2. J. S. Seol, S. Y. Lee, J. C. Lee, H. D. Nam, and K. H. Kim, *Sol. Energy Mater. Sol. Cells*, **2003**, *75*, 155. **DOI**: S0927024802001277
3. P. Jackson, D. Hariskos, E. Lotter, S. Patel, R. Wuerz, R. Menner et al., *Prog. Photovolt. : Res. Applications*, **2011**, *19*, 894. **DOI**: 10.1002/pip.1078
4. N. Muhunthan, O.P. Singh, M.K. Thakur, P. Karthikeyan, D. Singh, M. Saravanan and V. N. Singh, *J. Sol. Energ.* **2014,** 2014, 476123. **DOI**: 10.1155/2014/476123
5. L. Arora, P. Gupta, N. Chhikara, O.P. Singh, N. Muhunthan, V. N. Singh, B. P. Singh, K. Jain and S. Chand, *Appl. Nanosci.*, **2015**, 5, 193. **DOI**: 10.1007/s13204-014-0302-9.
6. W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov,Y. Zhu, et.al, *Adv. Energy Mater.*, **2014**, *4*, 1301465. **DOI**: 10.1002/aenm.201301465
7. J. Gifford, http://www.pv-magazine.com/News/details/betirag/solar-frontier-hits-223-on-clgs-cell_100022342/#ixzz3v755gdiz.
8. M. Dhankhar, O.P. Singh and V.N. Singh, *Renewable and Sustainable Energy Reviews*, **2014**, 40, 214. **DOI**: 10.1016/j.rser.2014.07.163.
9. O.P. Singh, N. Vijayan, K.N. Sood, B.P. Singh and V.N. Singh, *J. Alloys Compounds*, **2015**, 648, 595-600. **DOI**: 10.1016/j.jallcom.2015.06.276.
10. O.P. Singh, N. Muhunthan, B.P. Singh and V.N. Singh, *Advanced Science, Engineering and Medicine*, **2015**, 6, 1285. **DOI**. 10.1166/asem.2014.1633.
11. O.P. Singh, N. Muhunthan, V.N. Singh and B.P. Singh, *Adv. Mater. Lett*. **2015**, 6, 2. **DOI**: 10.5185/amlett.2015.6584.
12. K. Orgassa, H. W. Schock, and J. H. Werner, *Thin Solid Films*, **2003**, *431*, 387. **DOI**: S0040609003002578
13. S. A. Pethe, E. Takahashi, A. Kaul, and N. G. Dhere, *Sol. Energy Mater. Sol. Cells*, **2012**, *100*, 1. **DOI**: 10.1016/j.solmat.2011.11.038
14. M P Salom, J Malaquias, P. A. Fernandes and A. F. da Cunha, *J. Phys. D: Appl. Phys.* **2010**, *43*, 345501. **DOI**: 10.1088/0022-3727/43/34/345501
15. P.-cheng Huang, C.-ho Huang, M.-yong Lin, C.-ying Chou, C.-yao Hsu, and C.-guo Kuo, *Internat. J. Photoenergy*, **2013**, 390824. **DOI**: 10.1155/2013/390824
16. J. H. Scofield, A. Duda, D. Albin, B. L. Ballard, and P. K. Predecki, *Thin Solid Films*, **1995**, *260*, 26. **DOI**: 10.1016/0040-6090(94)06462-8
17. M. Khan and M. Islam, *Semiconductors*, **2013**, *47*, 1610. **DOI**: 10.1134/S1063782613140017.
18. O. Lupan, V. Trofim, V. Cretu, I. Stamov, N.N. Syrbu, I. Tiginyanu, Y.K. Mishra and R. Adelung, *J. Phys. D: Appl. Phys*, **2014,** 47, 085302. **DOI**: 10.1088/0022-3727/47/8/085302
19. O. Lupan, V. Cretu, M. Deng, D. Gedamu, I. Paulowicz, S. Kaps, Y.K. Mishra, O. Polonskyi, C. Zamponi, L. Kienle, V. Trofim, I. Tiginyanu and R. Adelung, *J. Phys. Chem. C*, **2014**, 118, 15068. **DOI**: 10.1021/jp5038415
20. X. Liu, H. Cui, C. Kong, X. Hao, Y. Huang, F. Liu, N. Song, G. Conibeer and M. Green, *Applied Physics Letters* **2015**, 106, 131110. **DOI**: 10.1063/1.4916994
21. Hovestad, P.M.M.C. Bressers, W.P. Voorthuijzen, R.M. Meertens and C.H. Frijters, *J. Appl. Electrochem* **2015,** **DOI:** 10.1007/s10800-015-0829-9
22. J. Li, Y. Zhang, W. Zhao, D. Nam, H. Cheong, L. Wu, Z. Zhou and Y. Sun, *Adv. Energy Mater*. **2015**, 1402178. **DOI**: 10.1002/aenm.201402178
23. J.H. Yoon, K.H. Yoon, W. M. Kim, J.K. Park, Y.J. Baik, T.Y. Seong and J. Jeong, *J. Phys. D: Appl. Phys*. **2011**, *44*, 425302. **DOI**: 10.1088/0022-3727/44/42/425302
24. K. Lee, R. Gatensby, N.M. Evoy, T. Hallam, and G.S. Duesberg, *Adv. Mater*. **2013**, 25, 6699. **DOI**: 10.1002/adma.201303230
25. J. Kibsgaard, Z. Chen, B.N. Reinecke and T.F. Jaramillo, *Nat. mater*.**2012,** 11, 963. **DOI**: 10.1038/NMAT3439
26. C.Y. Su, K.H. Liao, C.T. Pan, P.W. Peng, *Thin Solid Films* **2012**, 520, 5936. **DOI**: 10.1016/j.tsf.2012.05.027
27. S.A. Pethe, E. Takahashi, A. Kaul and N.G. Dhere, *Sol. Energ. Mater. Sol. Cell.* **2012**, 100, 1. **DOI**: 10.1016/j.solmat.2011.11.038
28. P. Huang, C. Huang, M. Lin, C. Chou, C. Hsu and C.Kuo, *Int. J. Photoenerg*., **2013**, 390824. **DOI**: 10.1155/2013/390824