

Na-Doped Mo Target Sputtering for CIGS Thin Film Solar Cells on Stainless Steel Substrate

Y. C. Lin, *Member, IACSIT*, Z. H. Shi, C. H. Shen, and Y. L. Chen

Abstract—This study deposited Cu(In,Ga)Se₂(CIGS) thin films on Mo/SiO_x/SS431 substrates using magnetron sputtering. Our objectives were to introduce a Mo-5%Na target as a source of incorporate Na to the chalcopyrite structure and investigate its influence on the crystallinity of CIGS thin films. Experimental results demonstrate that adding Na in this manner can enhance the distribution of Na on the surface as well as the depth profile. When the thickness ratio of Mo-5%Na: Mo was 2.8%, the atomic ratio of Na was 0.48%, which enhanced crystallinity of CIGS. Excess Na dopant led to the formation of NaInSe₂ phase, which increases the number of In vacancies in chalcopyrite, thereby reducing crystallinity. The results of bending tests demonstrate that the adhesion of SiO_x to SS431 is superior to the adhesion of SiO_x to Mo.

Index Terms—Cu(In,Ga)Se₂, crystallinity, Na dopant.

I. INTRODUCTION

Cu(In,Ga)Se₂ thin films (CIGS) provide high absorptivity and low cost and can be produced on flexible substrates. In the future, these materials will be produced using roll-to-roll deposition processes [1], [2] to enhance manufacturing speed and reduce costs. The flexible substrates used for CIGS include ZrO₂ [3], polymer [4], and stainless steel [5]. The thermal stability, and coefficient of thermal expansion of the substrates must conform to the standards of soda-lime glass; however, these substrates do not contain Na. Recent studies have found that the addition of Na can increase the crystallinity [6], open voltage [7], and fill factor [8] of CIGS absorber layers. The methods commonly used to incorporate Na into CIGS include evaporation [9], sputtering [10], and coating. In practice, the preparation of NaF film through evaporation leads to the uneven distribution of Na when applied in large-area production [10]-[15] and the deposition of NaF film on Mo back contact using RF sputtering is too slow deposition rate for mass production. Therefore, this study sought to apply Mo-5% Na on Mo electrodes via sputtering to resolve the difficulties involved in maintaining evenness while enabling large-scale production. Our approach involved the application of a Mo-5% Na target in order to incorporate

Na on Mo electrodes. In addition, few previous studies have discussed the conditions of flexible stainless steel substrates when the substrates are bent. Thus, we also investigated the influence of curvature on the adhesion

between Mo electrodes and a SiO_x barrier layer.

II. MATERIALS AND METHOD



$$R\% = a/(a+b) \times 100\%$$

Fig. 1. A schematic diagram of Mo-5% Na as the bottom of a Mo back contact.

We employed SUS431 stainless steel substrates (15mm x 10mm x 0.5mm) with surface roughness below 5 nm. A SiO_x barrier layer with a thickness of 300nm was deposited on the substrate using sputtering to reduce the diffusion of Fe and Cr during annealing. The thickness ratio between the upper and bottom layers of Mo bi-layer electrode was 1:2. Na content was represented using the ratio of Mo-5%Na to Mo electrode film thickness. The structure of the material is detailed in Fig.1. Quaternary CIGS (Cu:In:Ga:Se = 23:20:7:50 at.%) and Cu targets were co-sputtered to form a CIGS absorber layer of various concentrations. Deposition was performed using a Cu target power of 60W at 0.67Pa and a quaternary-CIGS target power of 125W on a substrate at 473K. The total thickness was 1μm. The substrate was then selenized annealed at 798K for 20 minutes under Se vapor. An external force bending machine was used to bend the Mo electrode to determine the resulting damage to the thin films, as shown in Fig. 2. The experiments in this study used X-ray diffraction (XRD, CuKα, λ=1.54052Å) to investigate the crystalline structure of the CIGS films with 0.5° ~ 10° incident angle. Raman measurements (Jobin Yvon Labram HR) were taken to check the phase structures of CIGS films at room temperature using a red laser with a 633 nm wavelength as the light source. The stoichiometric ratio and depth profiles of the CIGS films were analyzed by an energy dispersive spectrometer (EDS, Hitachi S3000N) and secondary ion mass spectrometer (SIMS, IMS-6f), respectively. The resistivity, carrier concentration and carrier mobility of the sample were measured using a Hall effect measurement apparatus (ECOPIA HMS-2000). Secondary ion mass spectroscopy (SIMS, IMS-6f) was used to understand the depth profiles of thin film elements before and after annealing treatment. The extraction voltages were 10 and 12.5 keV, respectively, and the current of the O²⁺ ion amounted to 80 and 120 nA, which impacted the sample

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surface with energy of 5.5 and 8 kV, respectively.

III. RESULTS AND DISCUSSIONS

Fig. 3 shows the electrical properties of thin films of various thicknesses. A Cu thickness equivalent to 2.8% the total thickness of the thin film produced a p-type conductivity with the highest carrier mobility. When the thickness was increased to 3.3%, the semiconductor material switched from a p-type to an n-type conductivity due to the formation of

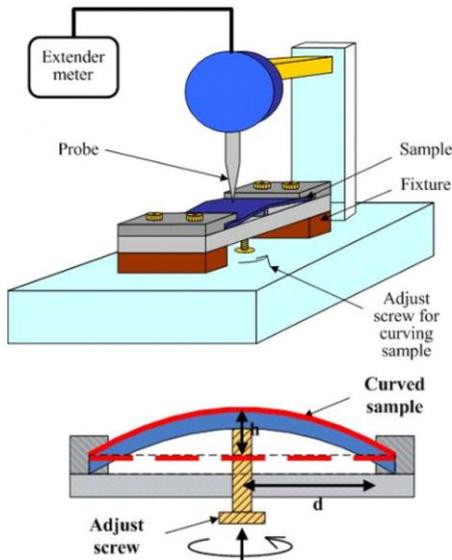


Fig. 2. A schematic diagram of curing sample mechanism for bending test.

In-Se or Cu-Se secondary phases. Table I lists the composition of the CIGS absorber layer produced under various deposition conditions followed by annealing at 798K for 20 minutes. When the thickness of the co-sputtered Cu was 3.3% (condition D) of the total thickness of the thin film, the composition ratio of Cu/III was 1.0. Previous studies have shown the formation of Cu-Se secondary phase under such conditions [16]; however, in n-type CIGS may form OVC-phases, such as CuIn_3Se_5 or $\text{Cu}_2\text{In}_4\text{Se}_7$ [17]. A composition ratio of 0.87 for Cu/III produced a narrowest full width at half maximum (FWHM).

TABLE I: THE COMPOSITIONS OF CIGS FILM FORM VARIOUS DEPOSITION CONDITIONS AFTER ANNEALING PROCESS AT 798 K FOR 20 MIN

Deposition condition	Compositions (at.%)				Composition ratio	
	Cu	In	Ga	Se	Cu/III	Ga/III
A	22.6	22.72	5.68	49	0.8	0.2
B	23.58	21.96	5.56	48.9	0.85	0.20
C	24	21.98	5.52	48.5	0.87	0.20
D	26.34	20.95	5.37	47.34	1.00	0.20

Fig. 4 shows the XRD patterns of CIGS films prepared at various Mo-5%Na thickness ratios. According to the Raman spectrum of CIGS thin films in Fig. 5, the optimal thickness ratio is 2.8, which produced the narrowest FWHM. It was found that excess Na content (above 2.8 %) does not contribute to the phase crystallization of CIGS chalcopyrite, and leads to the formation of NaInSe_2 phase. With a Mo-5%Na/Mo thickness ratio of 4.2%, chalcopyrite crystals

decrease in size [12]-[14], probably due to the formation of NaInSe_2 phase, which induced the number of In vacancies in the chalcopyrite structure, thereby compromising crystallinity.

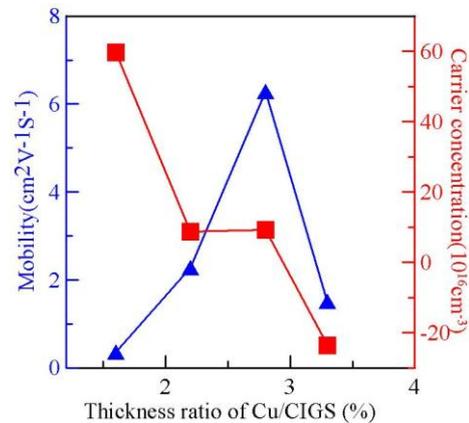


Fig. 3. The electrical properties of CIGS film as a function of thickness ratio of Cu/CIGS.

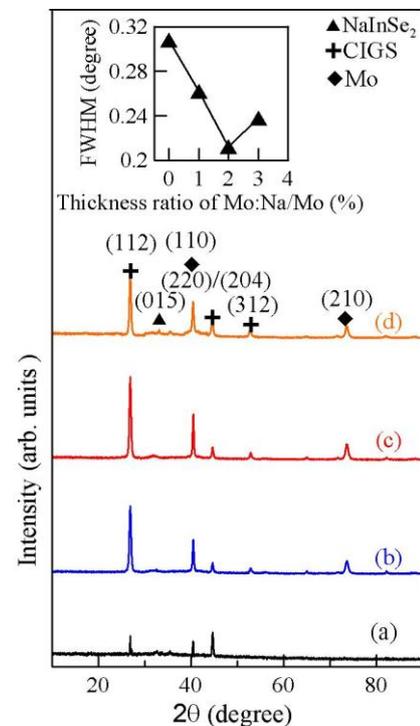


Fig. 4. The XRD patterns of CIGS film prepared at various thickness ratio Mo:Na:Mo: (a)without (b)1% (c)2% (d)3%.

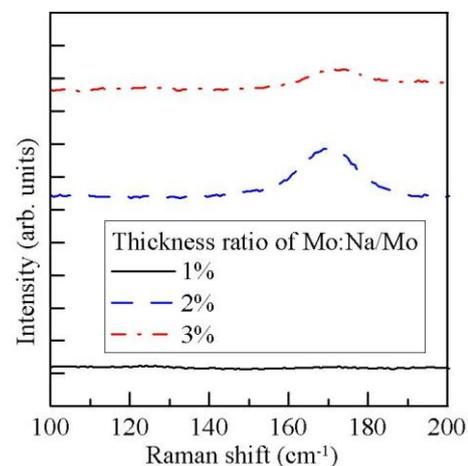


Fig. 5. The Raman shift CIGS film prepared at various thickness ratio Mo:Na:Mo.

Fig. 6 and Fig. 7 are EDS mapping images of the film surface and SIMS depth profile with a Mo-5%Na/Mo thickness ratio of 2.8%. Clearly, the diffusion of doped Na remains fairly even in both horizontal and vertical directions. This demonstrates that employing a Mo-5%Na target to supplement sodium by sputtering is an effective and feasible approach, capable of improving sodium distribution and applicable for large areas. We can see that the elemental In is richly distributed throughout the thin film and no signs of Se desorption from the surface are observed. The elements within the thin films are evenly distributed after annealing.

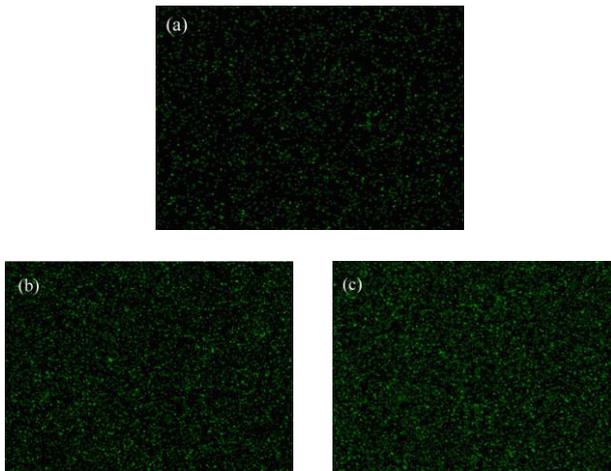


Fig. 6. The stoichiometry mapping image of Na element at various thickness ratio of Mo-5%Na/Mo (a) 1% (b) 2% (c) 3%.

Fig. 8 shows the surface morphology of Mo (700 nm)/SiO_x (300 nm)/SS431 (0.5 mm) films with various curvatures during the bending test. It can be seen that when the *h* value of curvature (see Fig. 2) increased to 0.5mm, the surface of the Mo electrode began cracking. Decreasing the radius of curvature increased the surface cracks to 1mm, leading to cracking within the SiO_x (300 nm). With a curvature of 0.75mm, cracks appear only on the Mo electrode, with no cracking observed on the SiO_x (under the Mo electrode). Clearly, the adhesion of SiO_x to SS431 is superior to the adhesion of SiO_x to Mo.

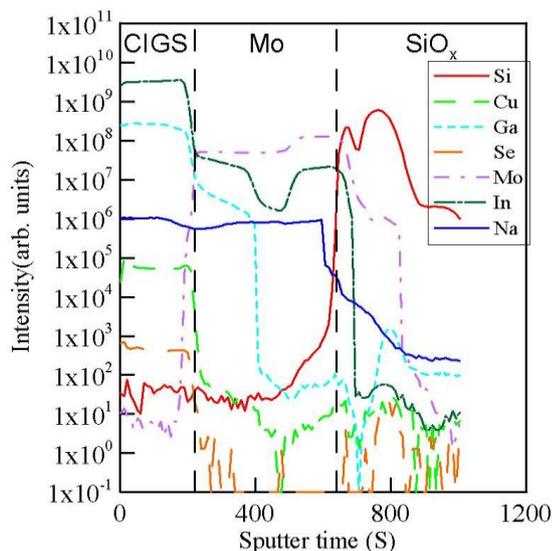


Fig. 7. Depth profile of each element of CIGS film at the thickness ratio of Mo-5%Na/Mo.

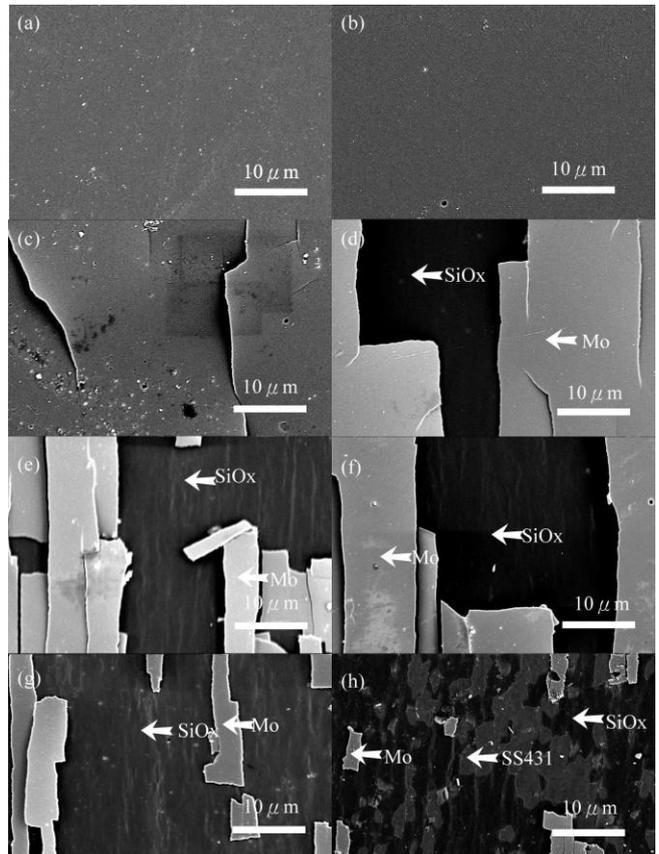


Fig. 8. SEM fractographies of Mo (700nm)/SiO_x (300nm)/SS431 (0.5mm) films with various curvatures during the bending test: (a) Before deflection (b)37mm (c)26mm (d)20mm (e)16mm (f)14mm (g)12mm (h)11mm.

IV. CONCLUSIONS

This study deposited CIGS thin films on Mo/SiO_x/SS431 substrates using magnetron sputtering. Our objectives were to introduce a Mo-5%Na target as a source of incorporate Na to the chalcopyrite structure and investigate its influence on the crystallinity of CIGS thin films. Experimental results demonstrate that adding Na in this manner can enhance the distribution of Na on the surface as well as the depth profile. When the thickness ratio of Mo-5%Na: Mo was 2.8%, the atomic ratio of Na was 0.48%, which enhanced crystallinity of CIGS. Excess Na dopant led to the formation of NaInSe₂ phase, which increases the number of In vacancies in chalcopyrite, thereby reducing crystallinity. The results of bending tests demonstrate that the adhesion of SiO_x to SS431 is superior to the adhesion of SiO_x to Mo.

REFERENCES

- [1] M. Kaelin, D. Rudmann, and A. N. Tiwari, *Sol. Energy*, vol. 77, 2004, pp. 749-756.
- [2] F. Kessler, D. Herrmann, and M. Powalla, *Thin Solid Films*, 2005, pp. 491-498.
- [3] S. Ishizuka, A. Yamada, K. Matsubara, P. Fons, K. Sakurai, and S. Niki, *Curr. Appl. Phys.*, vol. 10, 2010, pp. S154-S156.
- [4] K. Otte, *Thin Solid Films*, vol. 511-512, 2006, pp. 613-622.
- [5] T. Satoh, Y. Hashimoto, S. Shimakawa, S. Hayashi, and T. Negami, *Sol. Energy Mater. Sol. Cell*, vol. 75, 2003, pp. 65-71.
- [6] F. Kessler and D. Rudmann, *Sol. Energy*, vol. 77, 2004, pp. 685-695.
- [7] B. M. Basol, V. K. Kapur, C. R. Leidholm, and A. Halani, *25th Passaic Valley Sewerage Commissioners*, vol. 13-17, 1996, pp. 157-162.
- [8] Y. Sakurai, A. Yamada, P. Fons, K. Matsubara, T. Kojima, S. Niki, T. Baba, N. Tsuchimochi, Y. Kimura, and H. Nakanishi, *J. Phys. Chem. Solids*, vol. 64, 2003, pp. 1877-1880.

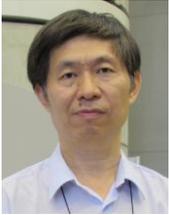
- [9] J. H. Yun, K. H. Kim, M. S. Kim, B. T. Ahn, S. J. Ahn, J. C. Lee, and K. H. Yoon, *Thin Solid Films*, vol. 515, 2007, pp. 5876-5879.
- [10] R. Caballero, C. A. Kaufmann, T. Eisenbarth, M. Cancela, R. Hesse, T. Unold, A. Eicke, R. Klenk, and H. W. Schock, *Thin Solid Films*, vol. 517, 2009, pp. 2187-2190.
- [11] I. Roca *et al.*, *Thin Solid Films*, vol. 519, 2011, pp. 7300-7303.
- [12] V. Izquierdo-Roca *et al.*, *Thin Solid Films*, vol. 519, pp. 7300-7303, 2011.
- [13] S. Roy, P. Guhaa, S. N. Kundu, H. Hanzawa, S. Chaudhuri, and A. K. Pal, *Materials Chem. Phys.*, vol. 73, 2002, pp. 24-30.
- [14] W. Witte, Robert Kniese, Michael Powalla, *Thin Solid Films*, vol. 517, pp. 867-869. 2008.
- [15] R. Caballero *et al.*, *Thin Solid Films*, vol. 517, 2009, pp. 2187-2190.
- [16] M. L. Fearheiley, *Sol. Cells*, vol. 16, 1986, pp. 91-100.
- [17] B. J. Stanbery, *Crit. Rev. Solid. State*, vol. 27, 2002, pp. 73-117.



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