

Improvement of the Corrosion Resistance of TCO/Ag/TCO Structure for Transparent Conductive Layer

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ABSTRACT

The corrosion resistance of TCO/Ag/TCO structure was improved by using new Ag alloy and TCO. These can inhibit corrosion defect which was one of the biggest challenges for practical use. It can be applied to various devices, such as display electrodes, touch sensor and IR cut film.

1 INTRODUCTION

1.1 Background

TCO/Ag/TCO structure (TCO : Transparent Conductive Oxide) has been proposed as a new transparent conductive layer [1-3]. The structure consists of a very thin Ag layer and TCO layers which are deposited above and beneath the Ag film by sputtering method. It has high conductivity and transmittance due to Ag layer under 10nm. Furthermore, since the interlayer is ductile Ag layer, the structure has also excellent flexibility, in other words, the resistance against bending. Examples of applications of the structure include flexible transparent electrode, and IR-cut transparent film that makes use of the high reflectivity at infrared range of Ag film.

One of the biggest challenges for practical use of the structure is the durability. Especially, the appearance of "spots" on the surface or the edge of TCO/Ag/TCO structure after the storage test such as thermo-hygrostat test is a serious problem [4]. These spots appear as shown in Fig. 1, the sizes are about several mm to several μm in diameter. And they also appear at the edge of the film like a band shape (Fig. 1). As mentioned later, these defects are caused by the corrosion of the Ag film in TCO/Ag/TCO structure. They not only impair the film appearance, but can also cause problems such as short circuit. Such corrosion problem is a major barrier to the practical application of the TCO/Ag/TCO structure.

In this study, the improved TCO/Ag/TCO structure which contained new materials (Ag alloy and TCO) layer was developed. The new structure can drastically inhibit the defects and bring new possibilities for the application.

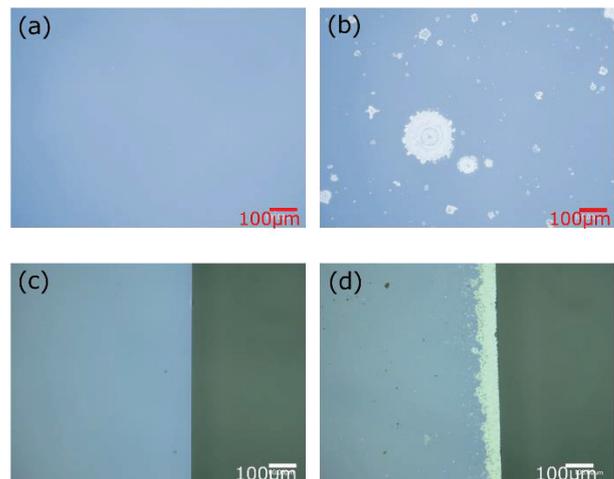


Fig. 1 TCO/Ag/TCO structure appearance
 (a) Normal film surface
 (b) "Spots" occurrence on surface
 (c) Normal film edge
 (d) "Spots" occurrence at edge

1.2 Cause of the "spots"

The "spots" were analyzed in order to understand the mechanism and consider the countermeasure. Fig.2 shows high magnification photos of the typical spots. In most cases, something like particle was observed in the center of the spot (the red circle in Fig. 2).

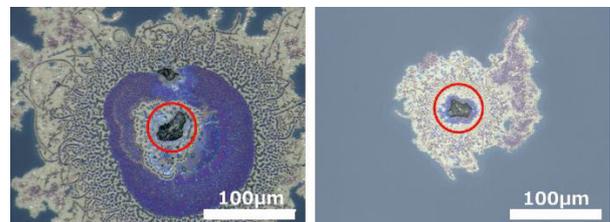


Fig. 2 High magnification photos of the "spots"

The elemental mapping images of the spot by Auger Electron Spectroscopy (AES) is shown in Fig. 3 as a more detailed analysis result. Carbon was mainly detected from the area shown by the red circle in Fig. 2.

Those are considered to be particles derived from the environment. Inside the spot, silver was scattered like islands and was no longer present as a continuous layer. Moreover, as the result of qualitative analysis, chlorine was detected inside the spot. The chlorine seems to be derived from the particles. From the result above, cause of the “spots” can be discussed. Namely, when particles containing chlorine attached the surface during storage test, the chlorine went through upper TCO layer and attacked Ag layer. Degradation of Ag film by chlorine was reported at previous paper [5], and the degradation often appeared as film peeling and reflectance reduction. It is considered that those were caused by chlorine-induced aggregation of Ag. And the aggregation can be accelerated by temperature and humidity.

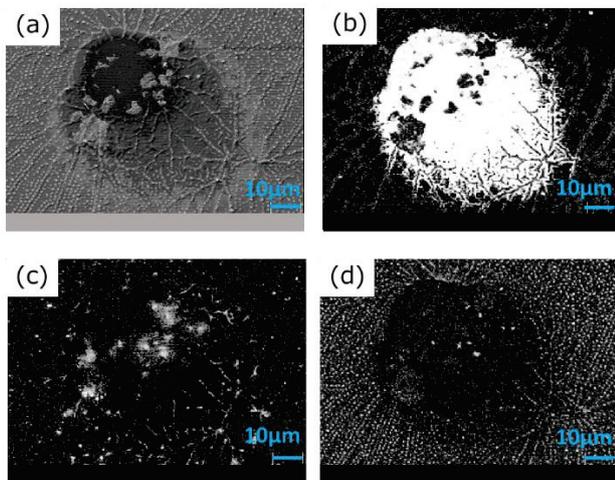


Fig.3 The analysis of the “spots”
(a) SEM image of the center of the spot
(b) C-mapping by AES
(c) Cl-mapping by AES
(d) Ag-mapping by AES

From the discussion above, the aggregation of Ag by chlorine must be suppressed in order to eliminate the “spots”. In this study, two methods were adopted. Those were the improvement of chlorine tolerance by optimization of additive element in Ag alloy and the improvement of aggregation resistance by optimization of under TCO layer. Those results are described in the following section.

2 EXPERIMENTAL METHOD

TCO/Ag/TCO structures were fabricated using the DC magnetron in-line sputtering system without substrate heating. All the layers of TCO/Ag/TCO were deposited continuously without taking it out of the chamber. ITO, new TCO and two Ag alloys were deposited using the parameters shown in Table 1. The composition of ITO was In₂O₃ 90wt% - SnO₂ 10wt%. The conventional Ag alloy

was our Ag alloy for TCO/Ag/TCO structure reported in IDW'17 [2].

Table 1
Sputtering conditions of ITO,
new TCO and Ag alloys

Materials	Sputtering Gas	Gas Pressure (Pa)	Power density (W/cm ²)
ITO	99% Ar + 1% O ₂	0.67	0.36
New TCO	99% Ar + 1% O ₂	0.67	1.34
Ag alloy (conventional)	100% Ar	0.30	0.45
Ag alloy (new)	100% Ar	0.30	0.45

Four types of TCO/Ag/TCO structure were used for the comparative experiments. Table 2 shows each TCO/Ag/TCO structure. The film thickness of all structures was TCO(40nm) / Ag(8nm) / TCO(40nm). Structure No.1 was our standard structure (ITO/conventional Ag alloy/ITO). Structure No.2 was in which Ag alloy layer was changed, and Structure No.3 was in which under TCO layer was changed. Both the layers in Structure No.4 were changed.

Table 2 Each TCO/Ag/TCO structures

Structure No.	Film structure
No.1	Sub. / ITO(40nm) / conv. Ag alloy(8nm) / ITO(40nm)
No.2	Sub. / ITO(40nm) / new Ag alloy(8nm) / ITO(40nm)
No.3	Sub. / new TCO(40nm) / conv. Ag alloy(8nm) / ITO(40nm)
No.4	Sub. / new TCO(40nm) / new Ag alloy(8nm) / ITO(40nm)

As the evaluation of the film characteristics, sheet resistance of the film was measured by four probe method and transmittance of the film was measured by spectrophotometer.

The durability, in other words, the “spots” suppression ability was evaluated by Salt-water dipping test as accelerated test. The dipping condition was in 5% NaCl aqueous solution for 24 hours at room temperature.

In order to discuss the mechanism, the analysis such as XRD was performed on the deposited film.

3 RESULTS AND DISCUSSION

3.1 Results

Fig. 4 shows each TCO/Ag/TCO structures appearance after the salt-water dipping test. Structure No.1 which was conventional one showed serious damage such as many defects and film peeling.

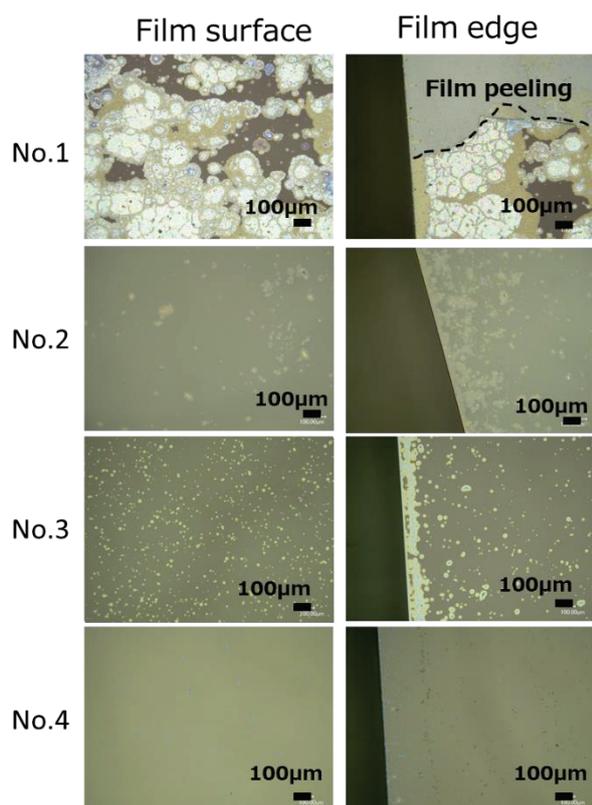


Fig.4 Film appearance of each TCO/Ag/TCO structure after salt-water dipping test

On the other hand, Structure No.2 and No.3 showed significant inhibition of the “spots” at the surface and the edge. From the result, it is confirmed that new Ag alloy and new TCO have a great effect on the suppression of the “spots”. Furthermore, Structure No.4 which used both showed more improvement (there were almost no “spots” including tiny ones), so the effect can be increased by the combination.

Table 3 shows optical and electrical characteristics of each structure. The sheet resistance was almost the same in all the structures. Regarding the optical property, Structure No.2, No.3 and No.4 showed slightly higher transmittance than Structure No.1, of those, Structure No.4 showed the highest transmittance. The result shows that new Ag alloy and new TCO each have the effect of improving not only the durability but also the transmittance.

Table 3 Optical and electrical characteristics (Optical property is an average at 380nm to 780nm)

	Structure No.1	Structure No.2	Structure No.3	Structure No.4
Sheet resistance (Ω/\square)	11.7	12.1	11.4	12.2
Transmittance (%)	84.5	85.7	85.3	86.3
Absorptance (%)	9.5	8.2	8.4	7.1

3.2 Discussion

The above improvement was achieved by two factors, that is, new Ag alloy and new TCO. In this section is discussed each mechanism.

It was reported that Ag film corrosion by chlorine could be inhibited by alloying [5-6]. The mechanism depended on the additive element, for example the inhibition of the chlorine adsorption on Ag surface or the chlorine capture by the formation chloride [5-6]. The new Ag alloy was designed to reduce its affinity with chlorine, and the type and amount of additive elements in the Ag alloy was optimized in order to achieve both such low affinity and excellent other properties (electrical / optical properties).

As an example showing the low affinity with chlorine, Fig. 5 shows the result of the contact angle measurement on each Ag film. Pure water and 5% NaCl aqueous on each Ag film surface (pure Ag and two Ag alloys) were measured by contact angle meter. First, regarding pure Ag film, the contact angle of salt water was much smaller than that of pure water. The extreme increase in wettability is considered to mean high affinity between Ag surface and chlorine ion. On the other hand, for two Ag alloys, such a difference in the contact angle was small. Especially new Ag alloy showed almost no difference. The result suggests that the new Ag alloy has a very low affinity with chlorine compared with pure Ag or the conventional one.

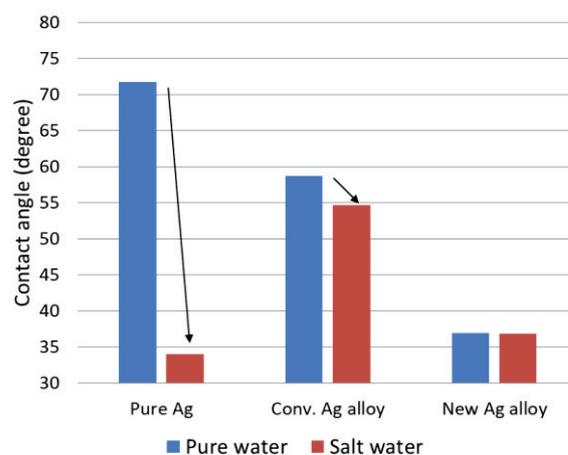
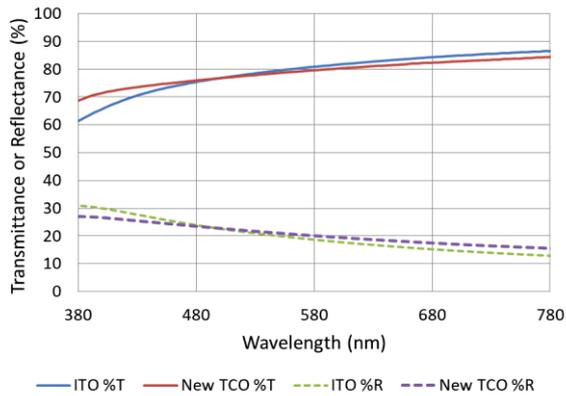


Fig.5 Contact angles of pure water and salt water on each Ag film surface

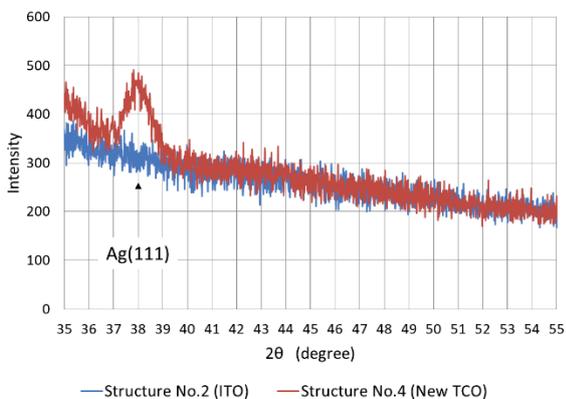
Second, the new TCO is discussed. Table 4 and Fig. 6 show film characteristics of the 40nm single layer of ITO or new TCO. The optical constants (refractive index and extinctive coefficient) were obtained by the Ellipsometry. Regarding the optical property, the new TCO had almost the same as ITO. However, the TCO had a quite higher resistivity than ITO, so it is difficult to use as a transparent conductive film by itself.

Table 4 40nm single layer characteristics

	ITO	New TCO
Film resistivity ($\Omega \cdot \text{cm}$)	4.7×10^{-4}	1.6×10^0
Refractive index @550nm	2.05	1.99
Extinction coefficient @550nm	<0.01	<0.01

**Fig. 6 %T and %R spectra of 40nm single layer**

The new TCO shows its advantage when it used as an under-layer for Ag. Intrinsically, it is considered that Ag film degradation by chlorine is the film agglomeration [6]. So it is effective to improve not only Ag alloy layer itself but also the interface with the under-layer. The new TCO can improve the interface than conventional ITO. The stronger interaction between TCO and Ag is considered to be a main factor (In other words, the stronger adhesion). Fig. 7 shows XRD result of each film structure. Despite the very thin Ag layer (8nm), Ag(111) crystal peak could be detected in the structure that the under-layer was new TCO. It means that the crystalline of Ag layer was improved by under-layer TCO. The Ag crystalline difference between two structures suggests the difference in growth mode during deposition, which seems to show one aspect of the stronger interaction. In the future, we will analyze further what kind of phenomenon occurs at the interface.

**Fig. 7 XRD result of Structure No.2 and No.4**

4 CONCLUSIONS

The new Ag alloy and the new TCO for transparent conductive layer were developed. By using these, we can realize the TCO/Ag/TCO structure which has high durability, in other words, cause no corrosion defects. The structure can be applied for display electrode (e.g. LCD, OLED), touch sensor and IR cut film, taking advantages of its high conductivity, flexibility and IR reflectivity.

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