Effect of annealing temperature on the structural and opto-electrical properties of TiO_2 thin films on AZO glass substrates by magnetron sputtering

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TiO_2 thin films were prepared on the AZO glass substrates by magnetron sputtering. The effect of annealing temperature on the structural、optical and electrical properties of TiO_2 thin films was investigated. The results show that the structures of TiO_2 thin films are closely related to annealing temperatures. The TiO_2 thin film annealed at 400°C is amorphous; the anatase TiO_2 is obtained by annealing at 500℃, whereas a rutile and anatase polymorph of TiO_2 is obtained when the TiO_2 thin film is annealed at 600°C The grain of TiO_2 thin film annealed at 600°C is spherical and the grain sizes are tens of nanometers. The optical and electrical properties of TiO_2 thin films on AZO glass substrates get worse than the AZO glass itself. The average transmittance of TiO_2 thin films annealed at 400°C, 500°C and 600°C is about 74.4%, 69.1% and 71.8% in the range of 400-800 nm. The sheet resistances of TiO_2 thin films on AZO substrates annealed at 400°C, 500°C and 600°C are about 45Ω/ϒ, 36Ω/ϒ and 23Ω/ϒ respectively.

(Received April 19, 2023; accepted November 24, 2023)

Keywords: TiO_2, Thin films, Structures, Optical and electrical properties, Sputtering

1. Introduction

Perovskite solar cells have become one of the research hotspots in the field of photovoltaic cells in recent years because of their low cost, good flexibility and high efficiency etc [1-3]. As far as we know that the highest power conversion efficiency of single-junction perovskite solar cells reached a value of 25.7% [4]. The carrier recombination will seriously affect the photoelectric performance of solar cells and significantly reduce photoelectric conversion efficiency. In perovskite solar cells, ohmic contacts between hole transport layers (HTL) and transparent conductive electrodes (TCE) cause recombination between the carriers, which will reduce the conversion efficiency of the solar cells. The compact layer between TCE and electron transport layer (ETL) can effectively avoid direct contact between the substrate and HTL, thus preventing electron migration from TCE to HTL [5]. Moreover, the compact layer can prevent the reverse migration of holes, so it can greatly reduce electron recombination and improve the device performance. The excellent compact layers need to meet three requirements as follows: good optical performance, the energy band structure matching with electrodes and sensitizing materials, and suitable thickness. TiO_2 is the most commonly used compact layer material（hole blocking layer-HBL）and ETL due to its good optical performance and suitable energy band structure [6,7]. The preparation methods of TiO_2 for compact layers and ETL mainly include spin-coating method [8], spray pyrolysis method [9], atomic layer deposition [10], sputtering [11] and so on. The spin coating method and spray pyrolysis method are widely used. T.M. Mukametkali et al. [12] prepared TiO_2 thin films on glass substrates used for electron transport layers by spin-coating methods, and revealed two competitive charge transport processes in TiO_2 : electron transport through the TiO_2 conduction band and electron trapping by deep trap levels formed by Ti^{+3} species. The optimal TiO_2 layer thickness is about 60 nm for perovskite solar cells. S. Mandati et al. [13] presents an economic, sustainable and scalable bar coating with high throughput for compact TiO_2 thin films on 50 mm×50 mm FTO glass substrates. M.A. Millan-Franco et al. [14] obtained anatase TiO_2 thin films on FTO glass substrates by spin coating method after a thermal annealing at 400-550℃, TiO_2 thin films annealed at 450 or 500℃ show a compromising between the crystalline structure and defect density, giving a better energy conversion efficiency of 16.3% of p-PSCs .The method of sputtering is also used for TiO_2 thin films or Ti-doped thin films [15]. H.Serrar et al. [16] prepared TiO_2 thin films with anatase structure on glass substrates by DC sputtering, and the effect of Ar flow rate on the optical waveguiding properties of TiO_2 thin films are investigated. H.Zhu et al. [17] Prepared TiO_2 thin films on FTO glass substrates by magnetron sputtering, the thickness and morphology of the TiO_2 thin films were controlled by sputtering time, the film transmittance showed a maximum value of 82.29% at 45 min of deposition, perovskite solar cells exhibited the highest photoelectric conversion efficiency of up to 12.42%. Most research of TiO_2 thin films used for perovskite solar cells is focused on the properties of TiO_2 deposited on the glass substrates or FTO glass substrates. The properties of TiO_2 thin films on AZO glass substrates deposited by magnetron sputtering is not researched fully.

In this paper, TiO_2 thin films were prepared on AZO glass substrates by magnetron sputtering. The effect of annealing temperature on structural, optical and electrical properties of TiO_2 thin films was investigated.

2. Experiment

TiO_2 thin films were prepared on AZO glass substrates by sputtering from the Ti target (purity: 99.99%). The deposition temperature was 200°C. The deposition pressure was 1.0Pa, and the sputtering power was 150W. The mass flows of Ar and O_2 were maintained at 90 sccm and 20 sccm respectively. The deposition time was 120min. The annealing temperatures were 400°C, 500°C and 600°C. The structural properties of the TiO_2 films were analyzed with X-ray diffraction (XRD, Empyrean, λ=0.154 nm) using Cu-Kα radiation. The transmittance of the films was measured by spectrophotometer (UV, Lambda 35) in the range of 300~900 nm. The electrical properties were characterized by four-point probes measurement system (RTS-9).

3. Results and discussion

3.1. Structures of the TiO_2 thin films

Fig. 1 shows XRD patterns of the TiO_2 thin films on the AZO glass substrates. It can be seen that the crystallinity of TiO_2 thin films is closely related to the annealing temperature. The TiO_2 thin films deposited at 200℃ and annealed at 400°C are amorphous, and there is no obvious diffraction peak. For TiO_2 thin film annealed at 500°C, there are two diffraction peaks at 2θ about 25.4°and 73.3° respectively, which is associated with (101) and (204) planes of anatase TiO_2. For TiO_2 thin film annealed at 600°C several diffraction peaks appear in the XRD pattern at 2θ about 27.8°(R-110), 43.5° (R-210), 63.6 °(R-310) and 73.3° (A-204), which correspond to rutile structure and anatase structure of TiO_2 respectively. The crystal structures of TiO_2 thin films are also related to the annealing temperature.When the annealing temperature is 500°C, the TiO_2 thin film is mainly anatase structure, which is the most used for the compact layer in perovskite solar cells and dye-sensitized solar cells [18-20]. When the annealing temperature reaches 600℃, the TiO_2 thin film is mainly rutile structure mixed with a small amount of anatase structure. Fig. 2(a), (b) and (c) are the SEM images of TiO_2 thin films annealed at 400°C, 500°C and 600°C. With the increase of the annealing temperature, the crystalline quality and density of the TiO_2 thin film increases. The grain of TiO_2 thin film annealed at 600°C is spherical and the grain size is tens of nanometers.

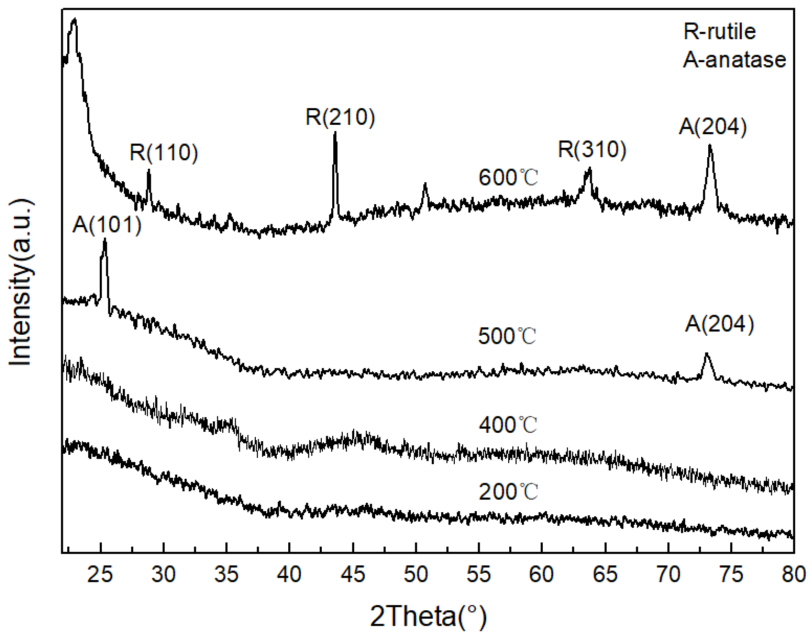

Fig.1 XRD patterns of the TiO_2 films on AZO glass substrates

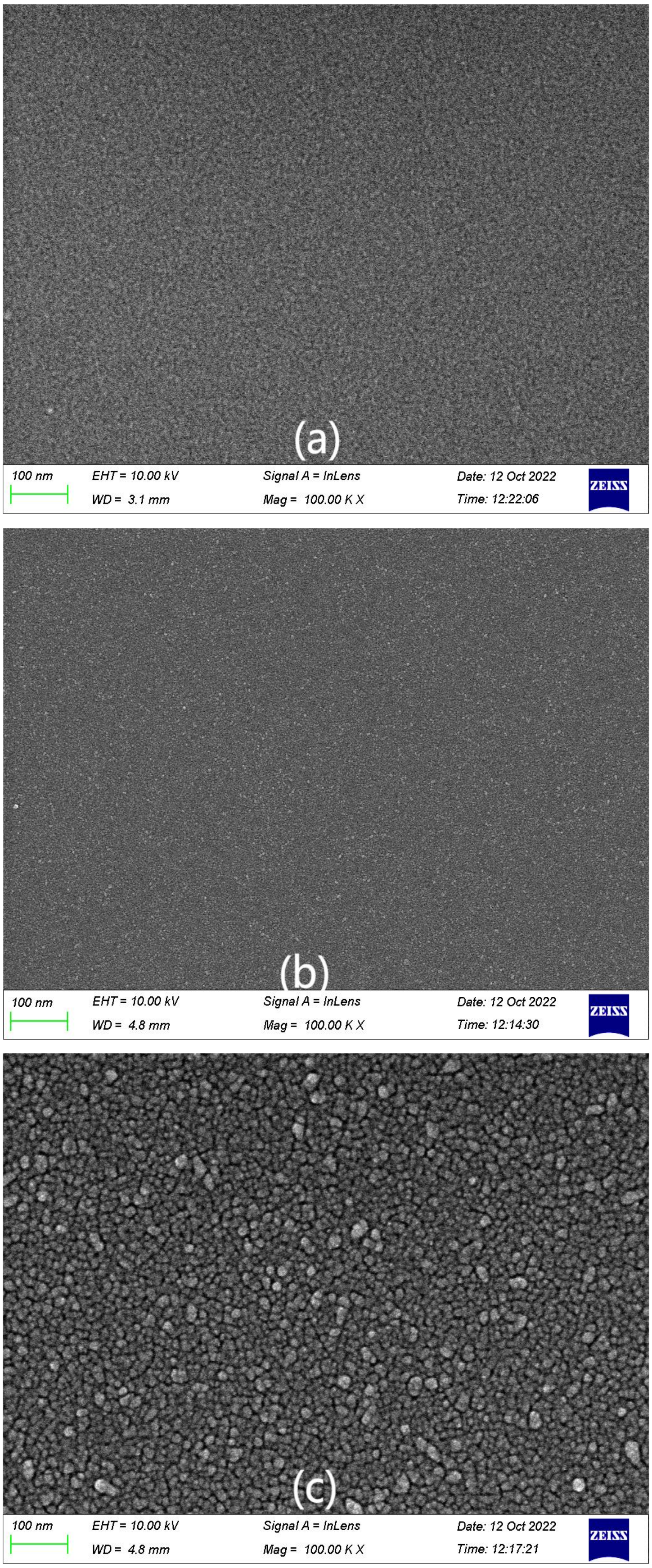

Fig. 2. SEM image of the TiO_2 films on AZO glass substrates annealing at 400°C (a), 500°C (b) and 600°C (c)

3.2. The optical properties of TiO_2 thin films on AZO glass substrates

Fig. 3(a) shows the optical transmittance of TiO_2 thin films and AZO glass substrates itself. It can be seen that the average transmittance of the AZO glass is above 90% in the visible region. The average transmittance of TiO_2 thin film deposited at 200°C is about 80% in the visible region. The average transmittance of annealed TiO_2 thin films is lower than that of unannealed TiO_2 thin film deposited at 200°C. As shown in Fig. 3(b), the average transmittance of TiO_2 thin films annealed at 400°C, 500°C and 600°C is about 74.4%, 69.1% and 71.8% in the range of 400-800nm.The lower transmittance of the annealed TiO_2 thin films on AZO glass substrates may be related to light scattering of the grain boundary [16].

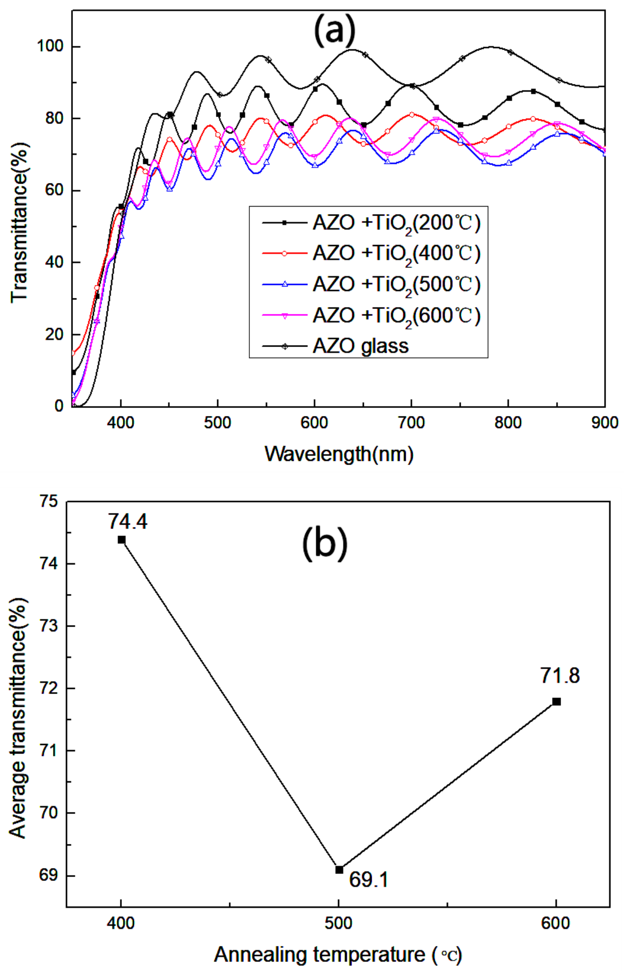

Fig. 3 Transmittance curves of the TiO_2 films on glass substrates (a),line chart of average transmittance of TiO_2 films annealed at 400°C, 500°C and 600°C (b) (color online)

The average transmittance of TiO_2 annealed thin films decreases firstly from 400℃ to 500℃ and then increases from 500°C to 600°C, which can be attributed to the structural changes in crystal quality. The larger grain size and fewer gain boundary results in the increase of transmittance of TiO_2 thin film annealed at 600°C. These can be verified by XRD and SEM results.

3.3. The electrical properties of TiO_2 thin films on AZO glass substrates

Fig. 4 is the sheet resistances of AZO glass and TiO_2 films on glass substrates annealed at 400°C, 500°C and 600°C. The sheet resistance of AZO glass substrate is about 9 Ω/ϒ. The electrical properties get worse for the TiO_2 thin films on AZO glass substrates, which is due to the poor electron conductivity of the TiO_2 material itself. The sheet resistance of unannealed TiO_2 thin film is 58Ω/ϒ, the sheet resistance of TiO_2 thin film annealed at 400°C, 500°C and 600°C are about 45Ω/ϒ, 36Ω/ϒ and 23Ω/ϒ respectively. The TiO_2 layers leads to a longer electron transport distance; thus, the sheet resistance of the sample increases compared to AZO glass substrates [17]. The sheet resistance of TiO_2/AZO thin films decreases with the increase of annealing temperature. According to the structural information, the improvement of crystal quality of TiO_2 thin films should be an important reason for the improved electrical conductivity performance.

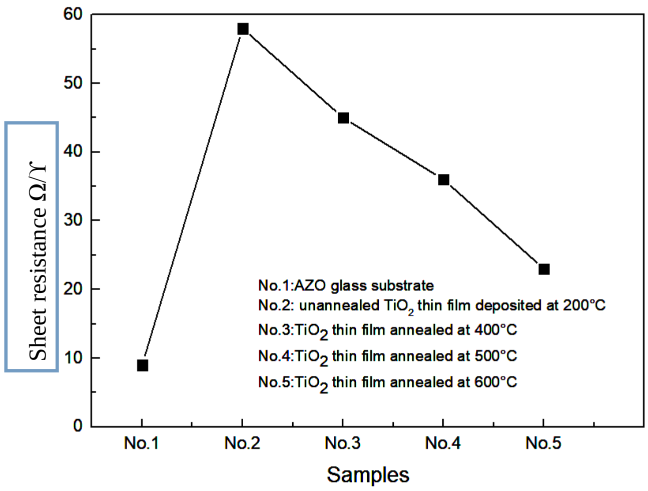

Fig. 4. The sheet resistances of AZO glass and TiO_2 films on AZO glass substrates

4. Conclusions

In this paper, TiO_2 thin films were prepared on AZO glass substrates by magnetron sputtering and annealed at 400-600℃. The structures and properties of TiO_2 thin films annealed at different temperatures were investigated. XRD and SEM results showed that the crystal quality and crystal structures of TiO_2 thin films are closely related to the annealing temperature. The structure of TiO_2 thin film annealed at 500°C is mainly anatase. The structure of TiO_2 thin film annealed at 600°C is mainly rutile mixed with a small amount of anatase. The grain sizes of the TiO_2 film annealing at 600°C are tens of nanometers. UV–Vis spectroscopy showed that all TiO_2 thin films were transparent with an average transmittance of more than 69% in the visible range. After annealing, the average transmittance of TiO_2 thin films decreases firstly and then increases. The electrical properties characterized by four-point probes measurement system showed that the lowest sheet resistance of TiO_2 thin film annealed at 600°C is 23Ω/ϒ. The electrical properties of TiO_2 thin films on AZO glass substrates are improved by annealing, which can increase crystal quality of TiO_2 thin films. The prepared TiO_2 thin films on AZO glass substrates may be useful for perovskite solar cells and other opto-electronic applications.

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