

# Intrinsic ZnO films fabricated by DC sputtering from oxygen-deficient targets for Cu(In,Ga)Se<sub>2</sub> solar cell application

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Intrinsic zinc oxide films, normally deposited by radio frequency (RF) sputtering, are fabricated by direct current (DC) sputtering. The oxygen-deficient targets are prepared via a newly developed double crucible method. The 800-nm-thick film obtains significantly higher carrier mobility comparing with that of the 800-nm-thick ZnO film. This is achieved by the widely used RF sputtering, which favors the prevention of carrier recombination at the interfaces and reduction of the series resistance of solar cells. The optimal ZnO film is used in a Cu (In, Ga) Se<sub>2</sub> (CIGS) solar cell with a high efficiency of 11.57%. This letter demonstrates that the insulating ZnO films can be deposited by DC sputtering from oxygen-deficient ZnO targets to lower the cost of thin film solar cells.

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High resistance transparent intrinsic zinc oxide (i-ZnO) thin film has been widely used as the front electrode in transparent electronics and photovoltaic devices because of its low cost and nontoxicity. Owing to its unique characteristics of high transparency and adjustable resistivity in a certain range, the use of i-ZnO thin films as diffusion barrier layers of a-Si/ $\mu$ c-Si, CdTe, and CIGS thin-film solar cells has been advantageous<sup>[1-7]</sup>. The i-ZnO layer not only hampers the interdiffusion of the contacts and the p-n junction, but also prevents the short-circuiting of the back- and front-contacts to enhance the uniformity and stability of the cell<sup>[8,9]</sup>.

ZnO films have been prepared by several methods, such as magnetron sputtering, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), physical vapor deposition (PVD), and metal organic chemical vapor deposition (MOCVD)<sup>[10-14]</sup>. Among these methods, magnetron sputtering is the most widely used technique because of its favorable features, such as lower process temperature, good film adhesion, and good uniformity of thickness distribution. Generally, ceramic intrinsic ZnO target is used and the radio frequency (RF) sputtering process is mandatory because of the poor conductivity of the target<sup>[15]</sup>. In industrial applications, RF power supply is difficult to be used in mass productions due to its high cost, whereas the direct current (DC) power supply platform is more popularly utilized because of its higher technique uniformity, controllable function, and lower cost. Researchers have tried to fabricate high resistance ZnO thin films with the conductive ZnO:Al (AZO) target by the DC sputtering method under a high oxygen atmosphere partial pressure<sup>[16-19]</sup>. However, the very high oxygen content in the plasma would damage the inner frontier films, which is deleterious to device

performance<sup>[20,21]</sup>. Furthermore, the Al impurity could scatter carriers and reduce its mobility.

In this letter, i-ZnO films were fabricated by DC sputtering with home-made ZnO targets, employing a new way of preparing the oxygen-deficient ZnO target. The ZnO targets were annealed in a reduced atmosphere via a double crucible method, and further applied in the DC magnetron sputtering because the as-sintered ZnO target is somehow electrically conductive in the direct acquisition of high resistance transparent ZnO films. The microstructure and the electrical and optical properties of the dc-sputtered ZnO films were investigated through comparison with the RF-sputtered ZnO films deposited from the commercial target.

ZnO targets were prepared from dry-pressed starting materials of ZnO sintered at 1350 °C for 4 h. The as-sintered targets were annealed via a double crucible method for 2 h at 1000 °C. During the annealing process, a small crucible containing the sintered target was placed inside a large one. In Fig. 1, the inner crucible was

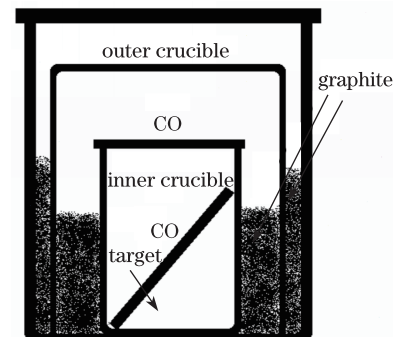


Fig. 1. Schematic diagram of the double crucible annealing method.

sealed by an upside-down crucible buried in graphite. When heated, the limited oxygen in the upside-down crucible reacted with the graphite. Carbon monoxide (CO) was produced, creating a reducing atmosphere in the inner crucible. The oxygen atoms in the ZnO lattice and on the grain boundaries were withdrawn by the reduced atmosphere, resulting in an oxygen deficient state in the target. The resistivity of the ZnO targets is  $0.185 \Omega\text{-cm}$  at room temperature.

ZnO films were deposited in a high vacuum magnetron sputtering system (JGP450) with a base pressure of  $2.0 \times 10^{-4}$  Pa, under a flow of high-purity Ar/O<sub>2</sub> mixture (0.9% O<sub>2</sub> content, 15 sccm). DC magnetron sputtering was employed to deposit films with the home-made oxygen-deficient ZnO target on glass slides with a holder-target distance of 90 mm. During the sputtering, pressure and the sputtering power were maintained at 1.2 Pa and 80 W, respectively. When used as the diffusion barrier in thin film CIGS solar cells, the thickness of the i-ZnO layer is normally controlled between 60–120 nm. In the current study, the film was deposited for 2 min and the thickness was measured to be 80 nm. One 800-nm sample was prepared for the accuracy of characterization. For comparison, another RF-sputtered ZnO film deposited from the commercial target was also prepared with the same thickness.

Bruker AXS Advance D8 Focus diffractometer using CuK $\alpha$  radiation was applied for X-ray diffraction (XRD) measurement. Field emission scanning electron microscopy (FE-SEM) was performed using LEO-1530VP. In combination with the use of a profilometer (Dektak 150), FE-SEM was used to evaluate the surface morphologies and thickness of the ZnO films. Transmission measurements were conducted on a Hitachi U-4100 spectrometer in the wavelength range of 300–2200 nm. The van der Pauw method was used with an Accent HL5580PC to measure the electrical transport properties, including electrical resistivity, carrier concentration, and hall mobility, at room temperature. A magnetic field of 3 T was applied in these measurements.

The XRD patterns of the as-deposited i-ZnO thin films are shown in Fig. 2. Three samples are shown to be oriented along the (002) direction, indicating a well-pronounced (002) preferential growth. The XRD peaks of the DC-80 W-80 nm ZnO film are weak and broad. As the thickness increased to 800 nm for the DC- or RF- sputtered films, the full-width at half-maximum (FWHM) of the (002) planes in the respective film decreased and the peak intensity measured in counts per second (CPS) increased, as listed in Table 1. For the same thickness, the DC-sputtered sample showed sharper peaks and stronger intensity than its RF-sputtered counterpart, indicating better crystallization.

The optical properties of the as-deposited ZnO films are depicted in Fig. 3. All the as-deposited samples showed a high transmittance of approximately 90% in the entire spectrum range of 400–2100 nm, and the DC-sputtered film achieved similar transmittance as the RF-sputtered one. The remaining extremely high transmittance in the near-infrared region is consistent with the low carrier concentration of the films, shown in Table 1, which depresses the plasma frequency.

The FE-SEM images of the surface morphologies of the

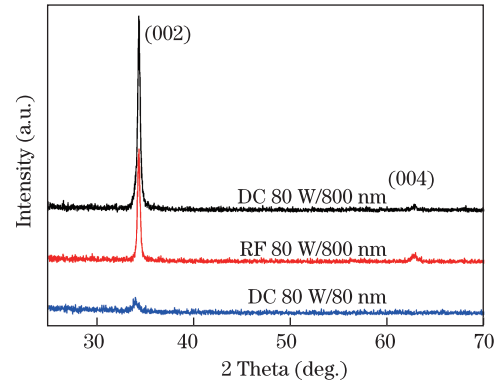


Fig. 2. XRD patterns of i-ZnO films deposited by DC and RF sputtering.

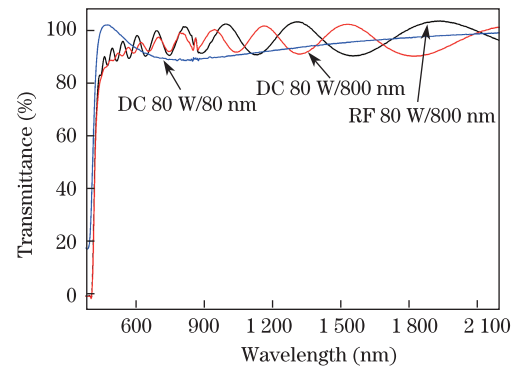


Fig. 3. (Color online) Transmittance of i-ZnO films deposited by DC and RF sputtering.

**Table 1. Structural and Electrical Properties of the As-deposited ZnO Films**

Sample	DC-80	DC-80	DC-80
	W/2 min	W/20 min	W/30 min
Thickness (nm)	80	800	800
CPS	30.7	382.2	222.1
FWHM ( $2\theta$ )	0.416	0.173	0.209
$R_{sq}$ ( $\Omega/\text{sq}$ )	$1.89 \times 10^6$	$1.91 \times 10^3$	$4.73 \times 10^4$
$\rho$ ( $\Omega\text{-cm}$ )	11.2	0.153	3.78
$\mu$ ( $\text{cm}^2/\text{V}\cdot\text{s}$ )	7.08	42.2	22.7
$N$ ( $\times 10^{17} \text{cm}^{-3}$ )	0.80	9.74	0.73

as-deposited ZnO films are shown in Fig. 4. The surface of the DC-80 nm film (Fig. 4(c)) is relatively flat, with a large quantity of densely packed and uniform grains. With the deposition time prolonged and the thickness increased to 800 nm, both DC (Fig. 4(a)) and RF (Fig. 4(b)) produced large and clear grains while the surfaces of which are different. The DC-sputtered film showed larger crystal size and higher crystallinity.

The electrical properties of the films are listed in Table 1. The 80-nm DC film obtained a square resistance of  $1.89 \times 10^6 \Omega/\text{sq}$ , which fits well with the application of the thin film CIGS solar cells as diffusion barrier. As the deposited time was prolonged and the thickness increased

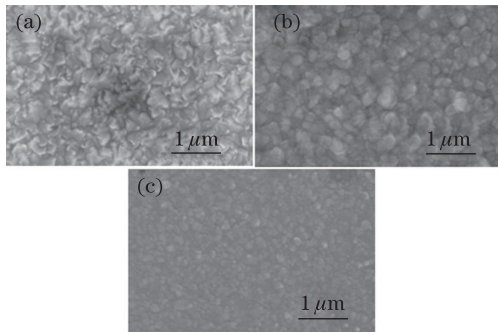


Fig. 4. SEM images of i-ZnO films deposited by DC and RF sputtering: (a) DC-800 nm, (b) RF-800 nm, and (c) DC-80 nm, respectively.

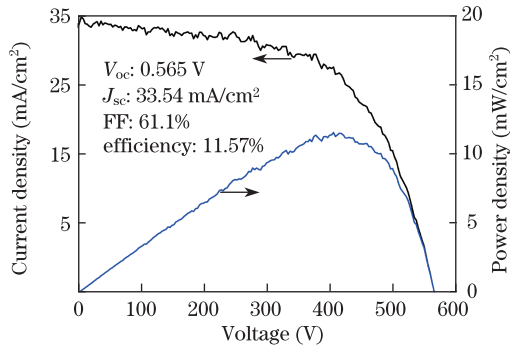


Fig. 5.  $I$ - $V$  characteristic of the CIGS solar cell.  $V_{oc}$  is open circuit,  $J_{sc}$  is short-circuit current, and FF is fill factor.

to 800 nm, the square resistance decreased to  $1.91 \times 10^3 \Omega$ , and the carrier mobility increased to as high as  $42.2 \text{ cm}^2/\text{V}\cdot\text{s}$ . Compared with the DC-sputtered sample, the RF-sputtered film exhibited lower conductivity and carrier mobility with the same sputtering power and thickness.

Relatively, the DC-sputtered film with the home-made oxygen-deficient target exhibited high conductivity and carrier mobility, which could be ascribed to the larger size of the grains and better crystallization. This induced a reduction in the height of the grain boundary potential barrier, as well as the number of grain boundaries that the carrier has to cross during electrical transport. For the application of thin film CIGS solar cells as the diffusion barrier, the enhanced carrier mobility of the ZnO thin film could considerably benefit the retardation of the recombination of the photon-generated electron-hole pairs in the interface and the prevention of the diffusion of the electrons. This would not only hamper the interdiffusion of the contacts and the p-n junction, but also favor the reduction of the series resistance of solar cells. Consequently, the open voltage and filling factor of the cell will be significantly improved.

To examine the performance of the DC-sputtered i-ZnO thin film in transparent electrode applications, the DC-sputtered 80-nm ZnO film prepared by home-made oxygen-deficient target was used as the diffusion barrier layer of a CIGS solar cell. The CIGS precursor layer with a molar ratio of Cu:In:Ga equals to 0.95:0.75:0.25 was deposited on the Mo/glass substrate, and annealed at  $500^\circ\text{C}$  in a Se-contained graphite box. CdS buffer layer, with a thickness of approximately 60 nm, was

deposited by chemical bath deposition (CBD). Subsequently, the DC-sputtered i-ZnO thin film was deposited by home-made oxygen-deficient target. The thickness was controlled to approximately 80 nm. The transparent front contact made of ZnO:Al with a thickness of 800 nm was placed on top of the cell to achieve the required conductivity.

The  $I$ - $V$  characteristic of the fabricated  $0.5 \times 0.5$  (cm) CIGS solar cell is shown in Fig. 5. The photocurrent density of the cell at air mass (AM) 1.5 illumination ( $100 \text{ mW}/\text{cm}^2$ ) and at room temperature is high, with values up to  $33.54 \text{ mA}/\text{cm}^2$ . The as-fabricated CIGS solar cell without an antireflective film has an efficiency of 11.57%. This result confirms that the DC-sputtered ZnO film is suitable as the diffusion barrier layer of CIGS thin film solar cells.

In conclusion, high performance i-ZnO films are deposited from oxygen-deficient targets by DC sputtering. The oxygen-deficient targets are prepared via a newly developed double crucible method. Aside from the comparatively high transmittance and suitable resistivity, considerably higher carrier mobility is obtained with the film by RF sputtering compared with commercial intrinsic targets. The enhanced carrier mobility of the ZnO film as a diffusion barrier provides significant advantage in the prevention of carrier recombination at the interfaces and in the reduction of the series resistance of solar cells. The optimal ZnO film is used in a CIGS solar cell with a high efficiency of 11.57%, indicating that our film satisfies the requirements for transparent electrode applications, particularly as the diffusion barrier layer of thin film solar cells.

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