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Electromagnetic shielder compatible ZnO transparent conducting oxides hybridized with various sizes of Ag metal nanoparticles

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Abstract

In this paper, the effect of different sizes of Ag-nanoparticles dispersed in ZnO matrix using sol–gel method has been focused. Low-temperature crystallized ZnO thin films was achieved by sol–gel process, using zinc acetate dihydrate and 2-methoxyethanol as starting precursor and solvent, respectively. Various sizes of Ag-nanoparticles could be prepared by the spontaneous reduction method with changing the preparation temperatures and mole concentrations of Ag 2-ethylhexanoate in dimethyl sulfoxide solvent. The crystallographic structure of the Ag–ZnO hybrid film was analyzed by X-ray diffraction. Ag-nanoparticle size and optical property of Ag–ZnO hybrid films were measured by UV–vis spectrophotometer.

Keywords: A. Sol–gel process; B. Nanocomposite; C. Electrical properties; D. ZnO

1. Introduction

By the development of telecommunication technology and electronic devices, electromagnetic (EM) shielding has been growing up in the last years. Especially application in the military sector is also very attractive, such as in protecting the electronic display systems of aircrafts from highly intensive electromagnetic fields emitted by radio emitters, TV, radars and telecommunication systems. Moreover the recent limits of radio frequency electromagnetic fields suggest the use of transparent shields for building windows. In this study, a new functional material reinforced in EM-shielding property has been developed.

EM-shielding effectiveness can be calculated by following equations [1]:

$$\mathrm{SE(Shielding\,Effectiveness)} = 20\log\left(\frac{E_b}{E_a}\right) = A_{dB} + R_{dB} + B_{dB} \quad (1)$$

$$A_{dB} = \mathrm{Absorption\,loss} = 8.686\sqrt{\pi f \mu \sigma t} \quad (2)$$

$$R_{dB} = \mathrm{Reflection\,loss} = 20\log\left|\frac{Z_w}{4Z_m}\right| = 20\log\left(\frac{1}{8\pi\gamma f\varepsilon_0\sqrt{2\pi f\mu/\sigma}}\right) \quad (3)$$

$$B_{dB} = \mathrm{Reflection\,correction} = 20\log(j - e^{-2t\sqrt{\pi t\mu\sigma}}e^{-j2t\sqrt{\pi f\mu\sigma}}) \quad (4)$$

From these equations, EM-shielding effectiveness is found to be dependent on the conductivity of materials.

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 [2]. It has therefore been considered a promising candidate material for the development of light-emitting structures and visible EM-shields. However, due to its low-conductivity compared to metal, the doping and hybridization with metal nanoparticles have been investigated [3]. Silver nanoparticles have been widely used in the electronics industry for the manufacture of conductive thick film circuits and for the internal electrodes of

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multilayer ceramic capacitors. It has been known that inclusion of nanoparticles in the materials offers unique properties in optical and electrical characteristics [4,5]. In the literature, Sarto et al. reported the electromagnetic shielding effect of Ag/ZnO multilayer film prepared by radio frequency ion sputtering method [6].

In this work, the size effect of Ag-nanoparticles on the crystallization behavior and electrical and optical properties of ZnO films prepared by sol–gel process at various preparation temperatures and mol concentrations of Ag-nanoparticles has been investigated.

2. Experimental procedure

ZnO thin films were prepared by sol–gel procedure [7]. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (98.0% Aldrich), 2-methoxyethanol (99.9% Aldrich), and monoethanolamine (MEA) (99.0% Aldrich) were used as starting precursor, solvent, and sol stabilizer, respectively. 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 (99.0% Strem chemicals) in the solvent of Dimethyl sulfoxide (99.9% Aldrich) [8]. Trisodium citrate (99.0% Aldrich) was used as a stabilizer of the solution. The concentrations of Ag 2-ethylhexanoates were 0.00015 M, and 0.00030 M and the molar ratio of trisodium citrate was 1.0. The colloidal dispersions were protected from the light during the preparation at 60 or 80 °C. 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 dihydrate were mixed together. The mixed solution was then spin-coated on the glass (Corning 1737) substrates at 2000 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 in the films. The films were annealed in a tube furnace for 1 h at 600 °C in the air atmosphere for crystalline phase formation. The crystallinity of the film was analyzed by X-ray diffraction (XRD, Rigaku) with Cu Kα radiation. The sheet resistance of the film was measured by using four-point probe method and the optical transmittance measurements were carried out by using UV–vis-NIR spectrophotometer.

3. Results and discussion

Fig. 1 shows the UV–vis-NIR spectrophotometer absorption spectrum of Ag-nanoparticles prepared with various preparation temperatures and mole concentrations of Ag 2-ethylhex-

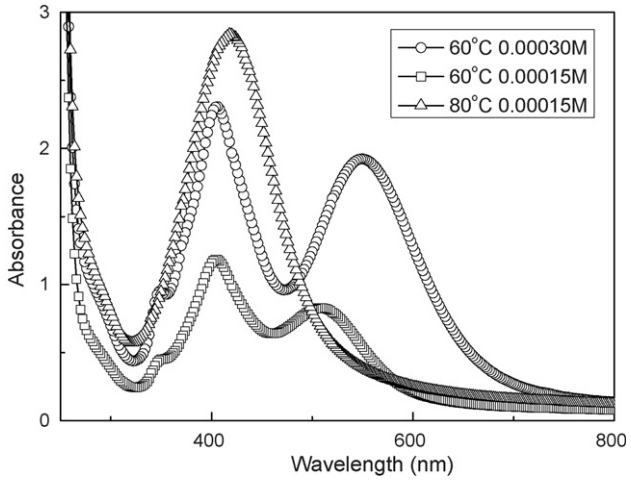

Fig. 1. UV–vis-NIR spectrophotometer absorption spectra of Ag-nanoparticles synthesized by spontaneous reaction method with various preparation temperatures and mole concentrations of Ag 2-ethylhexanoate.

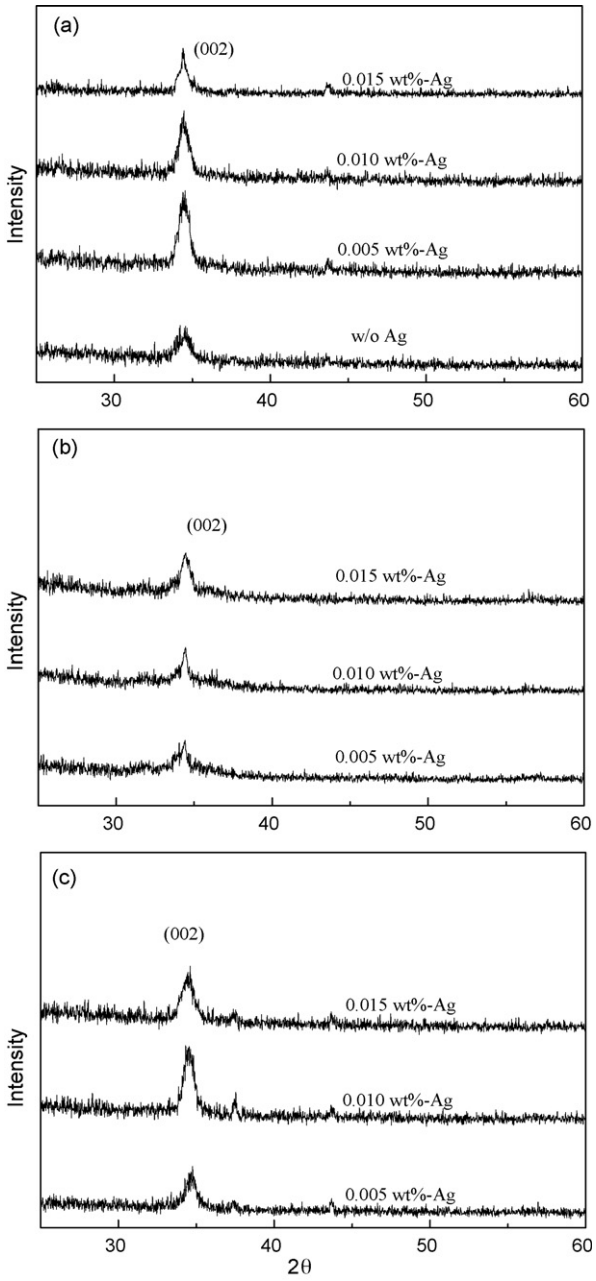

Fig. 2. The XRD patterns of Ag–ZnO hybrid films containing various size and amount of Ag-nanoparticles: prepared with (a) 0.00015 M at 80 °C, (b) 0.00015 M at 60 °C, and (c) 0.00030 M at 60 °C.

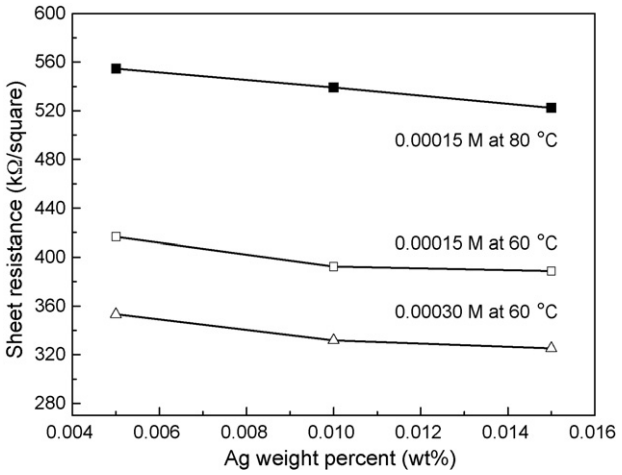

Fig. 3. The sheet resistances of Ag–ZnO hybrid films containing various size and amount of Ag-nanoparticles: prepared with 0.00015 M at 80 °C, 0.00015 M at 60 °C, and 0.00030 M at 60 °C.

anoate. The color of solutions was changed with synthesizing temperature and concentration of Ag 2-ethylhexanoate in DMSO. Trisodium citrate was used as a capping agent to stabilize the solution. As shown in Fig. 1, all samples exhibited intense absorption peak at 410 nm. The sample prepared at 80 °C with Ag 2-ethylhexanoate concentration of 0.00015 M showed a narrow absorption peak at 410 nm of wavelength. The Ag-nanoparticle exhibits two absorption peaks at the wavelength of 410 and 510 nm when the sample prepared at 60 °C with Ag 2-ethylhexanoate concentration of 0.00015 M. In this case, the intensity of the peaks was decreased with narrow absorption peak width. The absorption peak intensity (410 and 550 nm) and width of peaks region were increased with the concentration of Ag 2-ethylhexanoate from 0.00015 to 0.00030 M at the preparation temperature of 60 °C. This may be due to the increase in the nanoparticle size [9,10]. From UV–vis spectrum results, the 0.00015 M at 80 °C samples have the smallest size of Ag-nanoparticles comparing to other samples because this sample exhibits only a single peak at 410 nm and the 0.00030 M at 60 °C samples have the largest Ag-nanoparticle size.

Fig. 2 shows the XRD patterns of Ag–ZnO hybrid films synthesized at different size and weight percent of Ag-nanoparticles. The Ag–ZnO hybrid films exhibited a preferred orientation of (0 0 2) at $2\theta = 34.4^\circ$ with hexagonal wurtzite structure. The crystallinity of Ag–ZnO hybrid film was enhanced with the presence of Ag-nanoparticles (see Fig. 2 (a)). In the cases of Ag–ZnO hybrid films of 0.00015 M at 60 °C and 0.00030 M at 60 °C (Fig. 2(b) and (c)), an improvement in the crystallinity was observed with the increased Ag-nanoparticles. This may be due to the catalytic effect of Ag-nanoparticles to the nucleation and growth of ZnO matrix materials.

The sheet resistances of Ag–ZnO hybrid films are shown in Fig. 3. The ZnO film without Ag-nanoparticles showed high sheet resistance (781.4 kΩ/square). The sheet resistances of Ag–ZnO hybrid films were highly influenced on the Ag-nanoparticle size rather than the amount of Ag-nanoparticles. The Ag-nanoparticle (synthesized with 0.00015 M at 80 °C)-ZnO hybrid film exhibited the highest sheet resistance (554.7 kΩ/square) comparing with the other Ag-nanoparticles-ZnO hybrid films: 416.5 and 353.2 kΩ/square with the films of 0.00015 M at 60 °C and 0.00030 M at 60 °C, respectively. The effect of the amount of Ag-nanoparticles

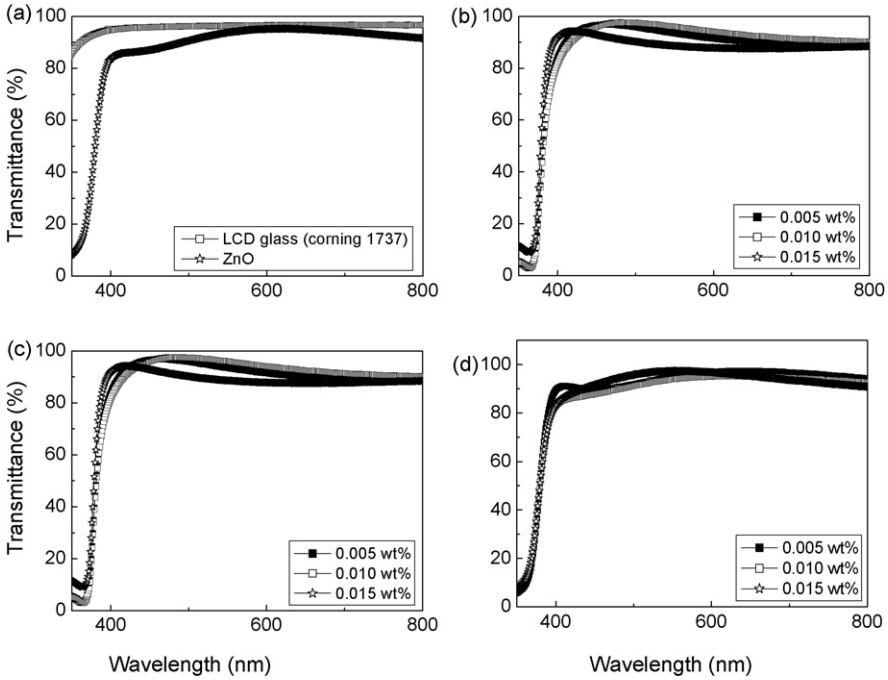

Fig. 4. Optical transmittance spectra of Ag–ZnO hybrid films: (a) LCD glass (corning 1737) and ZnO film and (b–d) Ag–ZnO hybrid films; prepared with (b) 0.00015 M at 80 °C, (c) 0.00015 M at 60 °C, and (d) 0.00030 M at 60 °C.

on the sheet resistance of Ag–ZnO hybrid films has been also studied, but there is no significant change in the sheet resistance with a change in the wt% of Ag-nanoparticles. From these results, it could be concluded that sheet resistance of Ag–ZnO hybrid film was effectively reduced by the control of Ag-nanoparticle size rather than the amount of Ag-nanoparticles. The better conductivity properties could be expected from the films with larger particle size because they have better quality of the grain boundary. The increase of Ag 2-ethylhexanoate concentration induces an increase in the particle size to generate an effective conducting path resulted in the enhanced electrical conductivity of Ag–ZnO hybrid films [11].

Optical transmittance spectra of Ag–ZnO hybrid films are shown in Fig. 4. All samples exhibited high optical transmittance above 90% in the wavelength range above 400 nm. Pure ZnO film shows the optical transmittance of 85% (Fig. 4(a)). When the weight percent of Ag-nanoparticle was embedded into ZnO films, the optical transmittance increased from 85% to 90% as shown in Fig. 4(b)–(d). These all hybrid films showed better transmittance than pure ZnO film. This increased transmittance seemed to depend on the increase in the crystallinity of ZnO film. The grain size of the films was calculated using the Scherrer's equation [12]. An increase in the grain size was observed with the incorporation of Ag-nanoparticles. The calculated values were 10.5 ± 2.5 and $(15.5 \sim 18.5) \pm 2.5$ nm for ZnO and Ag–ZnO hybrid films, respectively. The increase in grain size would induce an increase in the transmittance of light.

4. Conclusions

The Ag–ZnO hybrid films with various sizes of Ag-nanopartilcs were prepared by spin-coating technique. The sheet resistance and optical transmittance of Ag–ZnO hybrid films depended mainly on the Ag-nanoparticle size in ZnO film. The size of Ag-nanoparticles was controlled by varying the concentration of Ag 2-ethylhexanoate. The lowest sheet resistance of Ag–ZnO hybrid films was obtained with the film containing the largest size of Ag-nanoparticles. The crystallinity of the films enhanced with an increase in the amount of Ag-nanoparticles. The Ag–ZnO hybrid films showed high optical transmittance than pure ZnO film.

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