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Two-step preparation of laser-textured Ni/FTO bilayer composite films with high photoelectric properties

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ABSTRACT

A two-step strategy, i.e. sputtering Ni layers on FTO glass combined with magnetic-field-assisted laser irradiation, was proposed to prepare laser-textured Ni/FTO bilayer composite films. By analyzing surface morphology, crystal structure and photoelectric properties of Ni/FTO films with different Ni layer thicknesses, the Ni/FTO film with a 10-nm-thick Ni layer (Ni_{10}/FTO film), which had the best overall photoelectric property, was chosen to undergo magnetic-field-assisted laser irradiation with different laser fluences. Magnetic-field-free laser irradiation of the Ni_{10}/FTO film was also carried out for comparison purpose. It was found that magnetic-field-assisted laser irradiation using a fluence of 1.0 J/cm^2 was more effective for simultaneously achieving texturing and annealing, resulting in formation of ideal grating textures and significantly increased grain size. The corresponding film (MLI-NF1.0 film) showed the highest figure of merit of $22.8 \times 10^{-3}\ \Omega^{-1}$ compared to $13.1 \times 10^{-3}\ \Omega^{-1}$ of the FTO glass and $1.4 \times 10^{-3}\ \Omega^{-1}$ of the Ni_{10}/FTO film, suggesting that the two-step strategy is excellent for preparing textured Ni/FTO films with high photoelectric properties.

1. Introduction

Recently, the growing demand for high-efficient optoelectronic devices motivates researchers to develop more excellent transparent conducting oxide (TCO) thin films [1]. As window layers and front contact electrodes in thin-film solar cells, TCO films are expected to have high transparency (more than 80%) in the visible waveband and low sheet resistance (not larger than about 10 Ω/sq) [2,3]. The traditional TCO materials, such as tin-doped indium oxide (ITO), aluminum-doped zinc oxide (AZO) and fluorine-doped tin oxide (FTO), can satisfy the foregoing characteristics and have been confirmed to be the most attractive potential candidates [4]. Among these TCOs, FTO has attracted much attention due to its advantages of abundant resource, low cost, chemical inertness, thermal stability and being environmentally friendly [5,6]. However, FTO single-layer films have relatively low electrical conductivity and are difficult to pattern via wet etching as compared to ITO films [7]. Many researches indicated the possibility for improving photoelectric properties of FTO films [8–18]. In general, the improvement strategies mainly include coating an ultrathin metal or semiconductor layer [8–11], furnace or laser annealing [12–15] and fabricating anti-reflecting textures [2,16–18]. Coating a metal or semiconductor layer results in a decrease in transmittance of the FTO films although the conductivity can be effectively improved. Therefore, post-annealing has become imperative since annealing can give rise to a positive impact on improvement in both optical and electrical properties of the FTO-based films [19]. It is well known that laser annealing outperforms furnace annealing due to a variety of virtues, such as selectivity, short operating time, low thermal budget, avoiding escape of doping elements in the films and a gradient distribution of temperature that can restrain diffusion of impurities from the substrates [20,21]. More importantly, laser irradiation effect during laser annealing can also induce some special textures on the film surfaces, which will improve transmittance of the films through reducing light reflection [22]. Considering the difficulty of fabricating textured FTO-based films through traditional wet etching methods, employing a laser to simultaneously achieve annealing and texturing of the films will be a more effective strategy for optimizing photoelectric properties of the films. On the other hand, our previous research verified that laser annealing in an external

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magnetic field, rather than pure laser annealing, could help to form larger, denser and more uniform grains in FTO-based films, thereby resulting in higher transmittance and lower sheet resistance [23].

Consequently, in order to achieve performance optimization of single-layer FTO films, we propose a two-step preparation method of laser-textured nickel (Ni)/FTO bilayer composite films, which consists of coating Ni layers on FTO films and laser irradiation of the Ni/FTO films in an external magnetic field. In this study, Ni/FTO films with different Ni layer thicknesses were prepared to compare their photoelectric properties, so as to determine the optimal Ni/FTO film for subsequent magnetic-field-assisted laser irradiation. The external magnetic field was expected to help form a more compact Ni layer and improve the film crystallinity more effectively based on the roles of magnetization energy and magnetic force. The effects of laser fluence on structural, optical and electrical properties of the laser-irradiated Ni/FTO films were explored. To better understand the magnetic field effect, magnetic-field-free laser irradiation of the optimal Ni/FTO film was also performed.

2. Experimental details

Commercial FTO glass (15 mm × 15 mm) with a 750-nm-thick FTO layer on a 3-mm-thick plate glass was used as the substrate. The FTO glass was cleaned with deionized water, acetone and anhydrous ethanol in an ultrasonic bath each for 10 min and then dried by blowing high-purity (99.99%) nitrogen. The two-step preparation strategy is schematically shown in Fig. 1. Firstly, Ni layers with different thicknesses were coated on the pre-cleaned FTO glass by direct current (DC) magnetron sputtering at room temperature using a metallic Ni target (99.96% purity). Prior to deposition, the chamber was evacuated to $\sim 1 \times 10^{-3}$ Pa and introduced high-purity (99.99%) argon. The working pressure and current were 35 Pa and 100 mA, respectively. The thicknesses of the Ni layers were monitored in situ by a quartz-crystal-based thickness monitor. In the next step, the as-prepared Ni/FTO film with the optimal thickness was selected to undergo laser irradiation in an external magnetic field. The external magnetic field was formed by putting two identical permanent magnets (0.4 T in magnetic induction intensity) on both sides of the Ni/FTO film sample. The distances between the magnets and the film sample were both 15 mm. The diode pumped Nd:YVO_4 nanosecond pulsed laser with a central wavelength of 532 nm used here had the dual roles of texturing and annealing, which were achieved by adjusting the film surface to be after the focal spot of laser beam with a defocus amount of ~3 mm. The output laser beam was linearly polarized with a repetition rate of 1 kHz and a pulse width of 1–2 ns. The laser beam with a spot size of 100 μm scanned back and forth along a single direction with a spot spacing of 40 μm. The laser scanning speed was kept at 10 mm/s and various laser fluences were adopted. For comparison purpose, the optimal Ni/FTO film sample was laser irradiated using the same laser parameters without the presence of the external magnetic field.

The surface morphology of the films was observed by employing a scanning electron microscope (SEM) (Carl Zeiss EVO MA10). Cu Kα X-ray diffraction (XRD) (Bruker D8 Advance) analysis was adopted to characterize the crystal structure. The optical transmittance and reflectance spectra were measured using a spectrophotometer (Shimadzu UV-6100). The sheet resistance was obtained through a digital four-point probe instrument (Suzhou Baishen SX1944).

3. Results and discussion

3.1. Coating Ni layers on FTO glass

The surface morphology is an important factor in determining the performance of the films. Fig. 2 presents the SEM images of the pure FTO film and the as-prepared Ni/FTO films with a Ni layer thickness of 5, 10 and 15 nm (denoted as Ni_5/FTO, Ni_{10}/FTO and Ni_{15}/FTO), respectively. The pure FTO film, as Fig. 2a shows, was covered with small and densely-distributed SnO_2 particles. With increasing Ni layer thickness from 5 to 15 nm, the particles on the Ni/FTO film surfaces seemed to become comparatively larger and denser due to the coverage of the Ni layer with increased thickness, as shown in Fig. 2b–d. It is believed that enough material supply that corresponds to a larger layer thickness is essential to the large and dense particles [24]. Ni layer with a smaller thickness resulted in separated and randomly distributed Ni particles on the FTO glass. As Ni layer thickness increased, the Ni particles coalesced with each other and the gap between the particles was decreased, thus yielding larger and denser particles, which was similar to the result reported by Yun et al. [25]. By a detailed comparison, it was found that on the surface of the Ni_5/FTO film, some obvious micropores were observed between neighboring particles (Fig. 2b), which may be resulted from the smaller thickness of the Ni layer that formed sparsely distributed Ni particles on the FTO layer [26]. In contrast, the shapes of the particles on all the Ni/FTO films are clearer than those of on the pure FTO film, which may be resulted from the relatively higher electrical conductivity of the Ni/FTO films since the presence of the Ni layer can lead to an increased electron density [27]. This will be verified by the measured sheet resistances.

The XRD patterns of the pure FTO film and the as-prepared Ni/FTO films are shown in Fig. 3. All the films contained the SnO_2 tetragonal structure (JCPDS no. 41-1445) and exhibited preferred orientation along (200) plane. The presence of other diffraction peaks corresponding to reflexes along (110), (101), (211), (220), (310), (301) and (321) planes indicated polycrystalline nature of the films [28]. However, due to the continuous coverage of Ni layers on the surface of the FTO layers [29], the intensity of the SnO_2 (200) diffraction peak had been gradually weakened with increasing Ni layer thickness. In addition, it was noteworthy that Ni peak which supposed to appear at $2\theta = 44.5°$ and 76.4° had not been detected for all the as-prepared Ni/FTO film samples, which is similar to the results reported by Kim et al. and should be attributed to the very low thicknesses of 5–15 nm of the Ni layers [30].

Fig. 4 shows the average transmittances (T_{av}), sheet resistances (R_{sh}) and figures of merit (F_{TC}) of the FTO film and the as-prepared Ni/FTO films with different Ni layer thicknesses. The T_{av} values were obtained by averaging the transmittance values in the visible waveband (380–780 nm) which were extracted from the optical transmittance spectra, i.e. T_{av} was defined as

$$T_{av} = \frac{1}{n}\sum_{i=1}^{n} T_i, \tag{1}$$

where T_i is the transmittance value at a given wavelength and n is the number of the transmittance value. The FTO film had a T_{av} value of 80.2%. For the as-prepared Ni/FTO films, as the Ni layer thickness increased from 5 to 15 nm, the T_{av} value significantly decreased from 63.8% to 58.7%. This can be ascribed to the presence of Ni layer

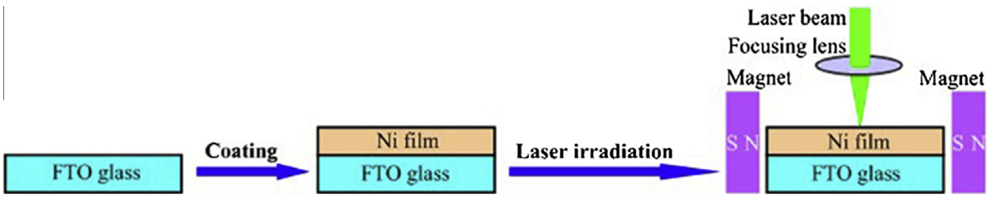

Fig. 1. Schematic diagram of two-step preparation of laser-textured Ni/FTO bilayer composite films. The first step is to prepare Ni/FTO bilayer films by coating Ni layers with different thicknesses on FTO glass, and the second step is to improve photoelectric properties of the Ni/FTO bilayer film with the optimal Ni layer thickness through laser irradiation in an external magnetic field.