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Effect of RF power on the properties of transparent conducting zirconium-doped zinc oxide films prepared by RF magnetron sputtering*

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Transparent and conducting zirconium-doped zinc oxide films with high transparency and relatively low resistivity have been successfully prepared by radio frequency (RF) magnetron sputtering at room temperature. The RF power is varied from 75 to 150 W. At first the crystallinity and conductivity of the film are improved and then both of them show deterioration with the increase of the RF power. The lowest resistivity achieved is $2.07 \times 10^{-3}\,\Omega\,\mathrm{cm}$ at an RF power of 100 W with a Hall mobility of $16\,\mathrm{cm^2V^{-1}s^{-1}}$ and a carrier concentration of $1.95 \times 10^{20}\,\mathrm{cm^{-3}}$. The films obtained are polycrystalline with a hexagonal structure and a preferred orientation along the *c*-axis. All the films have a high transmittance of approximately 92% in the visible range. The optical band gap is about 3.33 eV for the films deposited at different RF powers.

Keywords: sputtering, zirconium, zinc oxide, transparent conducting films
PACC: 8115, 7155G, 7360L, 7865K

1. Introduction

Transparent conducting oxides (TCO) are extensively used for a variety of applications in microelectronic systems such as liquid crystal displays, organic light emitting diodes, and solar cells.[1−5] Currently, indium tin oxide (ITO) film is the most widely used TCO film due to its high transparency, low resistivity and high work function.[6,7] In the applications involving transparent heaters and chemical sensors, it is required that the films be chemically stable as they cycle through high temperatures. However, ITO films are not stable and show degradation at temperatures above 700 K.[8,9] ZrO_2–ZnO films are stable and exhibit no evidence of micro cracking after multiple cycles over a wide range of temperatures.[10] Zr-doped ZnO (ZZO) is a promising substitute of ITO to work at high temperatures (> 700 K) stably.[11] Moreover, ZZO is nontoxic, inexpensive, and abundant as compared with ITO.[12]

ZZO films have been prepared using pulsed-laser deposition (PLD)[11,12] and sol-gel[13] methods. However, to our knowledge, ZZO films have been rarely prepared by RF magnetron sputtering. As a widely used method of depositing films, sputtering can prepare uniform and large area films more easily than PLD method, and can prepare films with higher quality than sol-gel method. Thus, we consider it is necessary to study the ZZO films prepared by sputtering.

We have reported the preparation of transparent conducting ZZO films using RF magnetron sputtering method and analysed the properties with the variation of film thickness and deposition pressure in our previous papers.[14,15] In this paper, the structural, morphological, electrical, and optical properties of the films are analysed in samples prepared at different RF powers.

2. Experimental Details

ZZO films were deposited onto glass (Corning #7059) substrates by RF (13.56 MHz) magnetron sputtering using a ceramic oxide target ZnO/ZrO_2 (95:5 wt.%; 6 cm diameter) with a purity of 99.99%. The sputtering was carried out in pure argon atmo-

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sphere and the deposition pressure was maintained constant at 0.6 Pa for all the films. During the sputtering, the substrates were not intentionally heated. The distance between the substrate and the target was 4 cm. In order to investigate the effect of the RF power on the properties of the films, the RF power was varied from 75 to 150 W. The film thickness was 300 nm in average for all the samples. Prior to deposition, the substrates were cleaned ultrasonically and degreased in acetone. The chamber was initially evacuated to 5.0×10^{-4} Pa, and then pure argon gas was introduced through mass flow controllers to achieve the required pressure.

The film thickness was measured using XP-2^{TM} profilometer (Ambios Technology Company, USA). The structural properties were analysed with a Philips X'pert MRD diffractometer using a Cu K_α radiation. Electrical properties (resistivity, Hall mobility and carrier concentration) were measured by the four-point probe method, and Hall effect was measured using the van der Pauw technique under a constant magnetic field of 0.5 T. The optical transmittance measurements were performed with a TU-1901 UV–VIS spectrophotometer. Surface morphologies were analysed by using Hitachi-S520 scanning electron microscope (SEM).

3. Results and discussion

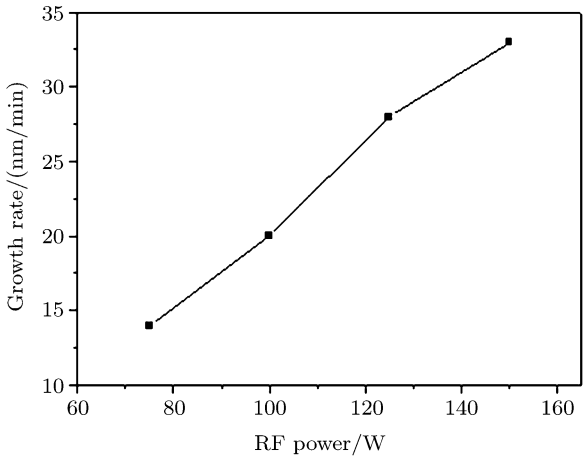


Fig.1. Dependence of the growth rate on the RF power for ZZO films deposited at room temperature.

Figure 1 shows the dependence of the growth rate on the RF power. It is found that the growth rate increases apparently from 14 to 33 nm/min with the increase of the RF power from 75 to 150 W. When the RF power increases, the self-polarization potential increases, leading to the increase of the kinetic energy of electrons and argon ions. Consequently, the argon ion density increases, resulting in the increase of the growth rate.[16]

The structural properties of the films are analysed by using their XRD patterns in Fig.2.

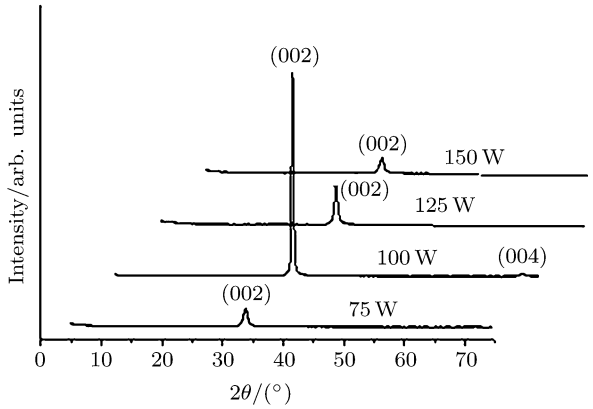


Fig.2. XRD patterns of ZZO films obtained at different RF powers.

For all the films, the ZnO (002) peak is clearly observed, and the ZnO (004) peak with a much weaker intensity is only observed for the film deposited at the RF power of 100 W. It is indicated that all the films are polycrystalline with a hexagonal structure and have a preferred orientation with the *c*-axis perpendicular to the substrate. The same structure has also been observed in the ZZO films prepared by PLD[11] and sol-gel.[13] The 2θ value of the (002) peak is very close to that of the standard ZnO crystal (34.45°) for all the films, which indicates that Zr replaces Zn in the hexagonal structure.[17] The *c*-axis lattice parameters can be calculated from the XRD patterns. All the parameters have values between 5.25 and 5.28Å, which are larger than the value of 5.207 Å for bulk ZnO. The radii of Zr^{4+} and Zn^{2+} are respectively 0.59 and 0.60 Å in the structure with a coordination number of 4. The increase of lattice parameter *c* is different from what was observed by Kim *et al.*[18] They reported that the lattice parameter *c* became shorter when Al^{3+} replaced Zn^{2+} in Al-doped ZnO (AZO), which was attributed to the smaller radius of Al^{3+} than that of Zn^{2+}. However, Qadri *et al*[19] still attributed the increase of the lattice parameter *c* to the substitution of Zr^{4+} for Zn^{2+} in the lattice. We suggest that this substitution may cause some lattice deviation which results in the increase of the lattice parameter. The

increase in the lattice parameter should be also attributed to the incorporation of Zr ions in the interstitial positions.[20] Oxygen deficiency and strain effect resulting from the thermal expansion coefficient mismatch between the film and the glass substrate may be another reason for the increase of the parameters.[20]

The (002) peak intensity increases sharply and the crystallite size (evaluated by the Sherrer formula[21]) increases from 15.1 to 20 nm when the RF power increases from 75 to 100 W, which indicates an obvious improvement of the crystallinity. However, the (002) peak decreases clearly and the crystallite size decreases from 20 to 10.3 nm when the RF power increases from 100 to 150 W, which indicates a deterioration of the crystallinity. The increase of RF power can lead to two effects: (1) The kinetic energy of the sputtered particles increases, which causes an increase of the particles' mobility in the surface of the film. The particles (including molecules, atoms, ions and their clusters) under a larger driving force can migrate to more suitable lattice sites and adjust their own bond direction and length to obtain optimum bonding to the adjacent ones, which are helpful for nucleation and growth, and consequently the crystallinity is increased.[22] (2) The surface damage caused by bombardment of the sputtered particles increases[23] and the film becomes non-stoichiometric.[24] It was proposed that the kinetic energy of particles increases with increasing sputtering power, so higher sputtering power can enhance the lattice damage by the high-energy particles, which deteriorate the crystallinity. While the oxygen deficiency at a higher sputtering power leads to the growth of less homogeneous films with more crystallographic faults, and the long-range order in the structure decreases,[25] which also results in a poor crystallinity. When the RF power increases from 75 to 100 W, the first effect should be dominant and the crystallinity is increased. As the RF power increases further to 150 W, the latter effect is much more important and thus the crystallinity is deteriorated.

Figure 3 shows the SEM micrographs of ZZO films deposited at different RF powers. The surface morphology transforms from small and individually distributed grains to a much more compact structure as the RF power increases from 75 to 100 W, indicating the improvement of crystallinity. When the RF power increases further to 150 W, the surface roughness increases obviously and the surface is composed of grains surrounded by voids. Such a deterioration of crystallinity can be attributed to the bombardment of the more energetic sputtered particles. A surface with porous structure can be favourable for amorphous silicon solar-cell application as rough surface will help in trapping more light.[26] The result is consistent with the XRD measurements.

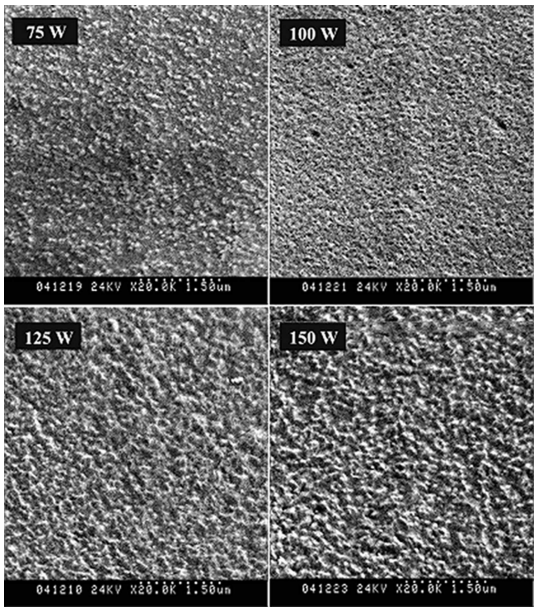


Fig.3. Surface morphologies of ZZO films deposited at different RF powers.

Figure 4 shows the dependence of the electrical properties (resistivity, Hall mobility and carrier concentration) of the ZZO films on the RF power. From the XRD results discussed above, it is concluded that Zr^{4+} is substituted for Zn^{2+} as donor in the hexagonal structure. Thus, two free electrons are produced for each Zn^{2+} replaced by Zr^{4+}, which contribute to the electric conduction of the films as free carriers. A similar explanation has been presented for Al and Tb doped ZnO films.[27,28] The mobility of the film is mainly determined by grain-boundary scattering and ionized-impurity scattering in extrinsic doped semiconductors.[29] The resultant mobility μ can be obtained from

$$1/\mu = 1/\mu_{\mathrm{GB}} + 1/\mu_{\mathrm{IS}}, \tag{1}$$

where μ_{GB} is the mobility due to grain-boundary scattering, and μ_{IS} is the mobility due to ionized-impurity scattering. In this experiment, the variation of the mobility can be attributed to grain-boundary scattering because of the obvious change of the crystallize size.

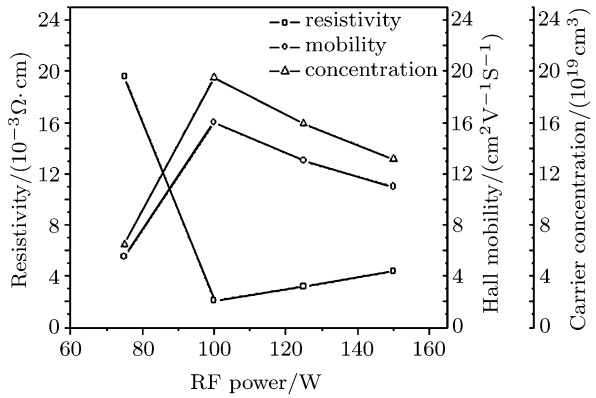


Fig.4. Dependence of the electrical resistivity, Hall mobility and carrier concentration on the RF power for the ZZO films deposited at room temperature.

As the RF power increases from 75 to 100 W, the resistivity decreases sharply from 1.96×10^{-2} to $2.07 \times 10^{-3}\Omega$cm and the Hall mobility and carrier concentration both increase. However, the resistivity shows a continuous increase from 2.07×10^{-3} to $4.4 \times 10^{-3}\Omega\cdot$cm with the simultaneous decrease of Hall mobility and carrier concentration as the RF power increases from 100 to 150 W. Similar variation of resistivity with RF power was reported in SnO_2:Sb films.[30] The lowest resistivities of 5.8×10^{-4} and $3.07 \times 10^{-2}\Omega$cm have been reported for ZZO films prepared by PLD method,[11,12] and Paul *et al*[13] reported the lowest resistivity of $7.2 \times 10^{-2}\Omega$cm for ZZO films prepared by sol-gel method. The increase of conductivity can be attributed to the improvement of crystallinity. When the RF power increases from 75 to 100 W, the crystallite size increases and the crystallinity is improved. When the RF power increases from 100 to 150 W, the crystallite size decreases and the crystallinity shows a deterioration. A larger crystallite size results in a lower density of grain boundaries, which behave as traps for free carriers and barriers for carrier transport. Hence, an increase in the crystallite size can cause a decrease in grain-boundary scattering and an increase of carrier lifetime,[31,32] and consequently leads to an increase of conductivity due to the increase in both carrier concentration and Hall mobility. With the improvement of crystallinity, the concentration of electrically active donor sites is improved,[33] which can also increase the carrier concentration.

Figure 5 shows the optical transmittance in the UV–VIS region of ZZO films grown at different RF powers. The average transmittance in the visible range is approximately 92% for all the films, which is comparable to that of pure ZnO films.[34] The average transmittance is calculated by taking the average value of the transmittance of the film in the range of wavelength from 500 to 800 nm for each sample. The optical band gap (E_g) is determined by extrapolation of the linear region of the plot of the square of the absorption coefficient α^2 versus photon energy ($h\nu$). The optical band gap value is about 3.33 eV for the films deposited at different RF powers.

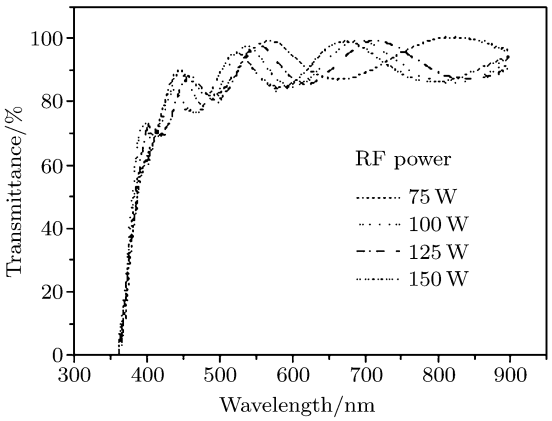


Fig.5. Optical transmittance as a function of wavelength for ZZO films grown at different RF powers.

4. Conclusion

Transparent conducting ZZO films have been prepared by RF magnetron sputtering at room temperature. The RF power dependence of the structural, morphological, electrical, and optical properties of the films has been studied. The films are polycrystalline. The lowest resistivity achieved is $2.07 \times 10^{-3}\Omega$cm at an RF power of 100 W. All the films present a high transmittance of about 92% in the visible range.

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