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THERMAL DEGRADATION BEHAVIOR OF Ag NANOWIRE-COATED TRANSPARENT CONDUCTIVE FILM FOR FLEXIBLE DISPLAY APPLICATIONS

For the reliable applications of silver nanowires, AgNW, which is used as a conductive transparent film in electronic devices, the isothermal degradation behaviors of AgNW films with and without overcoating were investigated. Accelerated isothermal degradation was performed as a function of temperature, time, and atmosphere. Electrical resistance and optical transmittance were measured and correlated with the microstructural damages, such as formation of oxide particles and fragmentations of AgNW, which were quantitatively determined from the scanning electron micrographs. The overcoating retarded the formation of oxide particles and subsequent fragmentations as well as resulting degradation in electrical resistance without affecting the optical transmittance.

Keywords: Silver nanowire, isothermal degradation, electrical resistance, overcoating

1. Introduction

As a substitute for indium tin oxide (ITO), which is widely used as a transparent conductive electrode material, AgNW films have been extensively investigated for applications in flexible electronics, such as display, energy devices, and heating elements, owing to their low electrical resistance, high optical transmittance, as well as mechanical flexibility [1-6]. To ensure the reliable application of AgNW films, their durability under field environment should be secured. Degradations caused by mechanical [1], thermal [2], and atmospheric [3] stress are a matter of major concern.

Particularly, due to the very high surface-area-to-volume ratio of AgNW, they have limitations of undergoing atmospheric degradation such as oxidation and corrosion [2-5]. Some studies on the atmospheric degradation due to elevated temperatures [2], humidity [3], light exposure [4], and high electrical currents [5] have been reported. However, the thermal degradation mechanism and quantitative correlation with property have not been studied much so far. In this investigation, the effect of isothermal exposure and overcoating on electrical resistivity and optical transmittance was studied based on the quantified structural damage including the oxide particle formation and fragmentation of AgNW.

2. Experimental

A commercial AgNW suspension (N&B Co. Ltd., Korea, model: SNW-004, purity >99.5%, diameter: 40 nm, length: 10 μm) was coated on a polyethylene terephthalate (PET) substrate film (thickness: 50 μm) by a roll-to-roll process. A PET film was used for a flexible substrate. Physical and mechanical properties of the PET film were as follows: glass transition temperature of 78°C, crystallizing temperature of 120°C, tensile strength of 110 MPa, and elongation of 15% [8]. The initial electrical resistance and optical transmittance were optimized as about 23 Ω/sq and about 93%, respectively, by controlling the various process variables. The roll-to-roll coating process was performed by using a micro-gravure coater. Detailed step of the coating process consists of a specific formulation of the coating solution to achieve initial electrical resistance of 23 Ω/sq, gravure coating of the AgNW solution, overcoating of an ultraviolet (UV) curable transparent polymer and final calendaring to increase contact surface of the AgNW. One overcoating (O/C) on this AgNW layer was additionally performed for comparison with the non-overcoated specimen. This additional layer, which does not contain AgNW, is for protecting AgNW from environmental attacks. The O/C with a specific chemical composition to prevent oxidation of AgNW was made by a micro-gravure coating and then UV-cured at a wavelength of about 380 nm. Both the films, non-overcoated and overcoated, were isothermally exposed to 100, 120, and 140°C up to 7 days or exposed to 160°C and 180°C up to 60 minutes in natural air and inert Ar atmosphere in an oven. Electrical resistance and optical transmittance were measured after exposure for specific time periods. In order to probe the material damage mechanism, AgNW was observed by using

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a scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). An average number of oxide particles and fragments per unit area was determined from at least 5 SEM micrographs per specimen, and were then correlated with the measured electrical resistivity. Optical transmittance was determined by a UV-Vis spectrometer in the wavelength range of 400-700 nm.

3. Results and discussion

Fig. 1(a) and (b) shows the change in the electrical resistance as a function of time, temperature, and atmosphere of isothermal exposure as well as overcoating. The electrical resistance of all the specimens increased with increase in exposure time and temperature. The overcoating on the AgNW film effectively retarded the increasing rate of the resistance, although the extent of retardation was not as much as the exposure to inert Ar atmosphere.

Fig. 2 shows the effect of isothermal exposure on the optical transmittance of the AgNW specimens with and without overcoating, respectively. The overcoating itself did not deteriorate the optical transmittance of the AgNW specimen. Optical transmittance of the non-overcoated AgNW specimen decreased after exposure to very high temperature of 160°C for 60 minutes in air, while little degradation occurred in the overcoated AgNW specimen even at such high temperature.

Fig. 3(a)-(d) are the scanning electron micrographs to show the effect of overcoating on the microstructural damage of the AgNW specimen. A large number of oxide particles on the AgNWs as well as fragmentations of the AgNWs were observed for both non-overcoated and overcoated specimens after isothermal exposure to 180°C for 60 minutes in air. The degree of these structural damages was less severe for the overcoated specimen.

Fig. 4 shows a high resolution XPS spectrum in Ag 3d binding energy regions of the non-overcoated specimens. The Ag 3d peak showed a typical peak split into $3d_{5/2}$ and $3d_{3/2}$

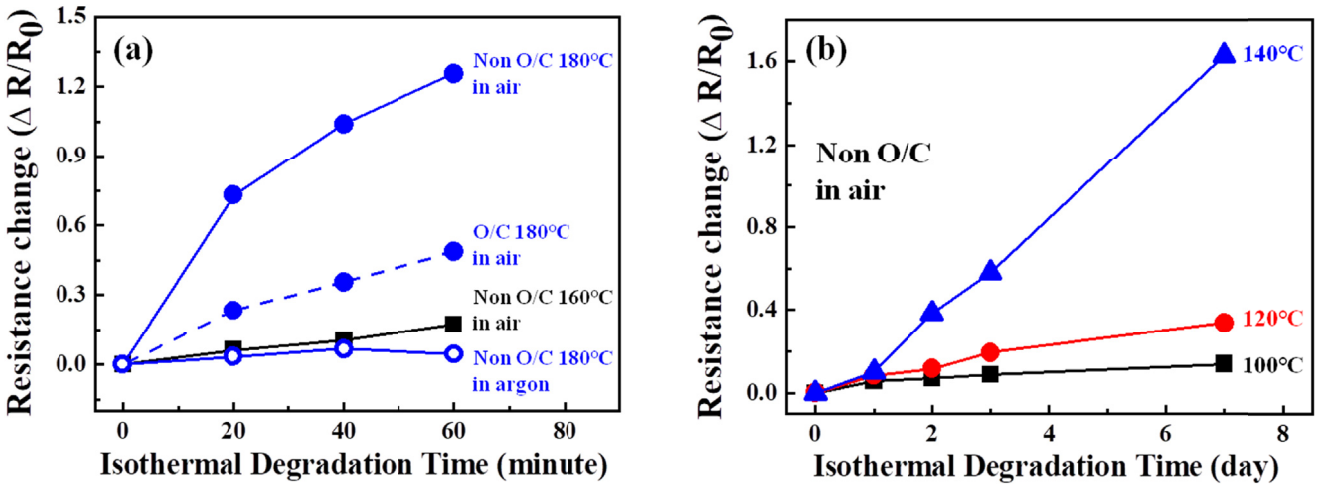

Fig. 1. Change in the electrical resistance of AgNW film with isothermal exposure at (a) 160°C and 180°C up to 60 minutes, and (b) 100, 120, and 140°C up to 7 days

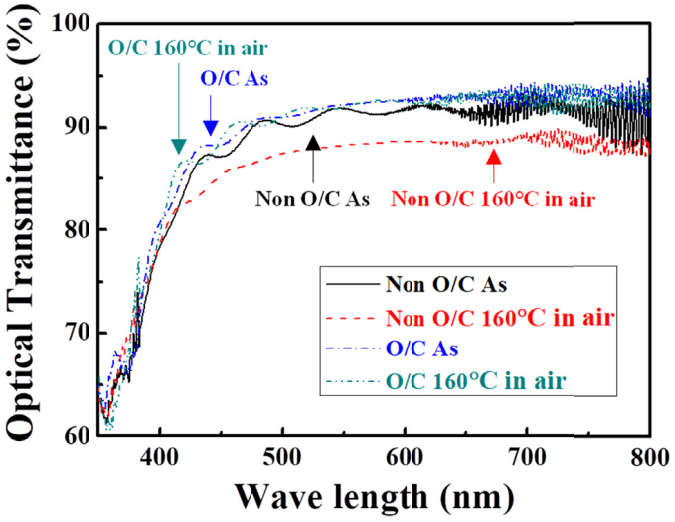

Fig. 2. Effect of overcoating on the optical transmittance of AgNW film exposed to 160°C for 60 minutes in air

peak with separation energy of about 6 eV. Ag $3d_{5/2}$ peak was observed at 368.2 eV for the as-received specimen and 367.8 eV for the isothermally exposed specimen, which corresponds to the metallic silver (Ag°) and the silver ions in Ag_2O (Ag^+), respectively [9]. According to these XPS results, the particles formed by thermal exposure (Fig. 3b, 3c) are believed to be Ag_2O phase.

According to the magnified micrographs for revealing the damage mechanism shown in Fig. 5, the oxide particle seems to form preferably at the junction of the AgNW network and the subsequent fragmentation of the AgNW occurs at some oxides particles. These oxide particles can cause the optical degradation observed in Fig. 2 due to increased light scattering at the large number of oxide particles. Fragmentation as well as formation of non-conducting oxide particles can increase the electrical resistance by blocking the current flow along conductive AgNW, as shown in the results of Fig. 1.

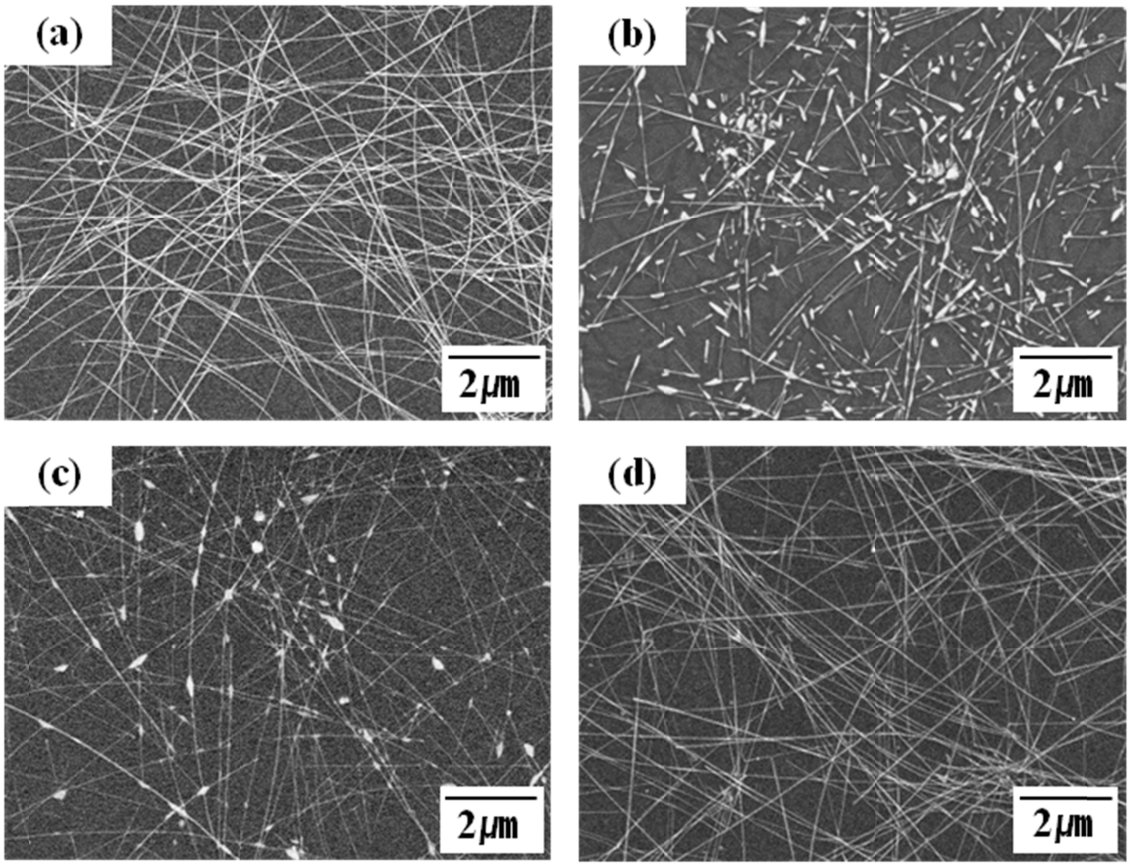

Fig. 3. Scanning electron micrographs showing microstructural damages under various isothermal exposure conditions: (a) as-received (non-overcoating), (b) 180°C in air (non-overcoating), (c) 180°C in air (overcoating), and (d) 180°C in Ar (non-overcoating)

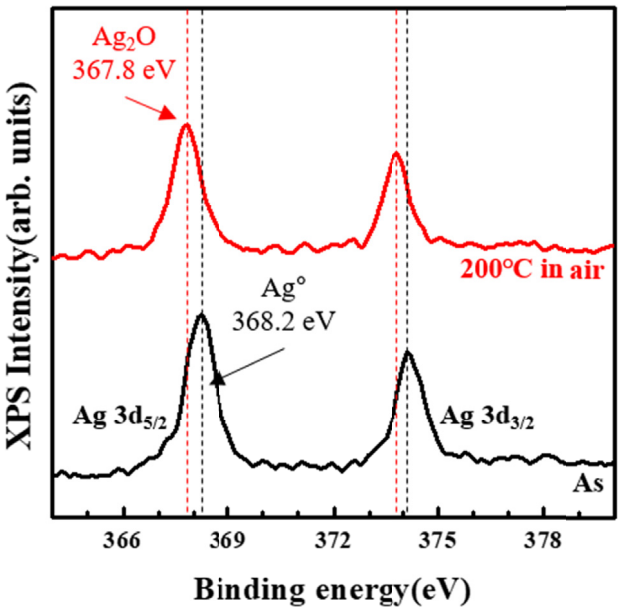

Fig. 4. High resolution XPS spectrum in Ag 3d binding energy regions of the non-overcoated specimens: (a) as-received specimen and (b) isothermally exposed specimen at 200°C for 60 minutes in air

For a detailed investigation on the correlation between microstructural damages and property degradation, the number of fragments and particles were quantitatively determined as a function of exposure time for the non-overcoated specimen (Fig. 6). The number of oxide particles is about four times larger than that of the fragments. Both the average number density of the fragments and the particles increased with time, temperature, and oxidative environment, respectively. These increasing trends are similar with that of the electrical resistance presented in Fig. 1, implying that the observed microstructural damages are likely to have correlation with the degradation of electrical resistance due to the isothermal exposure.

Fig. 7 compares the resistance change of the isothermally exposed specimens having damages from oxide particles and fragments with that of the tensile-strained AgNW specimen having damage from fragmentation only. In our previous investigation [8], a large number of fragments of the AgNW were reported after tensile strain up to 12% under room temperature and air condition. Electrical resistance of the tensile-strained AgNW specimen increased as a linear function of number density of the AgNW fragments measured from the interrupted specimens after various tensile strains. On comparing the slopes of the linearly fitted lines, the isothermally exposed specimen has a higher value than that of the tensile-strained specimen, implying that another damage mechanism besides fragmentation (i.e., formation of oxide particle at high temperature) is effectively acting to increase the electrical resistance at high temperature.

These oxidation damages observed under the accelerated condition can occur after long-term use of the electronic device using AgNW film in an actual field condition such as in a car

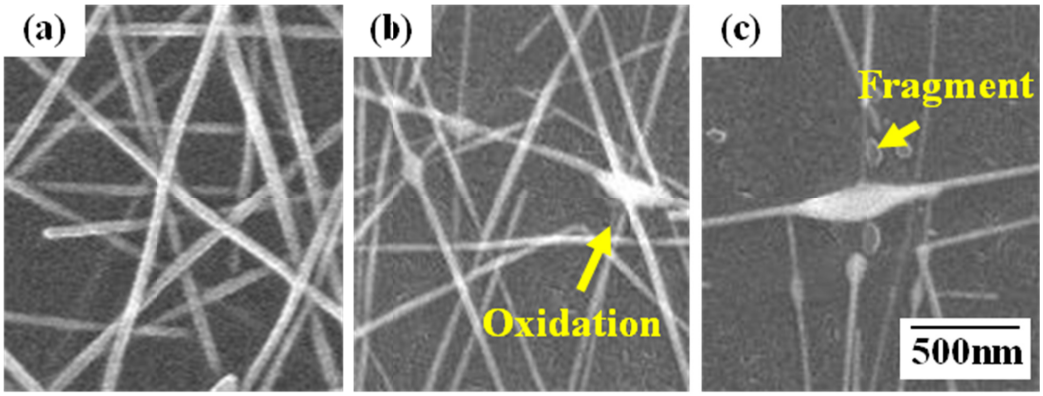

Fig. 5. Magnified scanning electron micrographs showing isothermal damage mechanism of the non-overcoated AgNW film: (a) as-received, (b) formation of oxide particle, and (c) fragmentation of AgNW

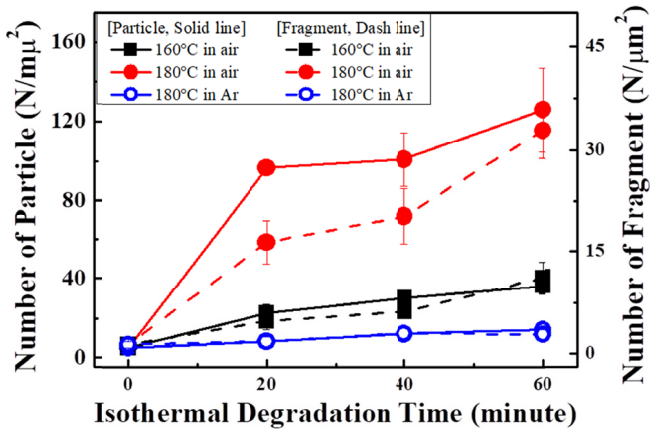

Fig. 6. Quantification of number of oxide particles and fragments per unit area as a function of temperature, time and atmosphere of isothermal exposure

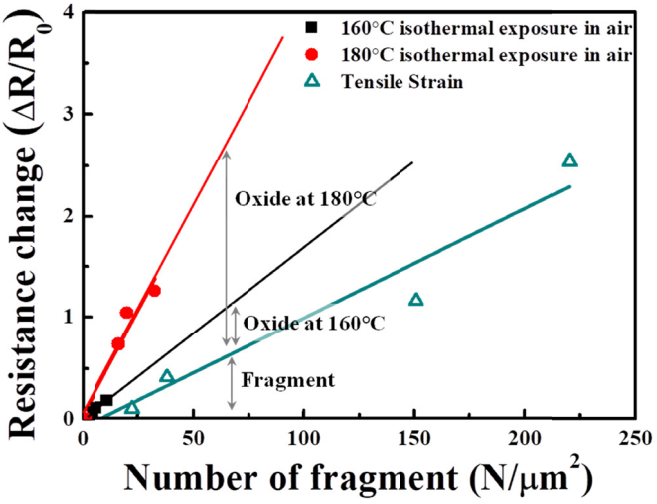

Fig. 7. Comparison of resistance change between isothermally-exposed and tensile-strained AgNW specimen as a linear function of number of fragments

in hot weather. In order to reduce the oxidation damage, a suitable protection such as overcoating on the AgNW-coated film as proved in this work, as well as protective organic coating on individual AgNW [8] can be a feasible solution.

4. Conclusions

Isothermal exposure of AgNW film in air atmosphere caused microstructural damages including preferable formation of non-conducting Ag-oxide particles at the junction of the AgNW network and subsequent fragmentation. As a result, a large increase in the electrical resistance occurred for the non-overcoated specimen. Overcoating effectively retarded the formation of oxide particles and fragmentations, and hence degradation in the electrical resistance without deteriorating the optical transmittance.

Acknowledgments

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