Pronounced optical gain attained in Ag/AZO structure for solar cell applications

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Abstract

Recently plasmonic effect has attracted tremendous interests due to its ability of light trapping and improving the photovoltaic performances of solar cells. In this letter, we propose a solution method based fabrication route of Ag plasmons and realize a pronounced optical gain in ZnO:Al (AZO) thin film, which is strongly beneficial to harvest incident sunlight in thin film solar cells. Processing parameters, such as spinning speed, coating times and post-annealing temperature, could be regulated to optimize the plasmon effects of silver particles. The reflectance of silver particles coated AZO (Ag/AZO) is reduced by ~18%, and the transmittance is enhanced by ~40% simultaneously. The underlying mechanisms are discussed in combination with the microstructures of the silver particles.

Key words: Particles, AZO, Reflectance, Transmittance, Plasmons, Deposition

1. Introduction

In the last several decades, nano noble metal materials, such as silver (Ag) and gold (Au), have attracted intensive attentions due to their wide applications in medical optical imaging [1], drugs [2] and solar cells [3] etc. Silver particles with a lower cost could be elaborately controlled to form surface plasmon polaritons (SPPs) with various shapes [4] and sizes [3] to trap light, which is the underlying mechanism for antireflection. As an example, Temple and Dligatch [5] proposed a structure of Ag/SiO₂/Si where the introduction of Ag layer with an optimized thickness of 5 nm was able to reduce

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the surface reflection by ~10%. On the other hand, Ag particles coated on the surface of AZO thin film can enhance the light scattering and lead to an increased transmittance of Ag/AZO [6]. For example, Theuring, et al. [7] presented a sandwich structure of AZO/Ag/AZO whose transmittance was increased from ~70% to ~80% due to the introduction of the intermediate Ag layer. That is to say, the reflection (transmission) of window layers can be effectively minimized (enhanced) by applying Ag SPPs. However, it seems to be difficult to attain a pronounced optical gain via decreasing the reflection and simultaneously increasing the transmittance in the window layer, to harvest more incident sunlight [5, 7, 8] by using metal SPPs.

As for the fabrication of silver plasmons, physical methods, such as magnetron sputtering [9] and electron beam evaporation [5] are commonly used. However, these physical methods are practically limited by a high cost and a complicated processing procedure. Recently we have developed an easy chemical reduction method [10, 11] to make the fabrication process to be easier, safer and more controllable. The morphologies and microstructures of the silver particles can be effectively tuned by the processing parameters. It was found that both the as-fabricated and thermally annealed silver particles significantly enhance the light transmission, and simultaneously reduce the reflectance on the AZO thin film surface due to the SPPs effect.

2. Experimental details

Silver nitrate (AgNO_3) was used as a raw material to prepare silver particles. Citric acid three sodium ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), polyvinyl pyrrolidone (PVP) and deionized (DI) water were used as reductant, stabilizer and solvent, respectively. The substrate was 350 nm thick AZO thin film magnetron sputtering grown on glass substrate. The mixed solution of 18 mL DI water, 0.8 g PVP, 0.5 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 0.08 g AgNO_3 was stirred by a magnetic stirring apparatus to form a uniform

precursor solution, and then introduced into a sealed reaction kettle to avoid the atmosphere exposure. The reaction kettle was put inside a thermostat set at the temperature of 180 °C for 20 h for the formation of silver colloid. Silver colloid was subsequently deposited on the AZO substrate via a spin coater to form the Ag/AZO structure. Finally, as-fabricated Ag/AZO was thermally annealed in an annealing equipment as schematically shown in Fig. 1.

Light reflectance and transmittance spectra of Ag/AZO were measured by using Agilent UV/VIS/NIR spectrophotometer (Cary 5000). Scanning electron microscopy (SEM) measurements of Ag/AZO were taken on FEI Inspect F working at 20 kV. X-Ray diffraction (XRD) measurements were performed on Bede D1 whose working voltage, operating current and X-ray wavelength were set at 50 kV, 35 mA and 0.15402 nm, respectively.

Fig. 1. The schematic fabrication flow of the silver particles

3. Result and discussion

Fig. 2(a-d) show the XRD spectra of the bare and 17 times silver colloid coated AZO thin films: bare AZO without silver colloid coating (Ag-0/AZO) (a), coated AZO without post-annealing (Ag-17/AZO) (b), coated AZO with a 4-hour post-annealing at 150 °C (Ag-17/AZO/annealing with 150 °C) (c), and coated AZO with a 4-hour post-annealing at 200 °C (Ag-17/AZO/annealing with 200 °C) (d). Apart from the peak located at $\sim 34.3^\circ$ which is definitely recognized as the ZnO (002) plane shown in Fig. 2(a), another peak located at $2\theta = 62.540^\circ$ attributed to the AgO (-221) plane appears. The

occurrence of AgO should be ascribed to the oxidation of Ag in air. In Fig. 2(c) there are three diffraction peaks, apart from ZnO (002) and AgO (-221), another standard (111) plane of Ag is verified as $2\theta = 38.120^\circ$. The appearance of Ag associated diffraction peak indicates that the 150°C annealing makes Ag particle crystallize. As shown in Fig. 2(d), the diffraction peak of Ag disappears, which means that the annealing temperature of 150°C is more beneficial to crystallization of Ag particles than 200°C .

Fig. 2. XRD spectra of the bare and Ag particles coated AZO thin films (see text)

The surface morphologies of Ag/AZO were examined by SEM. Fig. 3(a) [(b)] shows the top-view image of Ag-0/AZO [Ag-17/AZO]. A typical surface morphology of crystal AZO is represented in Fig. 3(a). There are sparse Ag or AgO particles situated on the surface of Ag-17/AZO as shown in Fig. 3(b). Interestingly, the particles are irregular and separated with various shapes of hexagon and square (outlined in the figure by dashed lines). The underling mechanism is out of the scope of this letter and will be studied elsewhere. The morphology of Ag-17/AZO/annealing with 150°C is shown in Fig. 3(c), where the particle shape becomes sphere with a markedly reduced size. These observations mean that the 150°C post-annealing can lead to a discoalescence of the bigger silver

particles into chemically reshaped smaller particles. With an increasing annealing- temperature, the dewetting speed of silver colloid is accelerated to result in smaller particles [12]. Fig. 3(d) shows the SEM image of Ag-17/AZO/annealing with 200 °C, where the particle size is further reduced and the distribution is more homogeneous. It is concluded that the post-annealing treatment could lead to the continuous decomposition and make the particles to be more homogeneous [3].

Fig. 3. Top-view SEM images of Ag-0/AZO (a), Ag-17/AZO (b), Ag-17/AZO/annealing with 150 °C (c), and Ag-17/AZO/ annealing with 200 °C (d).

The effects of the surface particles on the optical properties of AZO were also investigated. The reflectance spectra of the AZO thin films with different coating times of silver colloid are shown in Fig. 4(a), in which the reflectance of AZO coated with silver colloid is lower than that of bare AZO in a wide wavelength range covering the UV-VIS-NIR span. Silver colloid coated on the surface of AZO thin film could form SPPs where the collective oscillations of Ag particles' free electrons after light incidence lead to surface plasmon resonances (SPRs) and hence result in light trapping [13]. Meanwhile, as shown in Fig. 4(b), the transmittance of the Ag particles coated AZO drastically increases, which can be also ascribed to SPRs. Ag particles located at the interface between two mediums (air and AZO thin film) with different refractive indices scatter the light predominately into

the higher one [6] as shown in Fig. 4(c). The reflectance and transmittance of Ag-17/AZO decreases and increases ~10% and ~25% respectively with respect to that of the bare AZO.

Annealing treatment is another significant factor influencing the optical properties of Ag/AZO. As revealed in prior SEM measurements, post-annealing significantly reduces the silver particle size. The smaller silver particle is inclined to form quadrupolar mode leading to a decrease in the reflectance due to forward-scattering as its size decreases [3]. Meanwhile, the extinction which is simply the inverse of the transmittance increases with increasing sizes of silver particle [3], therefore the transmittance of Ag/AZO increases with decreasing silver particle sizes. The reflectance and transmittance of Ag-17/AZO/annealing with 150 °C decreases and increases about 15% and 33% respectively in comparison to Ag-0/AZO. When the annealing temperature reaches 200 °C, the silver particle is the smallest as shown in Fig. 3(d). Consequently, the reflectance and transmittance of Ag-17/AZO/ annealing with 200 °C decreases and increases by about 18% and 40% respectively in comparison to Ag-0/AZO. In principle, there are two types of modes in the formed plasmon on the surface of AZO thin film, namely the SPPs mode and local surface plasmons (LSPs) mode. According to Fig. 4(a) and (b), the light absorption in the Ag silver colloid coated AZO is very low because of the high sum values of the reflectance and transmittance, and thus the effect of LSPs which tends to enhance absorption [14] is much weaker than that of SPPs in the present experiments. Furthermore, the occurrence of LSPs usually needs a small particle size (1-100 nm), and LSPs are prone to be transformed into SPPs when the particle size is increased [15]. As shown in Fig. 3(b-d), the size of Ag particle is much more than 100 nm, and thus a dominant role of SPPs should be expected in our case.

Fig. 4. The reflectance (a) and transmittance (b) spectra of the various samples. Ag particles scatters incident light into AZO thin film as shown in (c).

4. Conclusion

A pronounced optical gain is attained by a solution route based Ag SPPs on AZO substrate. The introduction of Ag SPPs with an appropriate post-annealing, which effectively tunes the microstructures and distribution of Ag particles, leads to a pronounced optical gain in the Ag/AZO structure: a ~18% decrease in the reflectance and simultaneously a ~40% increase in the transmittance. The present Ag/AZO structure shows its huge prospect in improving the photovoltaic performance of thin film solar cells due to the pronounced optical gain.

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