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Simultaneous realization of electromagnetic interference shielding, hydrophobic qualities, and strong antibacterial activity for transparent electronic devices

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ABSTRACT

Al (3 at%)-doped ZnO (AZO)/Ag/AZO multilayer films annealed at 100 °C for 20 min under an oxygen atmosphere were examined for electromagnetic interference (EMI) shielding, hydrophobic qualities, and antibacterial activity for use in transparent glass panels. The annealed AZO (45 nm)/Ag (9 nm)/AZO (45 nm)/glass multilayer films showed a high level of EMI shielding effectiveness in the Bluetooth frequency range (~39 dB) and strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. The annealed multilayer films demonstrated high levels of transmittance (~90%) and conferred hydrophobic qualities to previously hydrophilic as-deposited films.

1. Introduction

The rapid development of modern electronic devices that are packed with highly integrated circuits generates severe electromagnetic radiation, which leads to harmful effects on highly sensitive precision electronic equipment as well as to the living environment for human beings [1]. Electromagnetic interference (EMI) shielding of radio frequency (RF) radiation in electronic devices has become a serious concern in modern society in conjunction with the high demand for, and rapid growth of, RF radiation sources [2–4]. Recently, electrically conductive polymer composites [5–8], graphene foam composites [9], silver nanowires [10–12], and single-walled carbon nanotube films [13] have received much attention for EMI shielding applications because they possess many advantages compared with conventional metal-based materials. However, the antibacterial effects of the use of these materials have not been reported.

Functional glass panels have recently been recognized as important items because the display industry has developed rapidly. However, all the transparent glass panels that are used to display information are easily contaminated by many microorganisms such as various bacteria, and this can promote infection among human beings. Therefore, the antibacterial treatment of transparent glass panels is indispensable, but this treatment should not deteriorate the transparency of the glass panels. The glass panels that supply the various functions are required to have high transmittance that is comparable to glass, strong antibacterial activity, and good mechanical endurance. These must also possess hydrophobic properties so that the physical properties of the glass panels will not be degraded by contact with water. Silver nanoparticles (NPs) [14–17] or zinc oxide NPs [18–20] are known to have strong inhibitory and bactericidal effects. However, metal NPs or metal oxide NPs have traditionally been prepared using a solution technique, which resulted in an inhomogeneous antibacterial effect due to the severe agglomeration of the nanoparticles. Choi et al. [21] used zinc/Ti NPs to achieve qualities that were comparable to glass such as transmittance, strong antibacterial activity, and stable mechanical durability via touch and swipe. Although that study exhibited the predominate properties for electronic glass panel applications, it was impossible to exhibit EMI shielding because these properties were exhibited near an insulator. For hydrophobic qualities, protective layers such as fluoride films must be deposited onto a glass substrate coated by antibacterial agents [22,23].

Organic photovoltaics have attracted considerable attention as a

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renewable, cost-effective, and alternative energy source to Si-based solar cells, due to a simple device structure, and to a simple fabrication process [24–26]. To fabricate low-cost and large-area organic solar cells, it is necessary to develop low-cost transparent anode materials with low sheet resistance and high transparency. Recently, Ga-doped ZnO (GZO) and Al-doped ZnO (AZO) has been studied as replacements for indium-tin oxide (ITO) for use as anode electrodes. However, GZO and AZO electrodes grown at room temperature cannot be used because their electrical and optical properties can only be optimized by the activation of group III elements. To solve this problem, the combination of an oxide electrode and metal has been investigated for use as transparent and low sheet-resistance electrodes. GZO/Ag/GZO [27], ZnO/Ag/ZnO [28], and AZO/Ag/AZO [29–31] multilayer electrode structures with a low sheet-resistance (~5–8 Ω/square) have been reported via the insertion of an optimal 5-15 nm-thick Ag layer.

The simultaneous realization of effective EMI shielding and antibacterial activity that can maintain a transmittance comparable to glass panels has not been reported. Therefore, in the present study, we investigated the EMI shielding, antibacterial activity, and hydrophobic properties of AZO/Ag/AZO multilayer films grown at room temperature onto a glass substrate annealed at 100 °C for 20 min under an O_2 atmosphere. In particular, EMI shielding effects of AZO multilayer films were compared with commercial 60 μm-thick Cu foils and Ag thin films of various thicknesses with resistivity that is similar to AZO multilayer films.

2. Materials and methods

AZO thin films were grown onto reinforced (Corning Gorilla) glass substrates at room temperature via radio-frequency magnetron sputtering using a $ZnO{:}Al_2O_3$ ceramic target (2 wt % Al_2O_3). Details of the deposition conditions of the AZO and Ag films for a multilayer structure were described in a previous study [30]. The thickness of the AZO films grown on the glass substrate was maintained at 45 nm and that of the Ag films was maintained at 9 nm. The thicknesses of the AZO films grown onto the Ag (9 nm)/AZO (45 nm)/glass were varied from 20 to 100 nm in order to establish the effect of the AZO thickness on EMI shielding. AZO (45 nm)/Ag (9 nm)/AZO (45 nm) multilayer films annealed at 100 °C for 20 min under an O_2 atmosphere were used for analysis of EMI SE, antibacterial activity, mechanical durability, and hydrophobic qualities.

Transmittance and resistivity of the AZO multilayer films was measured using an HP 8453 UV-VIS spectrophotometer and the four-point probe method, respectively. The EMI shielding effect in the range of 1.5–3.0 GHz (Bluetooth function) was investigated using the AZO/Ag/AZO samples (10 × 5 cm^2) via the waveguide shown in Fig. S1 (Supplementary Information, SI). The hydrophobic qualities of the multilayer films were investigated via contact angle measurement using the as-deposited and annealed samples. Mechanical durability of the multilayer films was tested via touches. The sample size for the touches was approximately 4.5 × 4.5 cm^2. For touches, a piece of glass 7.8 cm in width, 11.3 cm in length, and 2.8 cm in height was repeatedly dropped onto the multilayer films from a height of 1 cm. The impact conditions of the mechanical touch test using the glass were approximately 1.85×10^{-3} N • m, which placed them within the range of both a finger (1.10×10^{-3} N • m) and a pen (2.50×10^{-3} N • m) (Han and Kim 2003) [32].

The antibacterial measurement using the multilayer films was performed at the AMORE PACIFIC CORPORATION (Korea) using the film-attachment method [33]. The measured bacteria are two types such as *Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli).* Film-attachment method was followed by the JIS Z 2801 [33]. For observation of the morphologies of each bacterium by field-effect scanning electron microscope (FE-SEM), *E. coli and S. aureus* bacteria were incubated for 24 h at 30 °C and 90% humidity. The controlled (blank) and multilayer coated glass substrates were dipped into the incubated bacteria for 24 h and then the glass substrates were removed from the incubated solution. For observation of the detailed image, the incubated solutions were frozen for 5 min via liquid nitrogen and the frozen solutions were spread onto the bare glass. The solutions were coated with 10 nm-thick Pt for SEM measurement.

3. Results and discussion

Fig. 1 compares Ag thin films of various thicknesses with AZO multilayer films for transmittance, resistivity, and EMI shielding effectiveness. The Ag films were grown at room temperature onto a glass substrate via direct current (dc) sputtering. Fig. 1a shows the variations in transmittance vs. wavelength for different Ag film thicknesses. Transmittance of the Ag thin films was abruptly decreased from 68 to 19% (at a wavelength of 550 nm) with increases in film thicknesses from 10 to 50 nm. The resistivity of the different thicknesses of Ag thin films is shown in Fig. 1b, the most noteworthy of which is a resistivity of approximately 7.4×10^{-5} Ω-cm for 10 nm-thick Ag films. The resistivity of the 20 to 50 nm-thick Ag thin films was slightly decreased from 1.4 to 1.0×10^{-5} Ω-cm. The resistivity of the 10 nm-thick Ag films showed values similar to that of AZO (45 nm)/Ag (9 nm)/AZO (45 nm) multilayer films [30]. Therefore, Ag films with thickness that ranged from 10 to 50 nm were determined in order to compare them with the transmittance, resistivity, and EMI shielding effectiveness of the AZO/Ag/AZO multilayer films.

For EMI shielding effectiveness of the Ag films, 10 × 5 cm^2 rectangular specimens were placed between the two sections of the waveguide, as shown in Fig. S1 (SI), and the S-parameters such as S_{11}, S_{12}, S_{22}, and S_{21} of each sample were recorded over the Bluetooth frequency range. Here, the overall EMI shielding effectiveness (SE) was calculated based on the S_{12} or S_{21} parameters as follows [34].

$$\text{EMI SE} = 10\log\left(1/|S_{12}|^2\right) = 10\log\left(1\Big/|S_{21}|^2\right) \quad (1)$$

Where $|S_{12}|^2$ and $|S_{21}|^2$ represented the power transmitted from port 1 to port 2 and vice versa, respectively. Fig. 1c shows the variations in the S_{12} parameter as a function of frequency for different thicknesses of Ag films. The S_{12} values increased with increases in Ag film thickness in the Bluetooth frequency range of 1.50–3.00 GHz. The results of Fig. 1c suggest that the S_{12} increased with increases in Ag film thickness. Calculation (Equation (1)) using the S_{12} values observed for each sample (Fig. 1d) showed the variations in the EMI shielding effectiveness as a function of frequency for different Ag thicknesses. Stable EMI SE values were observed at frequencies ranging from 1.75 to 3.00 GHz, and showed an overall EMI SE value of approximately 25 dB. Generally, the target value of the EMI SE that was required for commercial applications is approximately 20 dB, which indicates a less than 1% transmission of electromagnetic waves [35]. As a result, although the Ag thin films satisfied the EMI SE requirements in the Bluetooth frequency range, they were inadequate for transparent glass panels because their transmittances were too low in the visible range. Therefore, the results of the present study showed that the AZO/Ag/AZO multilayer film structure is recommended for enhanced transmittance, hydrophobic qualities, and antibacterial activity as well as mechanical durability.

Fig. 2a shows the variations in transmittance of the as-deposited and annealed AZO (45 nm)/Ag (9 nm)/AZO (45 nm)