Development of silver nanowire inks and overcoating agents for transparent conductive films with superior environmental resistance

SEIKO PMC CORPORATION
Technology Division Tomoaki Kawaguchi
Munetoshi Kurimura
Yasuhiro Ueta
Kazuki Nagao

1. Introduction

In recent years, display devices such as liquid crystal displays and organic electroluminescence displays, input sensors such as touch panels, and solar cells such as thin film-type amorphous Si solar cells and dye-sensitized solar cells are increasingly used. Consequently, transparent conductive materials, which are essential components for these devices, are also widely used.

ITO (indium tin oxide), which is a metal oxide, is widely used as a transparent conductive material. On the other hand, since the device is required to have a large area and high functionality, the transparent conductive material is required to be lightweight, have low resistance, have high transparency, and have high bending. Therefore, transparent conductive materials that replace ITO are being actively researched.

Among the ITO alternative materials, silver nanowires, which have the advantage of being able to produce flexible transparent conductive films by wet processes, are proposed for use in various applications. We are focusing on silver nanowires as a transparent conductive material to replace ITO and are developing them for a wide range of applications.

The transparent conductive material is used both indoors and outdoors because it is used in applications such as display devices, input sensors, and solar cells. It is expected to be used for a long time under high humidity and high temperature conditions, sunlight conditions, and artificial lighting conditions. On the other hand, since silver nanowires are made of silver, their conductivity tends to deteriorate when used under any of the conditions of high humidity and high temperature, sunlight, and artificial light. To utilize silver nanowires in a wide range of applications, it is necessary to improve their environmental tolerance.

In this report, first, the features of silver nanowires and examples of their use as transparent conductive films are described. After that, we will introduce silver nanowire inks and overcoating agents for transparent conductive films that have achieved environmental tolerance under high humidity and high temperature conditions, under sunlight and under artificial lighting.

2. Features of silver nanowires

Terms related to nanomaterials are defined in ISO / TS27687[1]. Length range approximately from 1 nm to 100 nm is defined as “nanoscale”. Discrete piece of material with one, two or three external dimensions in the nanoscale is defined as “nano-object”. Nano-object with two external dimensions in the nanoscale and the third dimension significantly larger is defined as “nanofiber”. Electrically conducting or semi-conducting nanofiber is defined as “nanowire”. Nanofiber made of silver is silver nanowire.

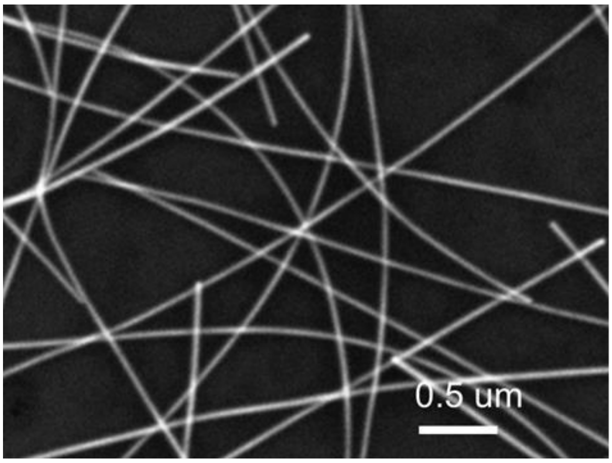

Figure 1. SEM image of silver nanowires

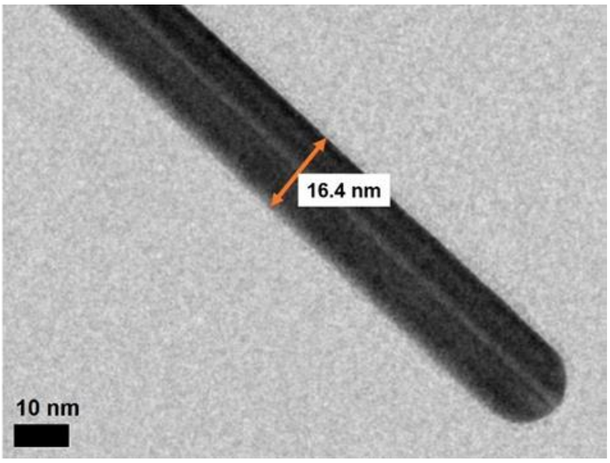

Figure 2. TEM image of silver nanowire

Figure 1 shows SEM image of our representative silver nanowires[2), 3)]. It can be confirmed that the length of the wire (wire length) is on the micrometer scale. Figure 2 shows TEM image of our silver nanowire. It can be confirmed that the diameter of the wire (wire diameter) is on the nanometer scale. Silver nanowires have unique features derived from its shape and the nature of silver.

When silver nanowires are randomly placed on the substrate, and the number of silver nanowires is more than the number of silver nanowires touching each other at two points per one silver nanowire, a conductive network of silver nanowires is formed on the substrate. That is, conductivity is imparted to the substrate. In addition to the high conductivity derived from silver itself, silver nanowires do not require high temperature treatment for crystallization like ITO does. It is possible to impart high conductivity even when a substrate with low heat tolerance is used. Furthermore, since light can pass through the gaps between nanowires, the network of silver nanowires also has light transmission. Therefore, the coating film of silver nanowires exhibits a function as a transparent conductive film. Due to the flexibility derived from silver itself, the transparent conductive film made of silver nanowires has high flexibility as compared with ITO, which is a brittle metal oxide. It has also been clarified that silver nanowires have high antibacterial properties derived from silver ions. From the above features, silver nanowires are expected to be used not only as an alternative to ITO but also in a wide range of applications.

3. Transparent conductive film of silver nanowires

3-1. Manufacturing process

As an example of the use of silver nanowires, a transparent conductive film coated with silver nanowires on a substrate will be described. By using silver nanowires dispersed in a dispersion solvent, silver nanowires membrane can be formed by a general wet process, and it is possible to impart the characteristics of silver nanowires mentioned above to various substrates.

Figure 3 shows the general manufacturing process of transparent conductive films using silver nanowires. First, in process (1), an ink containing silver nanowires is coated on the substrate and dried, a network of silver nanowires is formed on the substrate, and conductivity is imparted to the substrate. Conductivity and transparency can be adjusted by the shape and quantity of silver nanowires coated at this time.

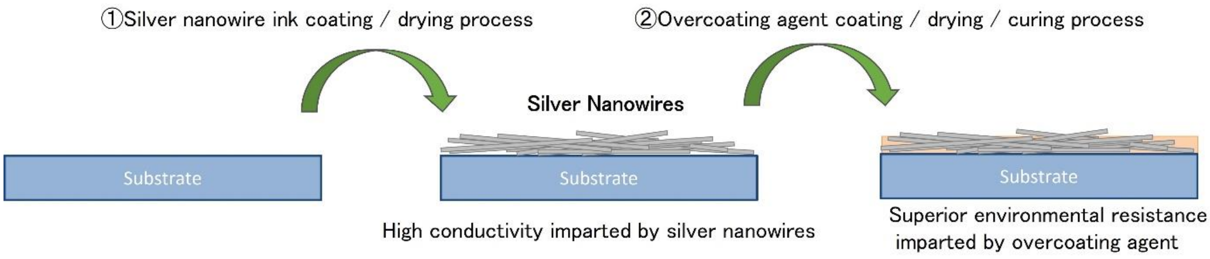

Figure 3. General manufacturing process of transparent conductive films using silver nanowires

Subsequently, in the process (2), an overcoating agent is coated, dried, and cured on the silver nanowire coating film to form a protective layer, thereby forming a transparent conductive film having scratch resistance and durability on the substrate. The overcoating agent needs to form a protective layer without breaking the silver nanowire network and needs to be selected according to the components of the silver nanowire coating film. Further, since the conduction changes from the surface of the protective layer according to the coating amount of the protective film, it is necessary to set the film thickness of the protective layer according to the application.

3-2. silver nanowire inks / overcoating agents

We are developing the "T-AG300 series" as silver nanowire inks with coating suitability. Table 1 shows the properties, and Figure 4 shows the appearance of the product. The contents and numerical values described are examples and can be changed according to the physical characteristics of the target and the coating method. Specifically, the silver concentration can be customized according to the target sheet resistance value. The wire length and wire diameter are shown as representative values, but these can also be customized according to the target physical characteristics. Further, although the main solvent is water, it is possible to adjust the coating suitability according to the substrate by adding alcohol when preparing the coating ink. As an overcoating agent formed on a silver nanowire coating film using the "T-AG300 series", we provide a two-component mixed type UV curable resin "T-YP476 / T-YP462". The properties are shown in Table 2 below.

Table 1. Properties of "T-AG300 series"

items	Unit	Properties
Product name		T-AG300 series
Product type		Ink
Main solvent		Water
Silver content	wt%	0.1 – 0.5
Viscosity	mPa・s	Depends on the coating method
Average wire length	μm	ca. 10 (Representative)
Average wire diameter	nm	ca. 25 (Representative)

Figure 4. Appearance of "T-AG300 series"

Table 2. Properties of T-YP476/T-YP462

Items	Properties
Product name	T-YP476/T-YP462
Product type	UV curable resin (Two-component mixed type)
Solvent	Alcohol solvents
How to use	Diluted with organic solvent

3-3. Electrical and optical properties

The electrical and optical properties of the silver nanowire coating film, which are formed on the PET substrate with the silver nanowire ink T-AG300 series and the overcoating agent T-YP476 / T-YP462 in the above manufacturing process, are described below. The properties of the transparent conductive film depend on the amount of silver nanowires. Figure 5 shows plots of surface resistivity against silver nanowire weight per unit area. Figure 6 shows plots of total light transmittance against surface resistivity by the solid symbols, which corresponds to the vertical axis on the left. Figure 6 also shows plots of inner haze against surface resistivity by the broken symbols, which corresponds to the vertical axis on the right.

The surface resistivity was measured by the eddy current method. The total light transmittance was measured according to JIS K7361-1, and the inner haze was measured according to JIS K7136. Both the total light transmittance and the inner haze are the values including the substrate. The inner haze was measured without the influence of surface scattering.

From Figure 5, it was confirmed that the silver nanowire weight per unit area and the surface resistivity are approximately inversely proportional. By changing the silver nanowire weight per unit area, the transparent conductive film can adjust the surface resistivity in a wide range from 10 Ω / □ or less to 100 Ω / □ or more.

From Figure 6, it is confirmed that as the surface resistivity decrease, that is, as the silver nanowire weight per unit area increases, the total light transmittance decreases and the inner haze increases. In general, the correlation between surface resistivity and total light transmittance as well as inner haze depends on the shape of the silver nanowires. It is effective to use silver nanowires having a small wire diameter to reduce inner haze.

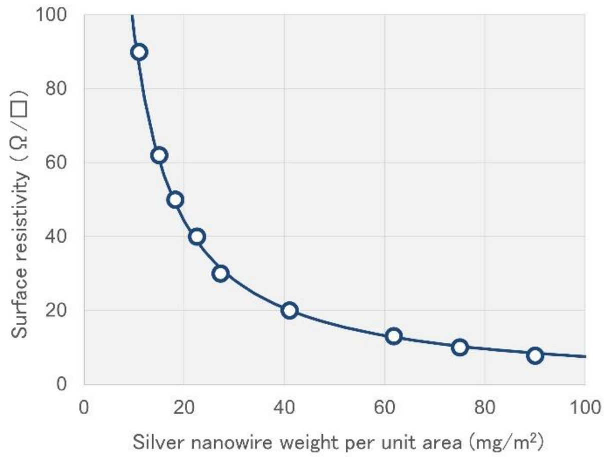

Figure 5. Plots of surface resistivity against silver nanowire weight per unit area

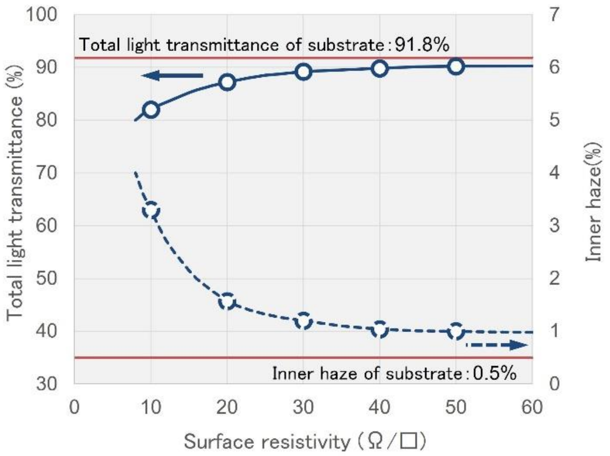

Figure 6. Plots of optical properties against surface resistivity

4. transparent conductive films with superior environmental tolerance

To utilize a transparent conductive film using silver nanowires in a wide range of applications, environmental tolerance is required under all of these conditions, such as high humidity and high temperature, sunlight, and artificial lighting. The environmental tolerance under these conditions is affected by the manufacturing method of silver nanowires, the ink composition, and the overcoating agent composition.

We have developed the silver nanowire inks T-AG300 series and the overcoating agents T-YP476 / 462 shown in the previous chapter. These are silver nanowire inks and overcoating agents capable of forming a transparent conductive film having environmental resistance without impairing electrical and optical properties.

4-1. High-temperature and high-humidity stability

First, we will explain the results of the high - temperature and high-humidity stability test of environmentally tolerant products in comparison with the conventional products. Table 3 shows the combinations of the silver nanowire inks and the overcoating agents used to form the transparent conductive film. Figure 7 shows the change in surface resistivity under an environment of 85 ° C and 85% RH. Figure 8 shows the change in resistance between two terminals created by printing silver paste on a silver nanowire coating film under an environment of 85 ° C and 85% RH.

From Figure 7, by using T-YP476 as the overcoat agent, long-term stability of the surface resistivity in a high temperature and high humidity environment can be achieved. From Figure 8, the long-term stability of the resistance between two terminals in a high -temperature and high-humidity environment can be achieved by using the T-AG300 series and T-YP476 together.

Table 3. Combinations of the silver nanowire inks and the overcoating agents

No.	Silver nanowire ink	Overcoating agent
1	T-AG300 series	T-YP476/T-YP462
2	T-AG300 series	T-YP476
3	T-AG300 series	conventional products
4	conventional products	T-YP476/T-YP462
5	conventional products	conventional products

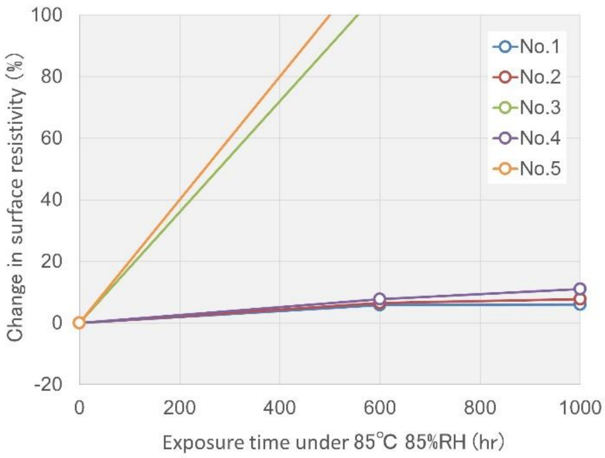

Figure 7. Plots of change in surface resistivity against exposure time under 85℃ 85%RH

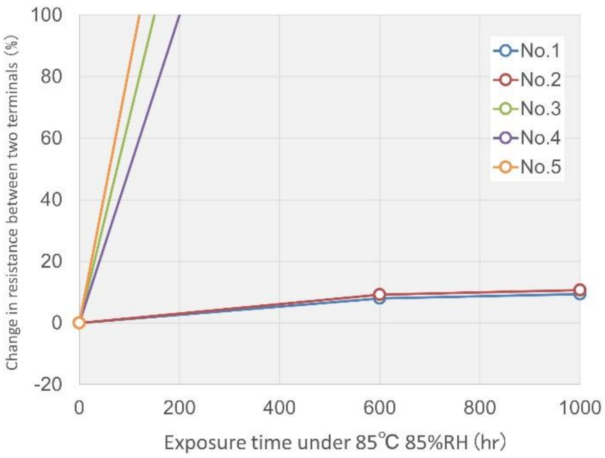

Figure 8. Plots of change in resistance between two terminals against exposure time under 85℃ 85%RH

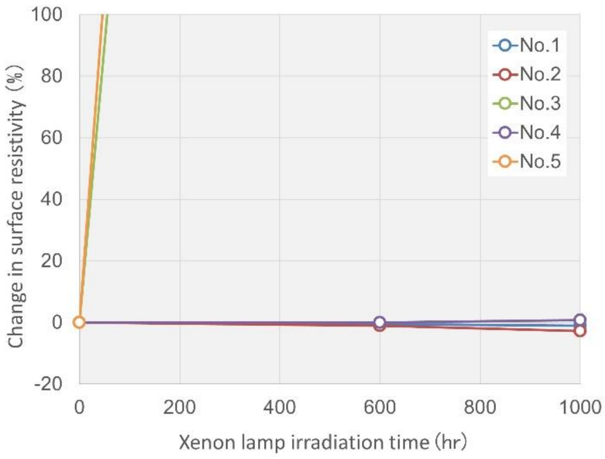

Figure 8. Plots of change in surface resistivity against Xenon lamp irradiation time

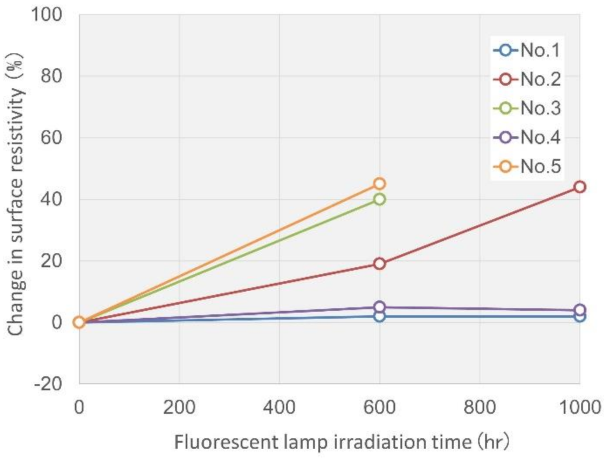

Figure 9. Plots of change in surface resistivity against fluorescent lamp irradiation time

4-2. Photostability under Xenon lamp irradiation

Secondly, we will explain the results of the photostability test under xenon lamp irradiation of environmentally tolerant products in comparison with conventional products. Similar to the high -temperature and high-humidity stability test, the transparent conductive film using the combination of the silver nanowire inks and the overcoating agents shown in Table 3 was tested.

Test conditions are black standard temperature of 60° C, irradiation intensity of 750 W/m2 (integrated value of spectral irradiance of wavelength 300 nm to 800 nm). Figure 9 shows the change in surface resistivity under xenon lamp irradiation. The surface resistivity was measured at the boundary between the irradiated part and the shielded part where the xenon lamp irradiation is blocked by the shield. At the boundary the silver nanowires are generally tends to deteriorate in sunlight.

From Figure 9, the long-term stability of the surface resistivity under sunlight can be achieved by using T-YP476.

4-3. Photostability under fluorescent lamp irradiation

Finally, we will explain the results of the photostability test under fluorescent lamp irradiation of environmentally resistant products in comparison with conventional products. Similar to the high-temperature and high-humidity stability test, the transparent conductive film using the combination of the silver nanowire inks and the overcoating agents shown in Table 3 was tested. Test condition is irradiation degree of 20000 lx. Figure 10 shows the change in surface resistivity under fluorescent lamp irradiation.

From Figure 10, long-term stability of the surface resistivity under artificial lighting can be achieved by using T-YP476 / T-YP462.

5. Conclusion

From the above results, the transparent conductive film using the silver nanowire inks T-AG300 series and the overcoat agents T-YP476 / 462 can adjust the surface resistivity in a wide range and has environmental tolerance under high-humidity and high-temperature, sunlight, artificial lights.

Currently, the required performance for transparent conductive films is diversifying due to changes in customer needs. As transparent conductive materials other than silver nanowires, not only highly functional ITO, but also new materials such as conductive polymers and carbon nanotubes are being actively developed. Although each has advantages and disadvantages, silver nanowires have high potential because they can impart high conductivity to various substrates and have high productivity that can be easily formed by a wet process.

＜References＞

1) Expert committee on the environmental impact of manufactured nanomaterials: Guidelines for preventing the environmental impact of manufactured nanomaterials, p.18 (2009).

2) Tomoaki Kawaguchi : Convertech, 42(10), 46 (2014).

3) Kinousei Film Kenkyukai : Sangyo wo sasaeru kinousei film [Functional films supporting industry] 2nd edition, p.196 (2020).

Profile

SEIKO PMC CORPORATION
Technology Division
New business develop-ment group
Manager
Tomoaki Kawaguchi

SEIKO PMC CORPORATION
Technology division
New business develop-ment group
Assistant manager
Munetoshi Kurimura

SEIKO PMC CORPORATION
Technology division
New business develop-ment group
Yasuhiro Ueta

SEIKO PMC CORPORATION
Technology division
New business develop-ment group
Acting general manager
Kazuki Nagao