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# The effect of light and humidity on the stability of silver nanowire transparent electrodes

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Transparent electrodes based on silver nanowires (AgNWs) films have attracted considerable attention owing to their high electrical and thermal conductivity, optical transparency, and flexibility. However, the long-term reliability of AgNWs electrodes, has seldom been studied. In the work, the effects of storing environment, such as, natural light, humidity, on the long-term reliability has been investigated in detail. The increase of electrical resistance with storage time greatly closed to natural light illumination, especially ultraviolet (UV) illumination, and high humidity seriously accelerated the failure of AgNWs electrodes. All these seems corresponded to the storing temperature. Some over-coating layers have been used to protect AgNWs electrodes considering the light and humidity from environmental factors and indicated that epoxy resin protecting layer exhibited the longest lifetime: over 40 days at 85°C and 85% relative humidity.

Key Words: Silver nanowires film, reliability, over-coating layer, natural light, humidity

## 1. INTRODUCTION

Since 2008, Lee et al. fabricated the first silver nanowires (AgNWs) transparent conductive films.[1] many attempts have been made to use AgNWs films in solar cells,[2–5] OLEDs, [6–8] touch screens,[9, 10] and sensors.[11, 12] Various detailed post-treatment techniques have been designed and developed to improve the conductivity and transparency of AgNWs films.[3–16] Hundreds of papers/books about AgNWs films are published annually; however, there have been no systematic studies about the reliability of AgNWs films although it is known that bulk silver is easily corroded or tarnished in air and sensitive to some gases.

Under ambient conditions, bulk silver reacts strongly with gaseous sulfur-containing compounds to form a $Ag_2S$ corrosion layer, the reactions are accelerated if water and oxygen are also present.[17–20] Similarly, silver nanoparticles (AgNPs) are also easily corroded via sulfidation /oxidization because, compared with bulk silver, silver nanomaterials have a much higher surface-to-volume ratio, which enhances surface reactivity. For example, the sulfidation rate due to chemisorption of sulfides on NPs is 7.5 times higher than that of bulk silver under the same conditions.[21-22]

As an emerging transparent conductive film, AgNWs films with low resistance, high transmittance and high reliability are very important to future applications. Some researchers have realized the serious problem of silver corrosion[23] and developed some barrier layers to prevent slow degradation of AgNWs films over time and enhance the film reliability. For example, AgNWs−rGO (reduced graphene oxide: r-GO) hybrid electrodes were exposed to 70°C/70% RH for 8 days with a sheet resistance increase of only 50%. [24] Jin et al. reported high performance of a AgNWs film coated by a non-conductive binder of poly(dopamine), which included a chemical-resistant substance (alginic acid); the AgNWs film exhibited long-term stability during 85°C/85% RH aging for 30 days.[25] However, a pristine AgNWs without any protective layer also showed long-term stability at same condition, which contradicts other observations of silver corrosion.[17–23] AgNWs–PEDOT:PSS composite films showed a 25% increase in sheet resistance when the film was exposed to 25°C/50% RH for only 40 h.[26] With UV-ozone treatment, a AgNWs-PDMS (Poly(dimethylsiloxane)) film maintained its original sheet resistance for only 300 min.[27] Other AgNWs/metal–oxide ($SiO_2$ or ZnO) films and Au-coated AgNWs films only

showed short lifetime below one week. [28-29] The results suggest that the reliability of AgNWs films remains an important issue, and most protective layers are only effective for very short periods. To our knowledge, efficient protective layers have not been developed yet, and the failure mechanism of AgNWs films remains unclear. Very recently, Simonato group reported that AgNWs films kept the stability in ambient atmosphere over two years without clear storing conditions. [30] They claimed concentrated $H_2S$ or light exposure did not cause sheet resistance change, however, an oxide shell around a metallic silver particles core has been observed under ambient conditions after light illumination for several hours.[31] These reports left many unsolved issues. In the work, AgNWs films were fabricated and coated with various materials; then the coated films were stored in ambient air under various conditions, including natural daylight, UV light, light shielding, high humidity, and vacuum. Microstructure and resistance of the AgNWs films were observed to identify failure factors and clarify failure mechanisms, and provided a real feedback concerning the stability of AgNWs films in practical applications.

## 2. EXPERIMENTAL SECTION

**Preparation of AgNWs films.** AgNWs were synthesized in a large scale using a modified polyol process.[32] Prepared AgNWs were dispersed in ethanol at a concentration of about 2.5 wt% to fabricate AgNWs film by drop-coating onto 3 × 3 cm polyethylene terephthalate (PET) or glass substrates, which were allowed to dry naturally at room temperature. These AgNWs films were treated with high-intensity pulse light illumination (PulseForge 3300, Novacentrix, Austin, TX, USA) at a fixed light intensity of 1.0 J/cm$^2$, similar to a recently reported method.[33] Finally, the films were over-coated and stored at real laboratory conditions which correspond to the season change. The detailed formation process for the AgNWs films is shown in a schematic diagram (Fig. S1a), unless stated otherwise. When a coating was too thick to measure sheet resistance, Au electrodes (each 0.3 × 3 cm) were placed on two sides of the film by sputtering at RT. These electrodes were used to evaluate the film's conductive performance. For every condition, three to five samples are tested to confirm the reproducibility.

**Optical, electrical, and microscopic characterization.** Transmittance spectra were recorded using a Jasco UV–visible-near-infrared spectrophotometer (V670, JASCO Corp.) with the corresponding substrate used as a reference. The films had 82%–87% transmittance, unless stated otherwise. Sheet resistance of the AgNWs films was measured using the four-probe method with a surface resistivity meter (Loresta GP MCP-T610, Mitsubishi Chemical Analytech Co. Ltd.) and resistance was obtained by a two-probe method with a multimeter (Sanwa, PC5000). Morphologies of the AgNWs films were observed and analyzed by SEM (JEOL JSM-6700F) and TEM (JEOL JEM-2100 at an accelerating voltage of 300 kV). Long-term reliability tests of the AgNWs films followed test standards in microelectronics in which the test temperature and humidity are defined as 85°C and 85% RH (ESPEC SH-240S3).

## 3. RESULTS AND DISCUSSION

**Effects of natural daylight.** As a transparent conductive film, AgNWs film is always exposed to natural daylight; therefore, the effects of light on the failure of AgNWs films should be understood. Here, bare AgNWs films without any coating were fabricated and kept under laboratory conditions. Some films were directly exposed to air and others were wrapped with Crecia Kim towels to avoid natural light but allow exposure to the same air environment. Sheet resistance was measured periodically to monitor temporal changes in conductivity (Fig. 1). The figure shows that sheet resistance generally increased with storage time although changes were small in the 1st week. After the 1st week, the resistance began to sharply increase, with the increase rate highly depending on the AgNWs film's state. For example, in the 2nd week, the resistance of films directly exposed to natural light increased by 3–5 factors compared with the original resistance (Fig. 1a). For all samples, the resistance increased by factors of over 25 in the 3rd week; this agrees with most reports on the stability of pristine AgNWs films.[24, 26–29] After 30 days, most samples were completely destroyed. Conversely, the films covered with a Kim towel showed slow increases in resistance. Under exposure to air, but not light, the increase in resistance was less that a factor of five over 30 days (Fig. 1b). This indicates that shaded storage decelerated the failure of AgNWs films.

Moreover, to further verify the effects of natural light and look for suitable coating materials, AgNWs films were coated with a Ripoxy SP-1509 vinyl ester resin (Showa Denko, Japan[34]). The resin was dissolved in ethanol with a concentration of 10wt% and then coated onto AgNWs films, which were left directly in air or wrapped with a Kim towel. The SP-1509 layer is transparent in visible range and cut a part of UV-light (Fig. S2), and serves as a barrier to moisture and gas to some extent. Sheet resistivity generally increased with storage time (Fig. 1c and d). The resistance of the protected AgNWs film remained low for 22 days, but afterward, it quickly increased by a factor of over 15 (Fig. 1c). In contrast, the AgNWs films wrapped in the Kim towel almost maintained low resistance for up to 50 days (Fig. 1d). This confirms that natural light truly accelerated the failure of AgNWs films again even when they were coated. However, comparing with those AgNWs film (Fig. 1a), the protected ones showed significant a clear delay in failure, which might imply the effect of coating layer that will be discussed later. Although it has been claimed that corrosion of silver is related to water and gases in air.[17–23] In the tests described above, these water and gases were kept in same conditions, therefore, the effect of natural light on silver corrosion cannot be ignored. Moreover, we also found that films with small values of initial sheet resistance always failed more slowly than those with high initial resistance (Fig. S3). Films with higher sheet resistance have sparser NW networks, so wire failure significantly depleted conductive paths, leading to the quick increase of resistance.[35]

SEM images give detailed information about AgNWs evolution over time. Fresh AgNWs films, coated or uncoated, always showed a normal random network structure with sharp wires (Fig. 2a). After 2 months, the wire shapes had changed from sharp to blurred (Figs. 2b-d). The films without coatings were broken into short thin rods, with some clear irregular particles between or around the rods. Some clear traces of the original wires remained (Fig. 2b). Apparently, thin NWs were more easily broken than thick ones. For example, a thick NW marked by the arrow in Fig. 2b remained a complete structure although some small particles appear on its surface. No clearly broken parts were observed for the coated films (Figs. 2c and d). These NWs maintained their original linear structures, although original smooth surfaces were replaced by rougher

surfaces. The high-magnification image in Fig. 2d shows that many tiny particles formed and surrounded these wires, and EDS analysis suggested that sulfur element has been observed (Fig. S5). These results agree will with other observations of many small protuberances (i.e., particles) after only 3 weeks of exposure to ambient air.[23, 35] Our results also confirm that AgNWs film prepared with the polyol process are unstable and undergo notable degradation in ambient air even when coated with a protective layer[26-29].

Yu et al. has reported that AgNP aggregation is accelerated by light irradiation due to the inherent redox instability of silver.[36] Grillet et al, have confirmed that a photo-assisted oxidation process always occurred on the surface of Ag nanoparticles to form an oxide shell.[31] Recently, a broadband, continuous light source was used to weld AgNWs via plasmonic mediated absorption and surface diffusion melting, indicating that light affects the AgNWs structure.[37-38] In our experiments, the films shaded with Kim towels showed slow increases in sheet resistance than those exposed to light, implying that natural light accelerated structural changes in AgNWs. However, shading and coating did not completely stop the failure of AgNWs films, strongly suggesting that ambient environment should be carefully considered. In the following sections, we individually address these factors under same natural light.

**Effects of thickness and materials of coating layers.** Failure was rapid when AgNWs films were directly exposed to air. However, the fact that a coating delayed the failure implied that the tailor of thickness and materials of the coating are importance. We firstly used the concentration of SP-1509 in ethanol, 5 or 20 wt%, to control the coating thickness. Figure 3a shows changes in film resistance with storage time under exposure to laboratory air and natural light. The films coated with a thin layer showed low resistance only over the first 2 weeks; thereafter, the resistance increased drastically by a factor of over 20 within 20 days. In comparison, films with thick coatings maintained the resistance near the initially low level for over 2 months. Then, the resistance started to increase with time. These results strongly suggest that a thick layer prolonged the lifetime of AgNWs films under natural light. The thin and thick layers of SP-1509 have same transmittance in the Visible and UV range. The light affect can be excluded. The resin SP-1509 is used as a matrix in conductive adhesives and can protect devices in ambient air by shielding them from moisture and gases. Hence, a coating

of SP-1509 initially protected the AgNWs films. However, over time, some harmful gases or moisture might penetrate the resin layer and reach the AgNWs surfaces depending on the thickness of coating. It should be stressed that a thin coating, such as GO, PEDOT, might be the main corrosion reason of the AgNWs films that showed very short lifetimes in those studies.[24–29] This implies that more attention should be given to the design of the protecting layers for AgNWs films.

Except the thickness, to look for suitable materials and confirm the effects of water[18-20] on AgNWs films in air is also an issue. Several kinds of gelatin, polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and epoxy resin (Showa Denko, Japan) were selected to make thick coating layer in the AgNWs films. Figure 3b and 3c shows temporal changes in the resistance of the coated AgNWs films in ambient air. The increase in resistance over time depended on the material used for the coating. For the films coated with gelatin, the resistance increased by a factor of three when the AgNWs films were kept in air for only 1 week; this increase was faster compared with films without coating (Fig. 1a). The films coated with gelatin completely failed after only 1 month (Fig. 3b). Films coated with PVP showed low rates of increase in resistance. After 20 days in air, these films had resistances that had increased by less than a factor of four; this was much lower than those for films coated with gelatin at the same ambient conditions. However, the PVP-coated films were generally damaged over time, and resistance was nearly 10 times higher after the films were stored in air for 30 days. Thereafter, resistance increased drastically and some films quickly failed. The PVA-coated films maintained low resistance over 45 days. It is found that these results are consistent with the properties of these coating materials. Gelatin is a widely used green food additive that can dissolve in hot water and has high water retentivity. When gelatin is coated on AgNWs films and dried, some moisture remains; this retained water is slowly released and contributes to the failure of NWs. PVP and PVA are both water-soluble polymers with a plurality of polar groups, so they are relatively strong hydrophilic materials. When the same amounts of PVA and PVP were kept in air at RT, the weight gain of PVP was always more than that of PVA. This water absorption capability might accelerate the failure of AgNWs films coated with PVP.

Epoxy resin was coated on surfaces of AgNWs films and cured with imidazole at 150°C for 30 min to form a uniform and hard layer in order to observe changes in resistance over time. Figure 3c shows a very stable resistance, except for deviations in measurements, without any change over 6 months. Owing to its special waterproof and chemical-proof properties, epoxy resin is widely used as a sealing agent for electronic devices. On the AgNWs films, the epoxy resin layer blocked penetration of moisture and protected the films from failure. A pure coating of epoxy resin on glass was placed in air at RT, and changes in weight were measured over time. The weight remained almost the same for over 2 months, demonstrating that the water-absorbing ability of epoxy resin is very poor. These results imply that blocking water from air might be a suitable method to extend AgNWs films' lifetimes. Reminding, the epoxy resin has shielding ability comparing other layers, which might protect the AgNWs films from failure to some extent (Fig.S2).

**Effects of water.** Water is a key factor for the corrosion of bulk Ag, and the materials discussed above also imply moisture in air affected the reliability of AgNWs films.[24–29] In order to further confirm the effects of water, uncoated AgNWs films were stored in a dry glass desiccator, which was periodically evacuated to remove moisture as possible, and a glass vessel containing hot water was introduced to generate a high humidity of about 70%–80% by evaporation of water under natural light. Figure 4 shows the resulting changes in resistance with storage time. In the first 2 weeks, the AgNWs films in the high-humidity vessel maintained low resistance without clear changes, but thereafter, three samples showed rapid increases in resistance and completely failed in the following 3rd week. Only one sample avoided failure until the 4th week. In contrast, the AgNWs films stored in dry vacuum almost maintained their initial low resistance without any change for over 2 months; thereafter, the resistance slowly increased. These results confirm that water significantly enhances the failure of AgNWs films stored in ambient air, just as water enhances corrosion of bulk silver.[17–20] It should be mentioned that the AgNWs films were rapidly failure when the temperature and humidity were increased at the same time, which are agree with the report. [30] However, although vacuum storage significantly decreased the effects of water vapor and other gas, the films exposed to the same natural light

still deteriorated over time. This strongly confirms that natural light is an inevitable cause of corrosion in AgNWs films again [31].

**Effects of UV light**. It has been tested above that films kept in the dark always showed slower rates of failure and partly cutting UV-light seems prolong the lifetime. To confirm the effect of UV-light, sheets of three different materials (glass, PET, and polyamide (PI)), were used to cover AgNWs films. These materials exhibit completely different transmittance (Fig. S2). Glass is almost transparent and cuts UV-light below 280 nm. PET has a slightly lower transmittance of about 75% at 550 nm and cuts wavelength below 310 nm. PI has the lowest transmittance to cut light below 480 nm. Each of these three sheets were placed on the surface of AgNWs film and sealed with commercial glue along the sides of the films; then the films were stored in air. Figure 5a shows that the increase in resistance over time depended on the material used for the sheets. The AgNWs films covered with glass showed slight changes in the first 30 days; thereafter, the resistance suddenly increased with failure. The films covered with PET maintained high conductivity after 30 days, but the resistance generally increased after that and failed until 60 days. More interesting are the results for PI sheets. Although the resistance increased similar to that for the glass and PET sheets, the rate of increase was relatively slow; after 60 days, the resistance had increased only by a factor of two. This implies that the PI sheet effectively prevented the failure of films; this might be due to the shading provided by PI below 480 nm. Reducing or eliminating UV light might be a suitable method to extend the reliability of AgNWs films in air. However, silver corrosion always involves many factors such as water, oxygen, light, and temperature. The three materials (glass, PET, and PI), provide different barriers for gas and water in air, and these differences are difficult to quantify in the present case. An accelerated test was therefore designed to confirm the influence of UV light.

Two types of AgNWs films were fabricated: an uncoated AgNWs film and an AgNWs film covered by a PI sheet. These films were illuminated with a UV lamp at 365 nm (SLUV-8, Asone Co. Ltd.) in ambient air. In the test range, no large changes in resistance were observed, but these films were easily and quickly destroyed in a short time compared with those stored in natural light (Fig. 5b). One blank (uncovered) AgNWs film was

damaged in the 3rd day, although it had a low resistance in the first 2 days. Another blank AgNWs film showed decreased resistance in the 2nd day, and then the resistance slowly increased until the 9th day. Similarly, the AgNWs films covered by the PI sheets showed decreasing resistance in the first 2 days, which might correspond to the UV light curing that enhances contacts between AgNWs.[27, 37-38] Thereafter, the resistance only increased slightly and remained almost stable until the 15th day. Similar to the blank AgNWs films, the covered films were completely destroyed. Compared with films stored in natural light, the short lifetimes observed here suggest that UV light is a strong failure factor. It has previously been observed that due to oxidation, the resistance of AgNWs films treated with UV-ozone was unstable after as little as 1 h.[27, 31] Therefore avoiding exposure to UV light should be considered in developing applications for AgNWs films.

**Accelerating test.** Before AgNWs films can be used in devices, they must be subjected to a standard microelectronics test to verify the film reliability. Here, AgNWs films with selected coatings were placed in an oven at 85°C/85% RH in the absence of natural light. Figure 6 shows temporal changes in resistance of AgNWs films. Except for the sample coated with epoxy resin, the resistance always increased with storage time. The rate of increase was largest for the sample coated with SP-1509 resin, followed by those coated with PVP and PVA, which showed almost the same rates of increase. The sample coated with epoxy resin gave the best results and maintained an unchanging resistance for over 40 days. To our knowledge, this is the longest lifetime that has been reported for any AgNWs film stored in a harsh environment. In comparison, films stored in air with the same coating materials (PVP, PVA, and SP-1509) always increased fast in resistance than they were placed in the high humidity oven. One reason might be the blocking of natural light, now UV-light, due to the thick metal container. Another reason could be heat treatment, which might densify coatings and prevent penetration of water vapor and other gases. Nevertheless, failure is only a matter of time; after some period of time, these films showed sudden increases in resistance and SEM image shown that many wires has been broken (Fig. S4). Moreover, SP-1509 and epoxy resin are similar resins that are used as sealing materials in many devices. The huge difference in failure for AgNWs films coated with these resins might be related to differences in curing methods. The SP-1509 resin was dried and hardened in air, which might result in

incomplete solidification and faulty sealing. In contrast, the epoxy resin was cured at 150°C for 30 min to form a complete and dense layer on the surface of the AgNWs film, thereby giving better protection. Furthermore, compared with the better adhesion of epoxy resin, SP-1509 always adhered weakly to the substrates; this might also affect the rapid failure of AgNWs films. However, the resistance of AgNWs film protected by epoxy resin has been increased with time over 60 days in present test, which suggested that humidity has a large impact on AgNWs reliability, as reported elsewhere. [18-23] Finally, in the accelerated test, all AgNWs films were protected from natural light, which has been confirmed to affect the failure of AgNWs films. Hence, for extensive applications of AgNWs films over long durations, the accelerating test conditions that more suitable for AgNWs films considering the discussed failure factors should be further investigated in the following studies for the evaluation of high-performance coatings.

It has been found that AgNWs films are always destroyed after a period of time even in totally different environments. EDS measurements (Fig. S5) show that sulfide is the main product at last, which agrees with the reaction between silver and $H_2S$ gas/OCS to form $Ag_2S$, and the reaction is significantly enhanced at high RH.[17–23] We also found that the stability of AgNWs films were worse in summer than in winter due to the difference of RT and humidity. Except $H_2S$ sources, OCS played a larger role because 3 million tons of OCS is released into the atmosphere each year. And sulfide formation can be enhanced by the presence of nitrogen dioxide and water,[39] which strongly indicates that the corrosion reaction of silver is ubiquitous. Moreover, we have to mentioned the ubiquitous natural light, especially UV-light, also unusually accelerated the silver corrosion, therefore, are more complicated the silver corrosion. On the other hand, we should also consider the Rayleigh instability effect. Many phenomena in nature exhibit Rayleigh instabilities, i.e. a solid cylinder will finally break up into a row of spheres, such as the formation of water drops, fiber spinning, and fission of charged finite systems. [40-42] Recently, silver nanobelts and NWs of other metals have been shown to fragment at temperatures far below their bulk melting temperatures because of Rayleigh instabilities.[43-45] Although our data supported the effect natural light, UV light, temperature, gas and humidity on reliability of AgNws films in ambient air, however, it do not exclude the possible effects of Rayleigh instabilities. More studies are

required to determine whether the instability of AgNWs in air is due to corrosion, Rayleigh instabilities, or some other mechanism.

## 4. CONCLUSIONS

We studied how natural light and humidity environmental factors affect failure of AgNWs films and found that natural light, especially UV light, temperature, and humidity often shorten the lifetime and decrease the reliability of AgNWs films. Shading the film from natural light was an effective method for enhancing the reliability of AgNWs films. Coating the films with a protecting layer always decreased the failure rate. Dry air also prolonged the lifetime. Those materials with good waterproofing ability always extended the stability of AgNWs films. AgNWs film coated with epoxy resin showed the longest lifetime of over 40 days under an atmosphere at 85°C/85% RH; this is longer than any lifetime previously reported for AgNWs films. Many factors always simultaneously or separately affect the reliability of AgNWs film, it may be useful to develop a multilayer structure in which each layer blocks one of the factors contributing to corrosion such as water vapor, gases, and light.

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# Figures

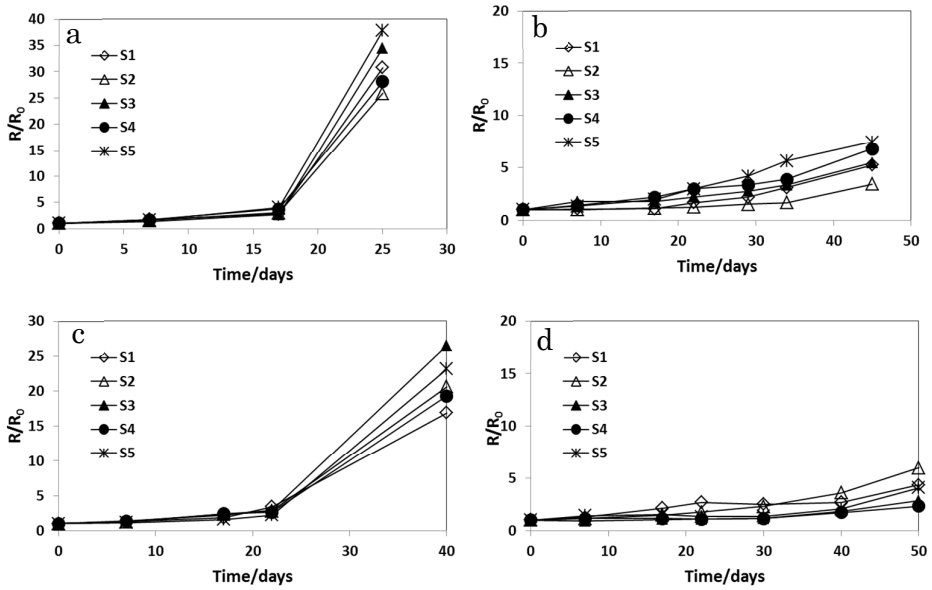


Figure 1. Temporal changes in sheet resistance for naked AgNW films (a) exposed to air and (b) wrapped in a Crecia Kim towel, and AgNW films coated with SP-1509 vinyl ester resin and (c) exposed to air and (d) wrapped in a Crecia Kim towel.

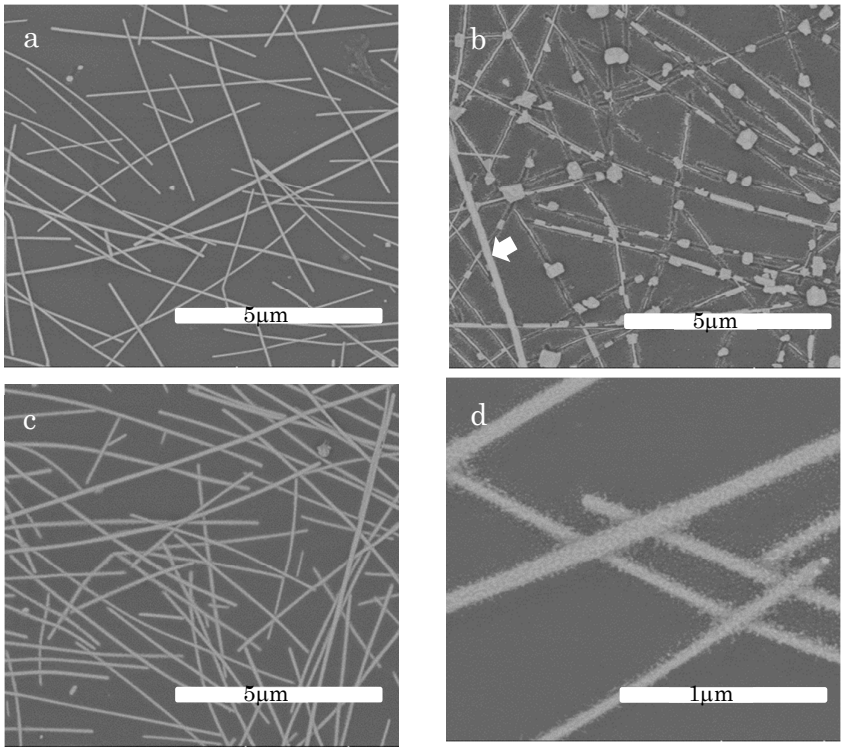


Figure 2. SEM images of pristine AgNW films exposed to air for (a) 1 day and (b) 60 days. (c) SEM image of AgNW film coated with SP-1509 resin and exposed to air for 60 days. (d) High-magnification image of a region in Panel (c).

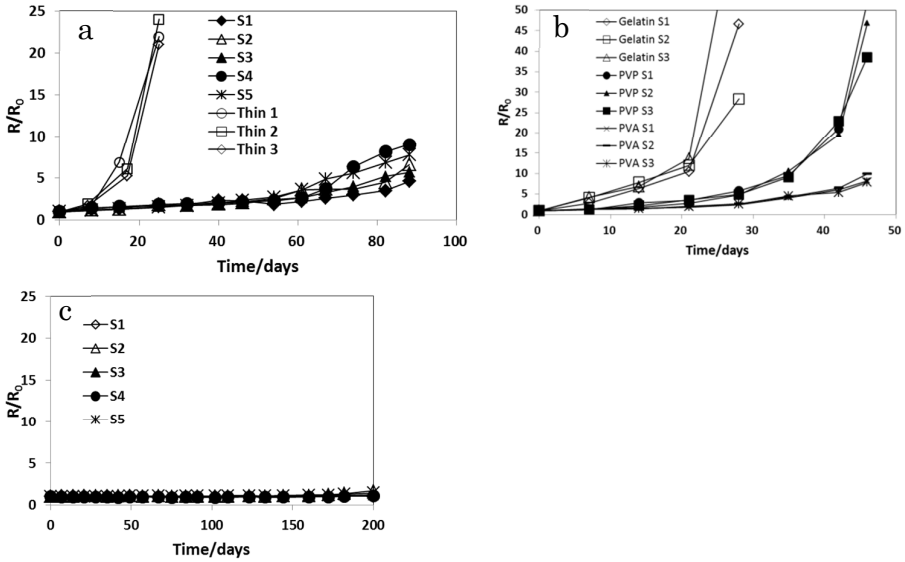


**Figure 3. Comparison of temporal changes in sheet resistance of AgNW films coated with a thick layer of SP-1509 resin and a thin layer (a), gelatin, PVP and PVA (b) and epoxy resin (c).**

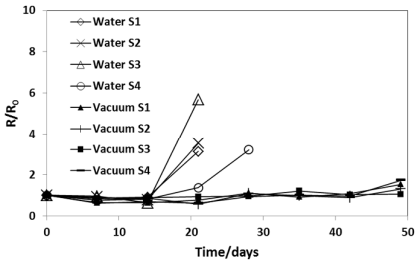


**Figure 4. Comparisons of temporal changes in sheet resistance of AgNW films stored in a vessel with hot water or in vacuum.**

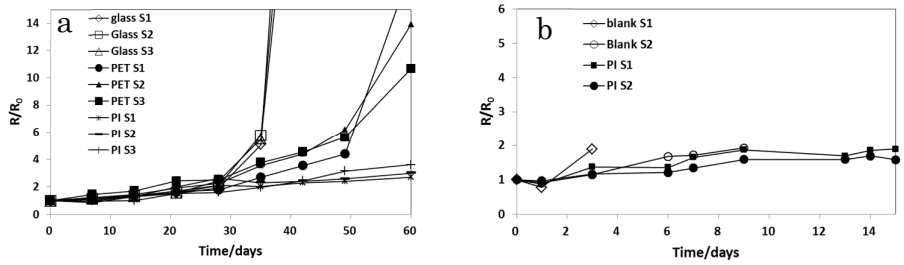


**Figure 5. (a) Temporal changes in sheet resistance of AgNW films stored in air but covered with glass, PET, or PI. (b) Temporal changes in resistance of AgNW films exposed to UV radiation with no coating (blank) and covered with a PI sheet.**

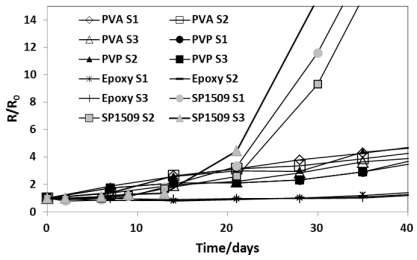


Figure 6. Temporal changes in resistance of AgNW films coated with selected materials and stored at 85°C and 85% RH.