Journal of Alloys and Compounds 602 (2014) 255–260

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Enhanced transmittance, mechanical durability, and anti-fingerprinting qualities of silver nanoparticles deposited onto glass substrates

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ARTICLE INFO

Article history:
Received 15 February 2014
Accepted 4 March 2014
Available online 13 March 2014

Keywords:
Silver NPs
Protective layer
Enhanced transmittance
Mechanical durability
Resistance to fingerprinting

ABSTRACT

Qualities such as an enhanced transmittance, mechanical durability, and resistance to fingerprinting were investigated for silver nanoparticles using a protective layer (fluoride/SiO_2 films) deposited onto a silver nanoparticles (NPs)/SiO_2/glass. The role of the protective layer in the enhancement of transmittance was investigated via localized surface plasmon resonance coupling and de-coupling using the protective layer/silver NPs/SiO_2/glass. The protective layer deposited onto the dense and uniformly distributed silver NPs showed an enhanced transmittance of approximately 91%, compared with that of about 75% in samples without a protective layer. In addition, the protective layer showed effective anti-fingerprinting qualities and good mechanical durability after repeated swipes and touches.

1. Introduction

Noble metal nanoparticles have been of widespread interest in the past few years as a result of advances in molecular plasmonic devices [1], biosensing [2], and other applications. Silver is one of the best conductive substances, because it contains unique properties in terms of high electrical conductivity, stretchability [3], salt spray mist corrosion durability [4], and electromagnetic interference (EMI) shielding [5]. Silver-coated Al-doped ZnO (AZO) [6] and AZO/Ag/AZO multilayer films [7,8] have been studied to improve electronic conductivity and high transmittance because Ag has a low resistivity of approximately $2 \times 10^{-6}\ \Omega$ cm. Many different approaches using silver nanoparticles or silver ions have been used to prepare silver nanoparticles (NPs) to investigate antibacterial activity [9–11]. However, metallic nanoparticles are the most promising as they show good antibacterial properties due to a large surface-area-to-volume ratio, which is currently on the rise as a main focus for researchers due to the growing microbial resistance against metal ions and antibiotics, and the resultant development of resistant strains.

Although the silver NPs showed good antibacterial effect, when prepared on transparent glass substrates, transmittance of the silver NPs/glass must be indispensably managed because the silver NPs deposited onto glass show a decrease in transmittance.

For an resistance to fingerprints by the electronic device panels with a glass substrate, fluoride films were deposited onto the glass substrate [12]. However, because of the adhesion problem between fluoride films and glass substrates, a thin SiO_2 layer should be inserted between the fluoride films and the glass. In particular, the problems with fingerprinting should be solved for applications of electronic device panels to products such as smart-phones.

To enhance the mechanical durability of the silver NPs deposited onto the glass substrate, silver NPs should strongly adhere to the glass substrate. A SiO_2 adhesion layer was inserted between the silver NPs and the glass substrate for strong adhesion. In order to satisfy the three different requirements using silver NPs deposited on the SiO_2/glass substrate, a 15 nm-thick protective layer (fluoride/SiO_2 films) was deposited onto the silver NPs/SiO_2/glass in the present study. Optical properties of the protective layer/silver NPs/glass and silver NPs/glass were investigated through study of the localized surface plasmon resonance (LSPR) coupling and de-coupling [13–16].

Based on the LSPR analysis, a protective layer deposited onto the silver NPs/SiO_2/glass was used to enhance transmittance using homogeneous and dense silver NPs deposited onto SiO_2/glass substrates. The mechanical durability of the samples was investigated via touches and swipes to test the mechanical role of the protective layer. The effect of anti-fingerprint measures via a protective layer was examined through the measurement of the wetting angle after mechanical tests.

2. Experimental procedure

For a strong attachment of the silver NPs with the glass substrate ($4.5 \times 4.5\ cm^2$), the 15 nm-thick SiO_2 buffered films were deposited via rf magnetron sputtering, using a SiO_2 quartz target (purity of 99.99%) with a diameter of 2

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http://dx.doi.org/10.1016/j.jallcom.2014.03.019
0925-8388/

in, onto the reinforced (Corning Gorilla) glass substrates. The deposition was performed under conditions such as a deposition rate of about 1 nm/min, a working pressure of 0.13 Pa, an argon flow rate of 20 sccm (standard cc min^{-1}), and an rf power of 100 W. The silver NPs consisted of a silver target (purity of 99.99%) 2 in. in diameter, and were prepared on the SiO_2 thin films using dc sputtering with deposition times that varied from 5 to 30 s at a dc power of 11 W under a working pressure of 0.13 Pa. Fluoride films were deposited onto the panels with silver NPs in order to prevent fingerprints. Here, fluoride films showed an inferior adhesion to the silver NPs. Therefore, SiO_2 buffered films, for a strong adhesion of the fluoride films, were deposited using electron-beam evaporation between the fluoride films and the silver NPs. The total thickness of the fluoride and SiO_2 films was approximately below 15 nm. Fluoride films consisting of fluorine and carbon were deposited using electron-beam evaporation (JNTC, Co. Ltd. in Korea) under a working pressure of 3.3×10^{-3} Pa. The anti-fingerprinting qualities of the protective layer/silver NPs/SiO_2/glasses were evaluated through the measurement of the wetting angle (Kruss, ESA100).

The optical properties (transmittance) of the nanocomposites with and without a protective layer of fluoride films/SiO_2 were investigated using an HP 8453 UV–VIS spectrophotometer. The distances between the silver NPs and the particle size of the silver NPs were measured using atomic force microscopy (AFM, Auto Probe CP). The localized surface plasmon resonance for the relationship between the silver nanoparticles and the protective layer was investigated using three-dimensional finite-difference time-domain (FDTD) methods. The surface image of the protective layer/silver NP/SiO_2/glass nanocomposites was observed using field-emission scanning electron microscopy (FE-SEM, Sirion, FEI (Netherlands)). The real structure of the silver nanocomposite deposited on the Si (001) substrates was observed using a field emission transmission electron microscope (FE-TEM: FEI, Tecnai G^2 F30S-Twin). A cross-section of the samples for FETEM analysis was prepared using the focused-ion beam (FIB) method instead of ion-milling, because conventional ion-milling can cause mechanical damage to the silver NPs. Platinum and carbon of about 20 nm were coated onto the protective layer/silver NP/SiO_2/Si nanocomposites to remove the charging effect and to protect the protective layer/silver NP/SiO_2/Si nanocomposites for sampling using FIB. The detailed identification of the layers deposited onto the silver NP was performed using X-ray photoelectron spectroscopy (XPS: ESCALAB 200R, VG Scientific). Sheet resistances of silver nanocomposites were measured using a four-point probe method.

Mechanical durability of the protective layer/silver NP/SiO_2/glass was tested via swipes and touches. Mechanical durability was tested using 4.5×4.5 cm^2 samples. For touch tests, a piece of glass 7.8 cm wide, 11.3 cm in length, and 2.8 cm in height was repeatedly dropped onto the samples 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 finger (1.10×10^{-3} N m) and pen touch (2.50×10^{-3} N m) [17]. The swipe tests were conducted using the same glass block.

3. Results and discussion

Fig. 1(a) and (b) shows the schematic and real structures of the silver-based nanocomposites, respectively. In the TEM cross-sectional image, the SiO_2 layer on the glass substrate was difficult to identify because of sample preparation, so the glass substrate was replaced by a Si (001) substrate. As shown in Fig. 1(b-1), small-sized silver NPs were embedded in the protective layer rather than large-sized silver NPs. No distinction was observed between the SiO_2 buffer layer and the fluoride films. Large-sized silver NPs were partially embedded in the protective layer, as shown in Fig. 1(b-1). In order to observe the embedded silver NPs in the protective layer, silver NPs coated with a protective layer are shown in Fig. 1(b-2), which shows that the large-sized silver NPs were not fully covered by the protective layer.

In order to investigate the existence of the protective layer on the silver NP, protective layer/silver NP/SiO_2/glass nanocomposites were investigated using XPS. Fig. 2(a) shows the XPS spectra of the protective layer/silver NP/SiO_2/glass nanostructure etched for (a-1) 0, (a-2) 5, and (a-3) 15 s. In order to remove the surface impurities from the air atmosphere, the surface of the samples was *in situ* etched within the XPS equipment. From the XPS spectrum of the unetched sample (see (a-1)), all elements such as fluorine, silver, Si, O, and C were observed, which consisted of the samples etched for 5 and 15 s. The depth resolution of the XPS is approximately 1–2 nm. When the XPS depth-resolution was considered, the sliver peak observed for the unetched samples indicated that the protective layer deposited onto the silver NP was very thin – less than 2 nm. Fig. 2(b) and (c) shows the AFM three-dimensional and SEM surface images, respectively, of the protective layer/silver NP/SiO_2/glass nanocomposites. Silver NPs are clearly shown in the AFM and SEM images after deposition of the protective layer. As shown by the AFM image, the root mean square (rms) roughness of the samples was approximately 1.5 nm.

The transparency of silver-based nanocomposites deposited onto the glass substrate was discussed. Fig. 3(a) and (b) shows

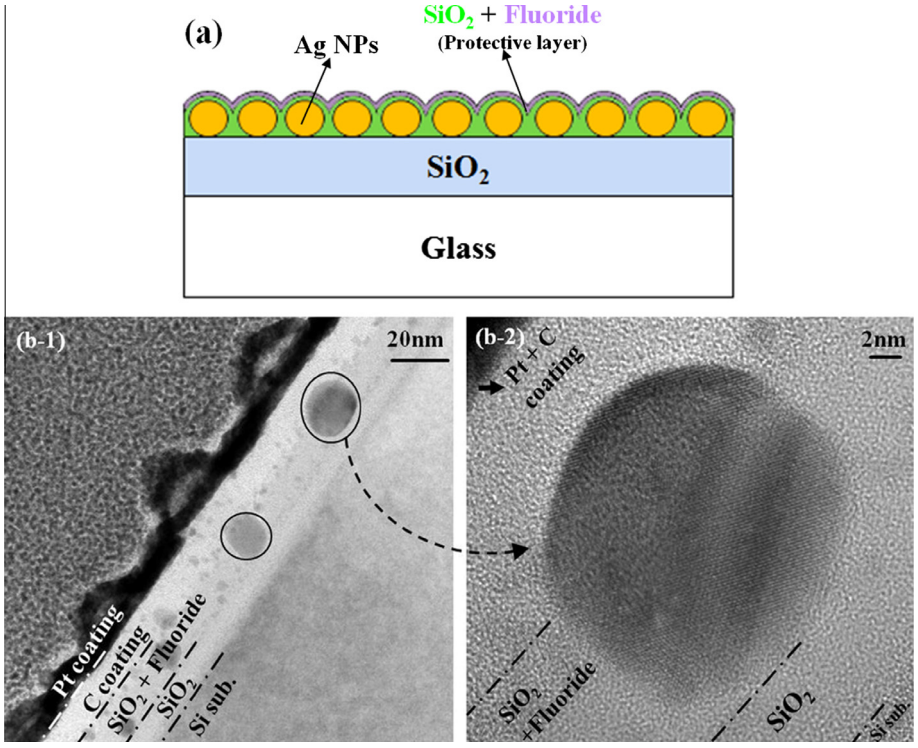

Fig. 1. (a) Schematic and (b-1) real structures of the protective layer/silver NPs deposited onto a SiO_2/Si substrate. (b-2) High-resolution image of the silver NPs shown in (b-1).