Preparation of a-IZO thin films by RF magnetron sputtering for Cu (In, Ga) Se2 solar cells

Haiyan Jiang, Shuai Wang, Ying Xu*, Shaopeng Yang

Hebei Key Laboratory of Optic-Electronic Information Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China

*Corresponding author e-mail: xuying4444@sina.com

Abstract. Indium zinc oxide (IZO) thin films were prepared by radio frequency magnetron sputtering at room temperature for the applications of Cu(In,Ga)Se2 (CIGS) solar cells. The effect of the RF power during the deposition process on the structural, optical, and electrical properties of the films was investigated. XRD analysis revealed that all films showed an amorphous phase. The average optical transmittance in the range of 300-1500 nm decreased with increasing deposition power. Hall effect measurements show that the optimal hall mobility of 34.22 cm$^2$/Vs and resistivity of 4.09×10$^{-4}$ Ω•cm were obtained at the power of 90 W. The optimized IZO film was applied to CIGS solar cells, and an efficiency of 13.81% in CIGS solar cell has been achieved.

1. Introduction

In the last couple of years, copper indium gallium diselenide (CIGS) based thin film solar cells are receiving worldwide attention for solar power generation [1, 2]. CIGS solar cell efficiencies up to 22.9% have been achieved by Solar Frontier [3]. Transparent conducting oxide (TCO) plays a crucial role in the devices. Various TCO films such as Indium tin oxide ITO [4], Al-doped ZnO (AZO) [5], B-doped ZnO (BZO) [6], and Ga-doped ZnO (GZO) [7] have been employed as window layers for electrical current collection in thin film photovoltaic devices [8]. The dominant TCO is ITO due to its superior electrical resistivity and good transmittance in the visible range [9]. However, ITO films with low resistivity and high optical transmittance were obtained at either high deposition temperatures or with high-temperature post-thermal treatments [4, 10, 11], which limited the application of ITO in CIGS solar cells [12, 13]. Although the CIGS solar cells have reached interesting conversion efficiencies using AZO, BZO, and GZO as transparent conductive electrodes. However, their resistivity of ZnO based TCO thin films is higher than that of other TCO films at the same thickness. Moreover, the optical transmittance is lower in the near-infrared (NIR) region by causing plasma oscillations [8].

Indium zinc oxide (IZO) is an n-type TCO with bandgap energies of 3.1-3.6 eV [8, 14]. IZO thin films exhibit superior electrical conductivity and optical transmission in the visible region and are widely used for solar cell applications [15]. Compared to the ZnO based TCO window layer in the CIGS solar cells, IZO exhibits the higher carrier mobility and moisture stability, which can also be deposited at low temperatures [13]. Furthermore, IZO can be applied in the perovskite/CIGS or perovskite/Si tandem solar cells as the intermediate transition layer, because the transmittance at wavelengths larger than 1100 nm is much better than for ITO or ZAO [16, 17].
The various methods were used to deposit IZO such as spray pyrolysis [18], hybrid inks [19], chemical bath deposition [20], atomic layer deposition [21], pulsed laser deposition [22, 23] and magnetron sputtering [24-26]. Among the above techniques, magnetron sputtering is one of the most applicable deposition routes due to its simplicity and maturity in industrial application. The properties of IZO thin films depend strongly on the deposition processes associated with different control parameters [27].

In the study, the IZO thin films are prepared by RF magnetron sputtering at different sputtering RF power (60-200 W) for application as window layers in CIGS thin films solar cells. The influences of the RF power on the sputtered films as well as corresponding CIGS thin film solar cells are investigated.

2. Experimental

In this work, the IZO thin films were prepared on soda-lime glass (SLG) by RF magnetron sputtering technique at room temperature with different RF power (60, 90, 120, 150, 180 and 200 W) using commercially 2 inches IZO target (99.95% purity, containing 10 wt.% ZnO). The substrates were cleaned ultrasonically, rinsed with deionized water and alcohol, dried with high purity nitrogen gas and then loaded into the deposition chamber. Argon was used as sputtering gas. The work pressure used during the sputtering was 1.0 Pa. The film thickness was controlled at approximately 360(±10) nm by adjusting the sputtering time.

To investigate the effect of various IZO films on the performance of CIGS solar cells, the solar cells were fabricated with the structure of SLG/Mo/CIGS/CdS/i-ZnO/IZO/Al. As our previous reports [28, 29], the CIGS layers (~2 μm) were deposited on Mo coated SLG substrates by the three-stage co-evaporation process in a high vacuum chamber. The CdS layers (~50 nm) were deposited by chemical bath deposition. The i-ZnO (~80 nm) and IZO (~360 nm) layers by RF magnetron sputtering were deposited in sequence. The Al contacts were finally formed by electron beam evaporation with a mask.

The structure of IZO films was studied by Bruker D8 Advance with Cu Ka radiation. The morphologies of the IZO films were identified by the field emission scanning electronic microscopy (FESEM) (FEI NOVA NANOSEM 450) and the atomic force microscopy (AFM) (Bruker Multimode 8). The electrical properties of the films were determined by Hall measurement with Van der Pauw method. The optical transmittance were investigated using a UV-Vis-NIR spectrophotometer (Hitachi U-4100). The current density–voltage (J–V) curves of solar cells were measured under the standard test conditions (AM 1.5G, 100 mW/cm², and 25 °C). The external quantum efficiency (EQE) of the solar cells was measured by an Enlitech QER3011 system equipped with a 150 W xenon light source.

3. Results and Discussion

3.1. Films Analysis

![X-ray diffraction patterns of IZO films deposited with various RF power.](image)

Figure 1. X-ray diffraction patterns of IZO films deposited with various RF power.

XRD patterns of IZO films deposited with different RF power are shown in Fig. 1. All patterns did not exhibit a crystalline peak. There only a broad amorphous shoulder at around 2θ=30–32° was observed,
indicating that all films are completely amorphous irrespective of the investigated working power range of 60W to 150W. As previously reported in the literature, IZO films usually grow amorphous on glass substrates [16]. A similar result was reported by Warasawa et al. [8].

The influence of RF power on the surface morphology of the IZO thin films is shown in the SEM image (Fig. 2). In general, all samples show a uniform, smooth, crack-free and well covered on the substrate surface. A regular surface and small grains, with dimensions below 50 nm, can be observed. Through AFM measurement, the surface roughness (root mean square deviation, Rq) of IZO thin films is 4.39, 2.85, 3.59 and 3.07 nm, when the sputtering power is 60, 90, 120 and 150 W, respectively. As seen in Fig.3.

**Figure 2.** SEM morphology images of IZO films deposited with various RF power, (a) 60W, (b) 90W, (c) 120W, (d) 150W, (e) 180W, (f) 200W.

**Figure 3.** AFM images of IZO films deposited with various RF power, (a) 60W, (b) 90W, (c) 120W, (d) 150W.

For further investigating the electronic properties of the IZO films, the Hall measurement was employed by van der Pauw method. Fig. 4 shows the electrical properties of IZO films as a function of RF power. It is clear that electrical properties are strongly affected by RF power. The carrier mobility (μ) of IZO films between 32.66 to 34.22 cm²/V and showed a slight variation when the sputtering power increases from 60 to 90 W, and then decreases sharply from 32.66 cm²/Vs to 18.46 cm²/Vs as the RF power increases from 90 to 150 W.
power increases from 90 to 200 W. The corresponding carrier concentration (n) increases monotonically from $3.55 \times 10^{20}/\text{cm}^3$ to $5.84 \times 10^{20}/\text{cm}^3$ with the RF power, the resistivity (ρ) first decreases to the minimum value $4.09 \times 10^{-4} \Omega \cdot \text{cm}$, then increases with RF power. In general, μ is limited by the carrier scattering processes, including those of grain boundary scattering, impurities scattering, and phonons scattering. Many studies reported that the amorphous structure can effectively eliminate scattering originating from grain boundaries [30]. Ionized impurity scattering is one of the most important mechanisms limiting the electron transport at high n [23]. Makise et al. suggested for films with $n > 3 \times 10^{20}/\text{cm}^3$, it is found that the μ is limited by ionized impurity scattering [31]. For amorphous IZO films, the Zn atoms are mostly placed in interstitial positions. The interstitial Zn$^{2+}$ ions, which act as dominant donors in the IZO films, would have increased due to oxygen deficiency in the sputter process. The increase of Zn$^{2+}$ ionized impurity result in an increase in the carrier concentration. The observation is in agreement with literatures [24, 32, 33].

![Figure 4](image1.png)

**Figure 4.** Resistivity, carrier concentration and mobility of IZO films deposited with various RF power.

The optical transmittance spectra of the IZO thin films with different sputtering power are shown in Fig. 5. The average transparency of every deposited film is 80%± 5% between 300 nm and 1500 nm, indicating meet the requirements for solar cells applications as the window layer. With increasing sputtering power, the average transparency sharply decrease in all regions. The optical band gap (Eg) values of IZO thin films were derived from the Tauc equation [34]. Fig.6 shows the $(\alpha h\nu)^2$ versus photon energy hν for the IZO thin films deposited different RF power. The obtained Eg of IZO thin films was given out in Fig.6. The optical band gap value increased from 3.15 eV to 3.24 eV as the sputtering power increased from 60 W to 200 W. The increasing of Eg is attributed to the increase in carrier concentration with RF power, which is explained by the Burstein–Moss effect [32, 35].

![Figure 5](image2.png)

**Figure 5.** Transmission spectra of IZO films deposited with various RF power.
Figure 6. Optical band gap of IZO films deposited with various RF power.

3.2. Devices Analysis

Figure 7. The J–V curve parameters of CIGS solar cells with various RF power.

CIGS thin film solar cells with the structure of glass/Mo/CIGS absorber/CdS/i-ZnO/IZO/Al grid without an anti-reflection layer were fabricated to study the influence of the sputtering power on the CIGS solar cells and compared to AZO thin films employed as the window layers. Fig. 7 shows the current density–voltage (J–V) curve for individual best CIGS solar cells with IZO window layers deposited at different sputtering power. The values of the short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$) and photoelectric conversion efficiency (PCE) of each solar cell were listed in the Table 1. The $V_{oc}$ of CIGS solar cells is between 633 to 644 mV. The $V_{oc}$ drops to 633.8 mV at the sputtering power of 150 W, at the same time the $J_{sc}$ decreases from 30.82 to 27.92 mA/cm$^2$. With increasing the RF power, the decreases of the QE can be ascribed to the higher absorption of the IZO layer in the whole range of spectra.

Table 1. The device parameters of CIGS solar cells based on different RF power.

| RF Power | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | Efficiency (%) |
|----------|--------------|----------------------|--------|----------------|
| IZO-60W  | 638.9        | 30.82                | 68.12  | 13.41          |
| IZO-90W  | 644.6        | 30.55                | 70.12  | 13.81          |
| IZO-120W | 643.5        | 28.93                | 68.70  | 12.61          |
| IZO-150W | 633.8        | 27.92                | 67.74  | 11.98          |
| AZO      | 640.4        | 30.31                | 67.37  | 13.07          |
4. Conclusion
The IZO thin films were prepared by magnetron sputtering with different RF power on SLG and on CIGS solar cells at room temperature. From XRD examination, the structure of all IZO films was amorphous. Hall effect measurements show that the optimal hall mobility of 34.22 cm²/Vs and resistivity of 4.09×10⁻⁴ Ω•cm were obtained at the power of 90 W. Both the resistivity and carrier concentration of IZO thin films increases with the increasing sputtering power. The increase of carrier concentration is mainly related to the enhancement of Zn²⁺ interstitials, while the decrease of carrier mobility might be mainly ascribed to the impurities scattering. The CIGS thin film solar cells with IZO thin films prepared at a moderate sputtering power show a high Jsc and a high FF. The highest efficiency CIGS thin film solar cell of 13.81% has been achieved without anti-reflection laye.

References
[1] J. Ramanujam, U.P. Singh, Copper indium gallium selenide based solar cells – a review, Energy Environ. Sci. 10(6) (2017) 1306-1319.
[2] M. Powalla, S. Paetel, E. Ahlswede, R. Wuerz, C.D. Wessendorf, T.M. Friedlmeier, Thin – film solar cells exceeding 22% solar cell efficiency: An overview on CdTe-, Cu (In,Ga)Se2-, and perovskite-based materials, Applied Physics Reviews 5(4) (2018) 041602.
[3] M.A. Green, Y. Hishikawa, E.D. Dunlop, D.H. Levi, J. Hohl-Ebinger, M. Yoshita, A.W.Y. Ho-Baillie, Solar cell efficiency tables (Version 53), Progress in Photovoltaics: Research and Applications 27(1) (2019) 3-12.
[4] C.L. Chuang, M.W. Chang, N.P. Chen, C.C. Pan, C.P. Liu, Improving Performance of CIGS Solar Cells by Annealing ITO Thin Films Electrodes, International Journal of Photoenergy 2015 (2015) 1-8.
[5] R. Menner, D. Hariskos, V. Linss, M. Powalla, Low-cost ZnO: Al transparent contact by reactive rotatable magnetron sputtering for Cu(In,Ga)Se2 solar modules, Thin Solid Films 519(21) (2011) 7541-7544.
[6] T. Koida, J. Nishinaga, H. Higuchi, A. Kurokawa, M. Iioka, Y. Kamikawa-Shimizu, A. Yamada, H. Shibata, S. Niki, Comparison of ZnO: B and ZnO: Al layers for Cu(In,Ga)Se 2 submodules, Thin Solid Films 614 (2016) 79-83.
[7] V. Garg, B.S. Sengar, P. Sharma, A. Kumar, Aaryashree, S. Kumar, S. Mukherjee, Sputter-instigated plasmon-enhanced optical backscattering layer in ultrathin solar cells: Application of GZO in CIGSe material system, Solar Energy 174 (2018) 35-44.
[8] M. Warasawa, A. Kaijo, M. Sugiyama, Advantages of using amorphous indium zinc oxide films for window layer in Cu(In,Ga)Se2 solar cells, Thin Solid Films 520(6) (2012) 2119-2122.
[9] M. Murugesan, D. Arjunraj, J. Mayandi, V. Venkatachalapathy, J.M. Pearce, Properties of Al-doped zinc oxide and In-doped zinc oxide bilayer transparent conducting oxides for solar cell applications, Materials Letters 222 (2018) 50-53.
[10] R. Hashimoto, Y. Abe, T. Nakada, High mobility titanium-doped In2O3 thin films prepared by sputtering/post-annealing technique, Applied physics express 1(1) (2008) 015002.
[11] G.H. Wang, C.Y. Shi, L. Zhao, H.W. Diao, W.J. Wang, Transparent conductive Hf-doped In 2 O 3 thin films by RF sputtering technique at low temperature annealing, Applied Surface Science 399 (2017) 716-720.
[12] X. Niu, H. Zhu, X. Liang, Y. Guo, Z. Li, Y. Mai, Air-annealing of Cu (In, Ga)Se2/CdS and performances of CIGS solar cells, Applied Surface Science 426 (2017) 1213-1220.
[13] A. Chirila, P. Reinhard, F. Pianezzi, P. Bloesch, A.R. Uhl, C. Fella, L. Kranz, D. Keller, C. Gretener, H. Hagendorfer, D. Jaeger, R. Erni, S. Nishiwaki, S. Buecheler, A.N. Tiwari, Potassium-induced surface modification of Cu(In,Ga)Se2 thin films for high-efficiency solar cells, Nat Mater 12(12) (2013) 1107-11.
[14] A.J. Leenheer, J.D. Perkins, M.F.A.M. van Hest, J.J. Berry, R.P. O’Hayre, D.S. Ginley, General mobility and carrier concentration relationship in transparent amorphous indium zinc oxide films, Physical Review B 77(11) (2008) 115215.
[15] J.S. Park, W.-J. Maeng, H.-S. Kim, J.-S. Park, Review of recent developments in amorphous oxide semiconductor thin-film transistor devices, Thin Solid Films 520(6) (2012) 1679-1693.

[16] R. Menner, M. Cemernjak, S. Paetel, W. Wischmann, Application of indium zinc oxide window layers in Cu (In,Ga)Se 2 solar cells, Thin Solid Films 633 (2017) 239-242.

[17] T. Wahl, J. Hanisch, S. Meier, M. Schultes, E. Ahlswede, Sputtered indium zinc oxide rear electrodes for inverted semitransparent perovskite solar cells without using a protective buffer layer, Organic Electronics 54 (2018) 48-53.

[18] Pasquarelli R, Solution deposition of amorphous IZO films by ultrasonic spray pyrolysis, 35th IEEE Photovoltaic Specialists Conference, Honolulu (2010) pp. 002471-002473.

[19] J.S. Lee, Low-temperature Processing of Inkjet-printed IZO Thin-film Transistors, (2014).

[20] T. Kodzasa, T. Nobeshima, K. Kuribara, M. Yoshida, Thin film transistor performance of amorphous indium–zinc oxide semiconductor thin film prepared by ultraviolet photoassisted sol–gel processing, Japanese Journal of Applied Physics 57(5S) (2018) 05GD01.

[21] A. Illiberi, I. Katsouras, S. Gazibegovic, B. Cobb, E. Nekovic, W. van Boekel, C. Frijters, J. Maas, F. Roozeboom, Y. Creyghton, P. Poodt, G. Gelinck, Atmospheric plasma-enhanced spatial-ALD of InZnO for high mobility thin film transistors, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 36(4) (2018) 04F401.

[22] M. Socol, N. Preda, A. Stanculescu, C. Breazu, C. Florica, O. Rasoga, F. Stanculescu, G. Socol, IZO deposited by PLD on flexible substrate for organic heterostructures, Applied Physics A 123(5) (2017).

[23] X.Z. Yan, X. Man, J.G. Ma, H.Y. Xu, Y.C. Liu, Modulation of electron transportation in amorphous and polycrystalline indium–zinc oxide films grown by pulse laser deposition, Journal of Non-Crystalline Solids 423-424 (2015) 18-24.

[24] N. Ito, Y. Sato, P.K. Song, A. Kajio, K. Inoue, Y. Shigesato, Electrical and optical properties of amorphous indium zinc oxide films, Thin Solid Films 496(1) (2006) 99-103.

[25] W. Witte, R. Carron, D. Hariskos, F. Fu, R. Menner, S. Buecheler, IZO or IOH Window Layers Combined with ZnO, S and CdS Buffers for Cu(In,Ga)Se2 Solar Cells, physica status solidi (a) 214(12) (2017) 1700688.

[26] R. Menner, S. Paetel, W. Wischmann, M. Powalla, Indium zinc oxide window layer for high-efficiency Cu (In,Ga)Se 2 solar cells, Thin Solid Films 634 (2017) 160-164.

[27] D.G. Jun, Fabrication of IZO thin films for flexible organic light emitting diodes by RF magnetron sputtering, Journal of Ceramic Processing Research 13(Special. 2) (2012) 260-264.

[28] X. Niu, H. Zhu, W. Zhang, X. Laing, Y. Guo, Z. Li, J. Chen, Y. Xu, Y. Mai, Control of oxygen for magnetron sputtered ZnO: Al window layer in Cu(In,Ga)Se2 thin film solar cells, physics status solidi (a) 214(10) (2017) 1700132.

[29] X. Liang, H. Zhu, J. Chen, D. Zhou, C. Zhang, Y. Guo, X. Niu, Z. Li, Y. Mai, Substrate temperature optimization for Cu (In, Ga)Se2 solar cells on flexible stainless steels, Applied Surface Science 368 (2016) 464-469.

[30] T. Koida, Y. Ueno, J. Nishinaga, Y. Kamikawa, H. Higuchi, M. Iioka, H. Takahashi, H. Shibata, S. Niki, Current status of transparent conducting oxide layers with high electron mobility and their application in Cu (In,Ga)Se 2 mini-modules, Thin Solid Films 673 (2019) 26-33.

[31] K. Makise, B. Shinozaki, T. Asano, K. Mitsuishi, K. Yano, K. Inoue, H. Nakamura, Relationship between variable range hopping transport and carrier density of amorphous In2O3–10 wt. % ZnO thin films, Journal of Applied Physics 112(3) (2012) 033716.

[32] M. Nisha, M.K. Jayaraj, Influence of RF power and fluorine doping on the properties of sputtered ITO thin films, Applied Surface Science 255(5, Part 1) (2008) 1790-1795.

[33] J.-W. Jeon, D.-W. Jeon, T. Sahoo, M. Kim, J.-H. Baek, J.L. Hoffman, N.S. Kim, I.-H. Lee, Effect of annealing temperature on optical band-gap of amorphous indium zinc oxide film, Journal of Alloys and Compounds 509(41) (2011) 10062-10065.

[34] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, Materials Research Bulletin 3(1) (1968) 37-46.
[35] V.S. Vidhya, V. Malathy, T. Balasubramanian, V. Saaminathan, C. Sanjeeviraja, M. Jayachandran, Influence of RF power on the growth mechanism, preferential orientation and optoelectronic properties of nanocrystalline ITO films, Current Applied Physics 11(3) (2011) 286-294.