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Optical and electrical properties of ZnO thin film containing nano-sized Ag particles

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Abstract Low-temperature crystallized ZnO thin film was achieved by sol–gel process using zinc acetate dihydrate and 2-methoxyethanol as starting precursor and solvent, respectively. Ag nanoparticles were prepared with uniform size at 4.4 nm by spontaneous reduction method of Ag 2-ethylhexanoate in dimethyl sulfoxide (DMSO). The optical and electrical properties of ZnO thin films containing various contents of Ag-nanoparticles were monitored. Light scattering and charge emission and scattering behaviors of Ag nanoparticles in ZnO film were found. The incorporation of Ag nanoparticles into Al-doped ZnO film was also investigated. The optical transmittance was not degraded but the increase of electrical sheet resistance was found. The effect of Al-dopant on the transmittance and electrical sheet resistance of ZnO film was found too great to distinguish the positive effect of the incorporation of Ag nanoparticles into Al-doped ZnO thin films.

Keywords ZnO thin film · Nano-sized Ag particles · Chemical solution deposition

1 Introduction

Zinc oxide (ZnO) exhibits numerous characteristics that may enable its efficient utilization in these novel devices. ZnO is n-type semiconductor with a wide band gap of 3.37 eV [1]. It has therefore been considered a promising candidate for the development of light-emitting structures and solar cells. However due to its low conductivity compared to metal, the doping and hybridization with metal-nanoparticles have been investigated [2]. Nanoparticles or quantum dots have received considerable attention due to their new quantum phenomena resulted from an increase in band gap with decreasing dimension and discrete electronic states with higher oscillator strength. Especially, Ag nanoparticles have been widely used in the electronics industry for the manufacture of conductive thick film circuits and for the internal electrodes of multilayer ceramic capacitors. It has known that inclusion of nanoparticles in the materials offers unique properties in optical and electrical characteristics [3, 4]. Sarto et al. reported the electromagnetic shielding effect by metallic Ag nanoparticles in ZnO [5]. Also some researchers have reported that nanoparticles could emit the electrons through the introduction of the various energy sources, especially electric field or some special light illumination. These electrons emitted from the applied electric field could contribute to the conduction of the matrix or gives the unique optical properties to the optical applications, e.g. photochromic effects [6, 7]. The doping of ZnO with 3^+ valence cations such as Al and Ga induces a great enhancement in the electrical property of ZnO [8, 9]. However there has been no detailed description on the role of metal-nanoparticles in ZnO, especially doped ZnO.

In this work, we investigated the effect of the incorporation of Ag-nanoparticles into ZnO film on the optical and electrical properties of ZnO. Furthermore, to clarify the hybridization effect of undoped or Al-doped ZnO with Ag metal-nanoparticles, Ag nanoparticles were prepared and nano-hybridization effect was investigated with undoped and Al-doped ZnO films.

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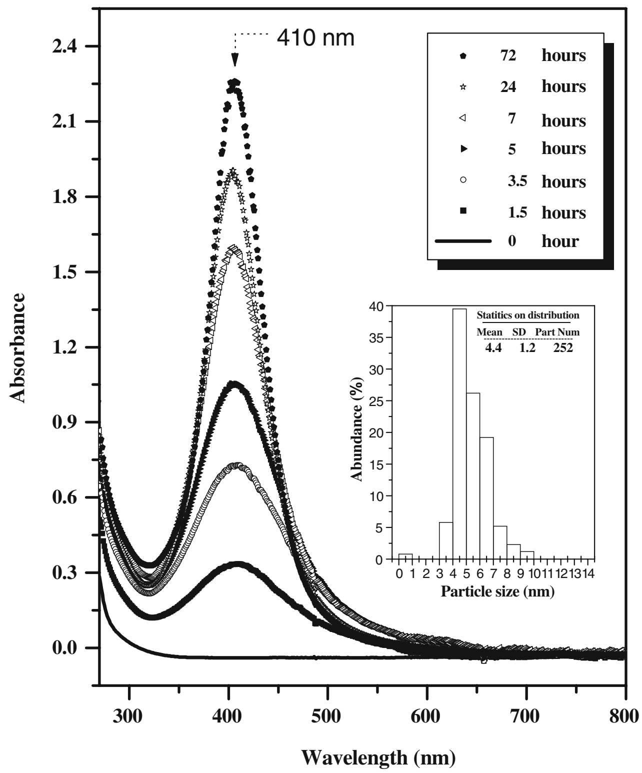

Fig. 1 UV–vis. spectra during the formation of Ag nanoparticles capped with a capping agent (trisodium citrate). *Inset* indicates the size distribution of nanoparticles

2 Experimental procedure

ZnO thin films were prepared by the sol–gel procedure [10]. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), 2-methoxyethanol, and monoethanolamine (MEA) were used as starting precursor, solvent, and sol stabilizer, respectively. Aluminum chloride ($AlCl_3$) was used as a dopant source for Al. Zinc acetate dihydrate and aluminum chloride were dissolved in 2-methoxyethanol and MEA was added for stabilization at room temperature. The concentration of zinc acetate dihydrate was 0.5 M and the molar ratio of MEA to zinc acetate dihydrate was 1.0. The solution was stirred at room temperature for 2–3 h. Silver nanoparticles were prepared by spontaneous reduction method of Ag 2-ethylhexanoate in the solvent of dimethyl sulfoxide [11]. Trisodium citrate was used as a capping agent for the size control of Ag-nanoparticles. The colloidal dispersions were protected from the light during the preparation. To obtain Ag-nanoparticle contained ZnO thin films, Ag dispersed solution containing the selected concentrations of Ag nanoparticles and zinc alkoxide solution derived from zinc acetate di-hydrate were mixed together. The mixed solution was then spin-coated on the glass (Fusion 1737) substrates at 2,000 rpm for 20 s. After spin coating, the coated films were dried at 250 °C for 5 min on a hot plate to remove the solvent and organic residuals. The films were then annealed in a tube furnace in air at 300 °C for 1 h for crystalline phase formation. The final thickness of the film was around 100 nm. The crystallinity was analyzed by X-ray diffraction (XRD, Rigaku) with Cu K_{α} radiation. The sheet resistance of film was measured by using four-point probe. Optical transmittance measurements were carried out by using UV–VIS–NIR spectrophotometer.

3 Results and discussion

Absorption spectrum of Ag-nanoparticles prepared by spontaneous reduction method with Ag 2-ethylhexanoate was given in Fig. 1. The size of Ag-nanoparticles was not changed with preparation duration because we had narrow and symmetric absorption peaks at 410 nm wavelength due to the surface plasmon resonance of conduction electrons of Ag. This kind of size control of Ag-nanoparticles with very narrow and uniform distribution could be possible by using trisodium citrate as a capping agent. The average size of Ag-nanoparticles was found to be around 4.4 nm [11].

Figure 2 presents an optical transmittance of ZnO thin films hybridized with various weight percent of Ag-nanoparticles after anneal at 300 °C. The ZnO film was crystallized with hexagonal wurtzite structure at 300 °C and preferred orientation of (002) was observed by XRD measurement. The transmittance of ZnO film-hybridized with Ag nanocrystals was slightly increased at 2.5 wt%, almost the same not-changed at 4 wt%, and reduced at 8 wt% of Ag content. The incorporation of 2.5 to 8 wt% of Ag nanocrystals with 4.4 nm size into ZnO matrix results in the inter-particle distance of 12.3 to 8.3 nm when we assume the ZnO matrix of theoretical density. The increase with small content of Ag-incorporation seemed due to the increase in crystallinity of ZnO film and the decrease with high content

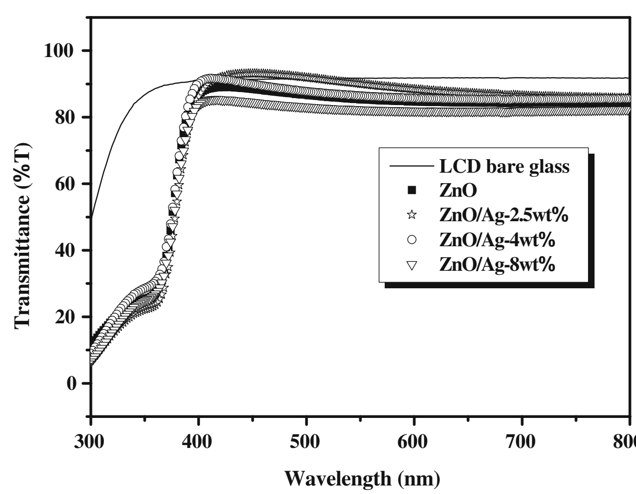

Fig. 2 Optical transmittance of ZnO thin films with different content of Ag nanoparticles

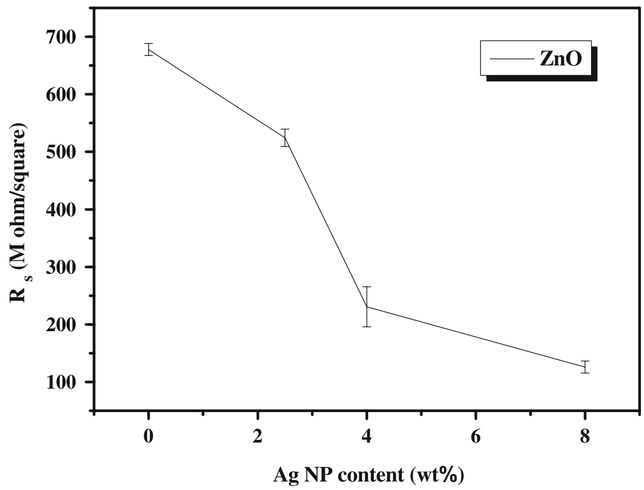

Fig. 3 Electrical sheet resistance of ZnO thin films with different content of Ag nanoparticles

was from the increased scattering of the light by Ag nanocrystals. The increase in grain size would induce the increase in transmittance but the increase of Ag-nanocrystals contributes to a scattering of the light.

The change in sheet resistance of ZnO film-hybridized with Ag nanocrystals was given in Fig. 3. As shown in the figure, a decrease in sheet resistance was observed with the increase of Ag content. ZnO film without Ag-nanocrystals shows about 600 MΩ/square of sheet resistance. This value is somewhat high and it can be said that charge carriers are not enough in pure ZnO film to show the conductivity comparable to that of metals. Ag-nanocrystals would emit charge carriers with applied field and these emitted carriers could contribute a decrease in sheet resistance.

ZnO is known to be non-stoichiometric n-type semiconductor. Then as previously described, doping has been continuously studied to decrease the resistivity and increase the grain size for minimizing the grain boundary area [12,

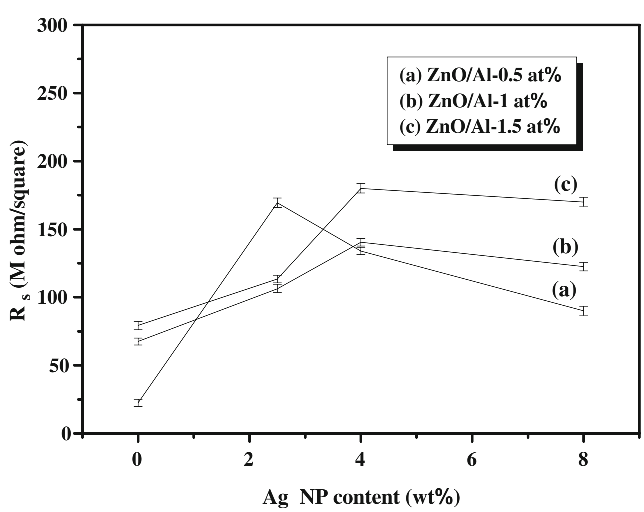

Fig. 4 Electrical sheet resistance of ZnO thin films with different concentration of dopant-Al

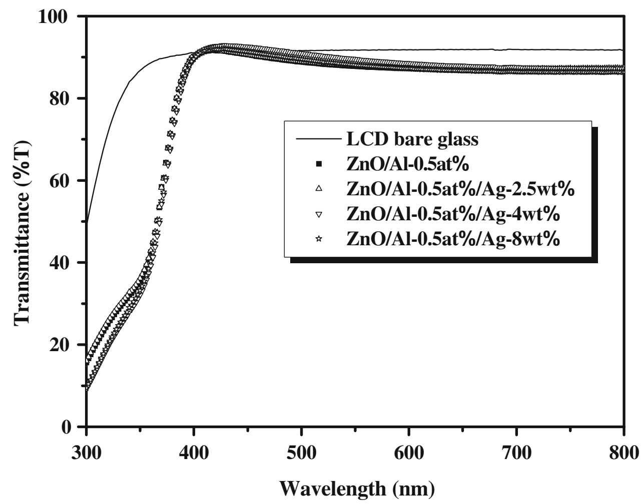

Fig. 5 Optical transmittance of 0.5 at.% Al-doped ZnO thin films with different content of Ag nanoparticles

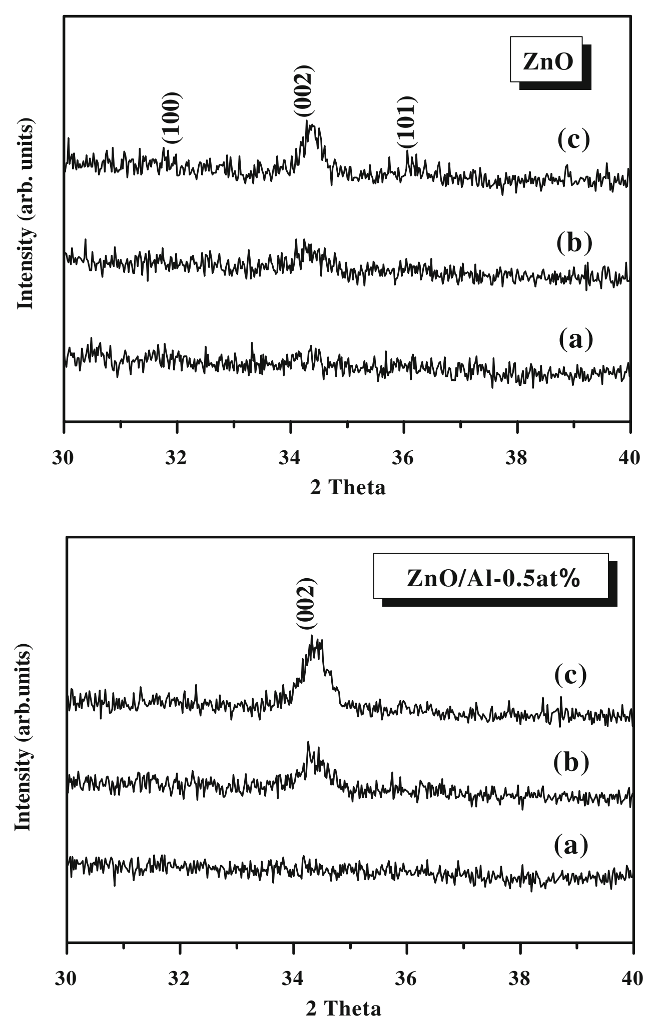

Fig. 6 XRD patterns of undoped and 0.5 at.% Al-doped ZnO thin films with different anneal temperature: (**a**) 250 °C, (**b**) 300 °C, and (**c**) 350 °C

13]. Especially, Al has been known to be an excellent dopant and ZnO doped with 1 at.% of Al shows greatly enhanced optical and electrical properties [10]. Figure 4 corresponds to the change in sheet resistance of Al doped ZnO film with various content of Ag-nanoparticles. The values were obtained from two different solution batches. The 0.5 at.% of Al-doped ZnO film showed greatly increased sheet resistance unexpectedly until the incorporation of 2.5 wt% of Ag-nanocrystals. This abnormal up-and-down change might be caused by an accidental and irreproducible doping with Ag during the incorporation of Ag nanoparticles. The 1 or 1.5 at.% of Al-doped ZnO films also showed an increased resistance behavior but not great as the case of 0.5 at.% of Al. The increase of sheet resistance with the increase of Al-dopant concentration is resulted from the increased scattering probability for carrier due to high dopant concentration [8, 10]. From these results, it can be said that the incorporation of Ag-nanocrystals into Al-doped ZnO films induced two opposite effects; decrease in resistance due to the emission of charge carriers and increase in resistance due to the increased scattering probability for carrier and plausible charge neutralization by accidental and irreproducible doping. However the latter effect seemed to be more dominant than the former except the case of ZnO films with 8 wt% Ag-nanocrystals.

Figure 5 shows the changes in the transmittance of ZnO film doped with 0.5 at.% of Al after the incorporation with various contents of Ag nanoparticles. Almost no-change was observed with the variation of Ag-contents and this situation was exactly the same with the cases of 1 and 1.5 at.% of Al doping. To clarify the reason, XRD measurements were carried out ZnO film doped with 0.5 at.% of Al and the results were compared with those of undoped ZnO film (Fig. 6). From the comparison, both films were found to crystallize after 300 °C. The crystallinity and preferred growth with (002) were intensified in the case of Al-doping. The grain size of undoped and 0.5 at.%-Al doped ZnO films could be calculated as 12.5 ± 2.5 and 22.5 ± 2.5 nm, respectively by using the Scherrer equation [14]. This means that the grain size of ZnO is more important for transmittance property than the incorporated Ag nanocrystals within 8 wt% of incorporation. From these result, it can be said that Ag nanocrystals can be applied to ZnO film without a degradation of transmittance property. However an important enhancement of electrical property of ZnO film was achieved by dopant application. Then it seems that the application of hybridization of Ag nanocrystals for ZnO is possibly applied for electromagnetic shielding.

4 Conclusions

The changes in electrical and optical properties of ZnO film were investigated after the incorporation with nano-sized Ag particles. The transmittance of ZnO was maintained with great enhanced conducting property. This kind of incorporation was applied also to the Al-doped ZnO film. Al-doping into ZnO film induced an improvement in the crystallization and conducting properties. Al-doping covered the advantages of the incorporation of Ag nanocrystals into ZnO film. With the case of Al-doped ZnO film, sheet resistance was increased with the incorporation of Ag nanocrystals. However no drop in the transmittance was found.

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