Study for double-layered AZO/ATO transparent conducting thin film

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Abstract. The purpose of this study is to provide transparent conductive composite films, used for such as dye-sensitized solar cells (DSSCs). In this work, transparent conductive oxide films with double-layer structure, ATO(antimony doped tin oxide) films covered on AZO(aluminum doped zinc oxide)films, were prepared on glass substrates by RF magnetron sputtering method. Subsequently the films were post-annealed at different temperature. The structure, surface morphology, optical and electrical properties of the films were investigated as a function of annealing temperature. Our results indicate that the composite films can maintain good electrical and optical properties at a temperature higher than 450°C compared to that of single-layer film.

Keywords: Transparent conductive oxide, composite, optical properties, electrical properties, thermal stability

1. Introduction

Transparent conductive oxide film, hereinafter referred to as TCO, is a functional thin film with low resistivity and high transmittance in the visible light range. TCOs are mainly used for optoelectronic devices such as flat panel displays[1] and photovoltaic fields[2-4] including inorganic and organic devices and dye-sensitized solar cells (DSSCs). The improvement of electrical and optical properties of TCO materials will greatly increase the efficiency and performance of these devices. The composite film technology can improve the shortcomings of the monolayer or achieve monolayer unattainable performance, which has become a hot research area of the film surface technology. Because optical, electrical and chemical properties of each layer material of the composite films are not identical, these composite films will have some unique characteristics. For example, the double-layer composite films,
FTO (fluorine doped tin oxide) films deposited on ITO (indium-tin-oxide) films coated on glass substrates, have excellent performance and make up their own defects as well as improve the efficiency of dye-sensitized solar cells\[^5\].

The main preparation methods of the composite films include physical vapor deposition (PVD)\[^6,7\] and chemical vapor deposition (CVD)\[^8\]. The former contains evaporation, sputtering, ion plating, arc plating, plasma plating, ion cluster beam (ICB) and molecular beam epitaxy (MBE), etc., and the latter covers vapor deposition, liquid phase deposition, electrolytic deposition, glow discharge deposition and the metal organic chemical vapor deposition (MOCVD), etc. There are many unique preparation methods such as ion implantation and laser assist deposition, etc. Among these techniques, RF magnetron sputtering is an attractive technique for the growth of composite films because it has advantages of high deposition rate, low substrate temperature, good adhesion of the film and large area coating capability\[^9\].

In this work, the double-layer composite films, ATO (antimony doped tin oxide) films deposited on AZO (aluminum doped zinc oxide) films coated on glass substrates, were developed without direct substrate heating by RF magnetron sputtering. The reason of growing double-layer structure is that the heat resistance of ATO films is better than that of AZO films in the high temperature process. In this article, we reported a detailed study about the temperature dependence of the structure and properties of these composite films.

2. Experimental details

2.1 Film preparation

AZO and ATO thin films were successively deposited on super white glass substrate (15×15×3mm\(^3\)) without direct heating by RF magnetron sputtering from the stoichiometric AZO and ATO ceramic targets (99.999% purity) of 2.4 in. diameter. The AZO ceramic target contained 2 wt% of Al\(_2\)O\(_3\) and the composition of ATO ceramic target was 6 wt % of Sb2O3. As the base pressure was smaller than 8 × 10\(^{-4}\) Pa, the Ar and O\(_2\) were introduced into the chamber. The total working pressure of films growth was fixed at 7 × 10\(^{-4}\) Pa and the oxygen partial pressure ratio (P\(_{O2}/(P_{O2}+P_{Ar})\)) was about 10-2 during AZO deposition and about 10-1 during ATO deposition. The applied RF power of composite films was 100 W and 80 W, respectively. Then, the AZO/ATO bilayer films were annealed in a rapid heating furnace at 150°C, 250°C, 350°C, 450°C, 550°C and 650°C, respectively, in the vacuum for 30 minutes in order to study the temperature dependence of the structure and properties of these composite films.

2.2 Film characterization

The film thickness was measured by a XP-2 step profiler. The crystal structure of the films was characterized by X-ray diffraction (XRD) using Cu Ka radiation. The surface morphology and cross-section of the films were studied using scanning electron microscope (SEM), the acceleration voltage was 20 kV. The transmittance in the 200–800 nm regions was performed using a UV-VIS spectrophotometer. Concentrations and mobility of charge carriers and resistivity of the samples were determined using Hall effect measurement system (Accent HL5500PC).
3. Results and discussion

Figure 1 shows the cross sectional SEM micrograph of the AZO/ATO composite transparent conductive film. As can be seen from the figure each monolayer including the first layer of the AZO film and the second layer of the ATO film is clearly seen. Because of the difference of the sputtering process parameters, the film thickness of the two layers in the AZO/ATO films is different. The thickness of AZO film is confirmed as approximately 380 nm and ATO has a thickness of about 75 nm as measured with XP-2 step profiler, which is in good agreement with the SEM result. It also can be seen from the figure that the ATO films are deposited tightly on the AZO films, which illustrates the conductive composite films could be prepared by this method.

Figure 1. A cross sectional SEM image of the double-layered film composed of AZO (1st layer) and ATO (2nd layer).

Figure 2. XRD patterns of bare AZO and 70 nm ATO-coated AZO films deposited at room temperature on the glass substrate. The inset shows XRD scan of as-deposited and 550°C annealed ATO (70 nm) film.
Figure 2 shows the XRD spectra of the bare AZO and the AZO/ATO films. The figure clearly presents the (002) diffraction peak of ZnO in the bare AZO films, which suggests good crystallized AZO films with wurzite hexagonal structure can be obtained. The diffraction peaks of the AZO/ATO films are dominated by the wurzite hexagonal characteristic peaks of AZO and do not show ATO characteristic peaks, which can be explained by the inset in Figure 2. Although the diffraction peaks of the SnO$_2$ in the ATO films deposited at room temperature are not observed, the inset shows the appearance of the tetragonal rutile peaks (110), (101), and (211) of pure SnO$_2$ when the ATO thin films are annealed at 550°C. This explains why AZO/ATO composite films deposited at room temperature mainly show the wurzite hexagonal characteristic peaks of pure ZnO: the AZO film deposited at room temperature is crystalline and ATO film deposited at room temperature is amorphous, even more, the thickness of AZO film is thicker than that of the ATO film.

![Figure 2. XRD spectra of AZO/ATO films.](image)

Figure 3 shows the XRD patterns of AZO/ATO composite films annealed in vacuum at different temperatures. The films were annealed at 150, 350 and 550°C for 30 minutes, respectively. The figure shows that the AZO/ATO as-deposited and annealed films are polycrystalline films with wurzite hexagonal structure. The strongest diffraction peak is the (002) direction. Because ATO films’ thickness is too thin, the diffraction figures do not show the ATO films’ characteristic peaks. In a temperature range of 150~550°C, with the annealing temperature increasing, the intensity of (002) peak increases gradually and the FWHMs of the peak are reduced accordingly, which reveals that the crystallization of the as-deposited AZO/ATO films could be improved after annealing. The crystal sizes of the films are estimated using Scherrer formula [10] to be about 21.2, 23.1, 26.2 and 30.8 nm for the samples as-deposited and annealed at 150, 350 and 550°C, respectively. The above results...
show that the crystal sizes of the films become larger and the crystallization becomes better with the increasing of the annealing temperature.

Figure 4 shows the optical transmittance spectra of the AZO/ATO films deposited at room temperature and annealed at different temperatures as a function of wavelength. The oscillations of the interference peaks in the visible region are observed in all the deposited and annealed AZO/ATO films due to the interference effect with respect to the increase in annealing temperature. Moreover, the optical transmittance increases slightly with increasing the annealing temperature. Particularly near the absorption edge, the transparency of the annealed films increases obviously, compared to that of films deposited at room temperature. Furthermore, the blue shift of the absorption edge with increasing the annealing temperature is mainly attributed to the Moss-Burstein effect, since the absorption edge of a degenerate semiconductor is shifted to shorter wavelengths with increasing carrier concentration\(^{[11]}\). The experimental results show that the optical properties of the bilayered films could be improved after this high temperature treatment. According to the preliminary analysis, this could arise from the corresponding optical band gap changes caused by structural changes after annealing. The results indicate that the composite films have good optical transparency.

![Optical transmittance spectra](image)

**Figure 4.** Optical transmittance spectra of glass substrate and AZO/ATO composite films before and after annealing at different temperatures in vacuum.

Figure 5 shows the resistivity, carrier concentration and Hall mobility of the AZO/ATO composite films as a function of the annealing temperature. According to quantum free electronic theory, the conductivity of the films depends on both the charge carrier concentration and transferring. The carrier comes mainly from oxygen vacancies and doping metal ions, while mobility are mainly originated from (derives mainly from) both the grain boundary scattering and ionized impurity scattering. As can be seen, within the temperature range from 350°C to 650°C, the carrier concentration increases with annealing temperature increasing, which is attributed to two different reasons: Sb\(^{3+}\) extinguishing and oxygen...
desorption. With increasing the annealing temperature, the mobility first increases and then decreases. The maximum mobility value is obtained for 450°C annealed sample, which is because once the charge carrier concentration is high enough to overcome the structural barriers, the ionized impurity scattering arises along with a decrease of the mobility. With the annealing temperature increasing, the resistivity of the AZO/ATO composite films declines sharply and the lowest resistivity of $6.1 \times 10^{-3} \ \Omega \cdot cm$ is obtained at 550°C, while as the annealing temperature increases to higher than 550°C, the resistivity of the composite films begin to rise again. Some literature reported that this phenomenon was considered to be due to the dispersion and the deviation of the grain caused by overhigh annealing temperature [12]. Some other literature speculated that hyperplasia and mobile mechanism of grain boundaries existed in the high annealing temperature, which promoted the splitting of the large grain and decreased the average grain size, and finally led to the deterioration of the conductive performance [13]. According to the figure 5, when annealing between 450 °C and 600 °C, the composite films have good conductivity, so the AZO / ATO composite conductive films can be used to prepare the dye-sensitized solar cells.

![Figure 5](image.png)

**Figure 5.** Resistivity, Carrier concentration and Hall mobility of AZO/ATO composite films annealed at different temperatures in vacuum.

4. Conclusions
AZO/ATO transparent conductive composite films have been successfully deposited on glass substrates by RF magnetron sputtering at room temperature. Post-annealing has a significant impact on crystallization as well as optical and electrical properties of the composite films. The transmittance in the visible region (400–800 nm) of the composite transparent conductive film is about 80–93%. Moreover, the optical transmittance increases slightly and the absorption edge is shifted to shorter wavelengths with increasing in the annealing temperature. An ATO protective layer could provide a fine thermal stability in terms of electrical conductivity at high temperatures and the lowest resistivity of $6.1 \times 10^{-3} \ \Omega \cdot cm$ was obtained at 550°C. In summary, the AZO / ATO composite conductive films can be used to prepare the dye-sensitized solar cells.
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