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Titanium dioxide-coated fluorine-doped tin oxide thin films for improving overall photoelectric property

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ABSTRACT

Titanium (Ti) layers were deposited by direct current (DC) magnetron sputtering on commercial fluorine-doped tin oxide (FTO) glasses, followed by simultaneous oxidation and annealing treatment in a tubular furnace to prepare titanium dioxide (TiO_2)/FTO bilayer films. Large and densely arranged grains were observed on all TiO_2/FTO bilayer films. The presence of TiO_2 tetragonal rutile phase in the TiO_2/FTO bilayer films was confirmed by X-ray diffraction (XRD) analysis. The results of parameter optimization indicated that the TiO_2/FTO bilayer film, which was formed by adopting a temperature of 400 °C and an oxygen flow rate of 15 sccm, had the optimal overall photoelectric property with a figure of merit of $2.30 \times 10^{-2}\ \Omega^{-1}$, higher than $1.78 \times 10^{-2}\ \Omega^{-1}$ for the FTO single-layer film. After coating a 500 nm-thick AZO layer by DC magnetron sputtering on this TiO_2/FTO bilayer film, the figure of merit of the trilayer film achieved to a higher figure of merit of $3.12 \times 10^{-2}\ \Omega^{-1}$, indicating further improvement of the overall photoelectric property. This work may provide a scientific basis and reference for improving overall photoelectric property of transparent conducting oxide (TCO) films.

1. Introduction

Transparent conducting oxide (TCO) films have received much attention due to their various technological applications in solar cells [1–3], flat panel displays [4], touch panels [5], light-emitting diodes (LEDs) [6], and gas sensors [7]. Among the TCO films, fluorine-doped tin oxide (FTO) film, which possesses virtues of relatively low cost (containing no expensive indium element), good thermal stability and high chemical stability, has been studied and applied abroad in recent years [8]. However, the electrical conductivity of FTO film is relatively low as compared to tin-doped indium oxide (ITO) film that has been widely used for many years [9]. On the other hand, the optical transmittance of FTO film shows the possibility of further improvement [10]. In order to meet the application requirements of high transparency and low sheet resistance, some FTO film-related researches have been focused on bilayer or multilayer composition [11–13]. It is well known that as a wide band gap semiconductor, titanium dioxide (TiO_2) has a large variety of potential applications and has been extensively investigated [14]. Its excellent performance, as evidenced by its high transparency at visible wavelengths, high refractive index, adjustable electrical conductivity, perfect chemical stability, and environmental non-toxicity [15,16], enables it to act as an ideal composited layer on some TCO films [17–19]. Kambe et al. [20] deposited an ultra-thin TiO_2 layer on FTO films by atmospheric pressure chemical vapor deposition (APCVD). In spite of almost unchanged average transmittance and slightly increased sheet resistance, the a-Si solar cells using the TiO_2-overcoated FTO films showed improvement of conversion efficiency by 3%. A recent report by Abdullah et al. [21] indicated that improvements in conductivity and optical properties of ITO films could be achieved by coating the ITO films with antireflective ZnO:TiO_2 layers. It is noteworthy that the electrical conductivity of TiO_2 films can be enhanced by annealing treatment, which has been reported by a number of studies [15,21,22]. However, to our knowledge, the preparation and annealing of TiO_2 films were carried out in sequence in previous reports. In this work, titanium (Ti) layers were deposited on commercial FTO glasses by direct current (DC) magnetron sputtering process. Subsequently, the as-deposited Ti/FTO bilayer films were oxidized to form TiO_2/FTO bilayer films and annealed to improve photoelectric properties simultaneously in a tubular furnace. The effects of temperature and oxygen flow rate on performance of TiO_2/FTO bilayer films were investigated. The TiO_2/FTO film with the optimal overall photoelectric property was adopted to be further optimized by

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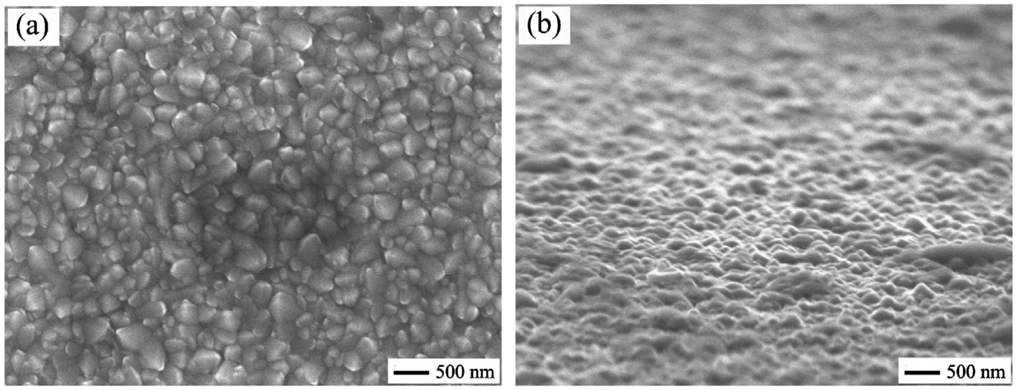

Fig. 1. SEM images of the FTO single-layer film: (a) top view; (b) oblique view.

coating a sputtered aluminum-doped zinc oxide (AZO) layer, since AZO itself has excellent photoelectric properties that are comparable with those of FTO or ITO [23] and always acts as upper layer in bilayer or multilayer films to achieve performance optimization [10,11].

2. Experimental details

The commercial FTO glasses with 700 nm-thick FTO single-layer films and 3 mm-thick plate glasses were prepared by chemical vapor deposition method. The FTO glasses were cut into small pieces of $2 \times 2\,cm^2$ and cleaned ultrasonically with anhydrous ethanol, acetone, and deionized water each for 10 min and then dried by blowing high-purity (99.99%) nitrogen. Subsequently, Ti layers were deposited on the FTO glasses by Peltier cooled high resolution coater (Emitech K575X) using a metallic Ti target (99.99% purity). The deposition chamber was evacuated to a base pressure of about 1×10^{-3} Pa, and then high-purity (99.99%) argon was introduced. The working pressure and current were 35 Pa and 120 mA, respectively. A research showed that optical matching of the refractive indices in glass/FTO/TiO_2/Si multilayers required an optimum TiO_2 film thickness of 50–60 nm [24]. Therefore, the ultimate thickness of the Ti layers was controlled at 50 nm and monitored in situ by a quartz-crystal-based thickness monitor. After that, the as-deposited Ti/FTO bilayer films were treated at a certain temperature (300, 400, or 500 °C) in an automatic temperature control tubular furnace (Hefei Risine CVD(Z)-06/60/3). During the treatment, high-purity (99.99%) nitrogen with a constant flow rate of 15 sccm and high-purity (99.99%) oxygen with a certain flow rate (10, 15, or 20 sccm) were firstly introduced into the furnace chamber. Ten minutes later, the oxygen flow was turned off, and the nitrogen flow was maintained for 30 min. Finally, one of the as-formed TiO_2/FTO bilayer films, which had the optimal photoelectric properties, was coated with a 500 nm-thick AZO layer by the K575X DC magnetron sputter coater using a zinc–aluminum alloy target (2 wt.% Al_2O_3).

The structural morphologies and thicknesses of the films were observed and verified with a scanning electron microscope (SEM) (Carl Zeiss EVO MA10). The crystal structures were examined with an X-ray diffractometer (XRD) (Rigaku D/max2500VB3+/PC) using Cu-Kα radiation of 0.15406 nm. The optical properties and sheet resistances were measured with a spectrophotometer (Shimadzu UV-2550) and a digital four-point probe instrument (Suzhou Baishen SX1944), respectively. The figures of merit of the different films were finally calculated and contrasted.

3. Results and discussion

3.1. Parameter optimization of TiO_2/FTO bilayer films

Fig. 1 shows the surface morphology of the commercial FTO single-layer film. The FTO film has a grain size in the range of 150–400 nm, as shown in Fig. 1(a). From the oblique view shown in Fig. 1(b), rugged morphology with some pyramidal shapes can be observed. The large and densely arranged grains will bring about a loss of light scattering at grain boundaries and enhance carrier mobility, resulting in high optical transmittance and electrical conductivity [25,26], which are demonstrated by the measured average transmittance of 82.7% and sheet resistance of 8.4 Ω/sq. listed in Table 1.

SEM images of the TiO_2/FTO bilayer films formed by adopting different temperatures and oxygen flow rates are presented in Fig. 2. All the films exhibit surface morphological features similar to that of the FTO film, i.e., containing large and densely arranged grains. The difference is that the shapes of grains on these films are more blurry, which may be due to the relatively lower electrical conductivity of TiO_2 layer [27]. In comparison, the grains on the TiO_2/FTO bilayer film formed by adopting a temperature of 400 °C and an oxygen flow rate of 15 sccm (expressed as TiO_2(400 °C_15 sccm)/FTO, the same below) are slightly larger (200–450 nm in diameter) and clearer than those on the other TiO_2/FTO bilayer films.

Table 1
Photoelectric properties and figures of merit of the FTO single-layer, TiO_2/FTO and Ti/FTO bilayer, and AZO/TiO_2/FTO trilayer films.

Sample	Thickness (nm)	Average transmittance (%)	Sheet resistance (Ω/sq.)	Figure of merit ($\times 10^{-2}\,\Omega^{-1}$)
FTO	700	82.7	8.4	1.78
TiO_2(300 °C_15 sccm)/FTO	50/700	78.3	7.6	1.14
TiO_2(400 °C_15 sccm)/FTO	50/700	82.3	6.2	2.30
TiO_2(500 °C_15 sccm)/FTO	50/700	72.0	5.7	0.66
TiO_2(400 °C_10 sccm)/FTO	50/700	81.4	6.0	2.13
TiO_2(400 °C_20 sccm)/FTO	50/700	78.9	6.5	1.44
Ti/FTO	50/700	50.2	5.7	0.02
AZO/TiO_2/FTO	500/50/700	83.2	5.1	3.12