Indium-saving effect and physical properties of transparent conductive multilayers

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Abstract. Indium-free transparent conductive multilayer structures consisting of top and bottom MoO$_3$ layers and an Ag interlayer (MoO$_3$/Ag/MoO$_3$; MAM) are deposited onto glass substrates by vacuum evaporation. The transmittance and sheet resistance of the structures are evaluated, and the optimum structure is determined to be MAM (20/14/30 nm) as it shows the best figure of merit (FOM), which is used as the index for transparent conductive films, with a value of $6.2 \times 10^{-3} \Omega^{-1}$. To further improve the performance of the films, we attempt to fabricate a multilayer consisting of MoO$_3$ and indium zinc oxide (IZO), based on previous results. The obtained IAM (30/14/50 nm) multilayer shows an FOM higher than that of the MAM, with a value of $32 \times 10^{-3} \Omega^{-1}$. Moreover, it reduces the amount of required indium as compared with the IZO/Ag/IZO multilayer.

1. Introduction
Display devices such as organic light emitting diodes (OLEDs) and organic solar cells generally use transparent conductive films as transparent electrodes [1, 2]. The most commonly used material in these films is indium tin oxide (ITO). However, it would be favorable to reduce the use of indium because its rarity causes its price fluctuation significantly [3]. In addition, a study has highlighted inferior mechanical properties of ITO films when used on flexible substrates [4]. Indium-free or indium-saving transparent conductive films have been intensively developed; an example of such a film is a sandwich structure consisting of top and bottom metal oxides and a metal interlayer (oxide/metal/oxide). Such a multilayer can reduce sheet resistance ($R_s$) due to the metal interlayer as well as the use of indium even if the top and bottom oxide is ITO compared to ITO single film [5]. In general, the same substance among various oxides has been introduced into the top and bottom layers and the properties have been recently reviewed [6, 7]. Previously, we reported the optimization of layer thickness and sputtering conditions for a multilayer consisting of indium zinc oxide (IZO) and Ag layers (IZO/Ag/IZO; IAI). It was shown to exhibit excellent properties as a transparent conductive film and used 80% less indium than an IZO single layer film with the same sheet resistance value. In addition, the optimized multilayer could be used as an anode in an OLED that demonstrated excellent EL properties [8].

Among the various metal oxides, MoO$_3$ [9, 10] has the advantage of being not only indium free but also an excellent hole injection material in OLEDs. It has already been shown that a MoO$_3$/Ag/MoO$_3$ (MAM) electrode can lower the barrier height for hole injection into an organic layer (hole transporting layer) when compared with an ITO electrode [9].

In this study, we first prepare indium-free MAM multilayers with different thickness combinations of the MoO$_3$ and Ag layers. Their transmittance, sheet resistance, and figure of merit (FOM) [11] are
subsequently obtained, and their structures are optimized. We then attempt to fabricate multilayers consisting of MoO$_3$ layers and sputtered IZO layers. We determine the optimum IZO/Ag/MoO$_3$ (IAM) multilayer structure. Finally, we compare the optimum MAM and IAM multilayers on FOM and indium-saving effect.

2. Experimental procedure

To begin with, we prepared the MAM structures. Commercial MoO$_3$ powders (99.9999% purity) and an Ag wire (99.99% purity) were deposited onto Corning Eagle XG glass substrates through vacuum evaporation after evacuation to below 4.0 x 10$^{-4}$ Pa. The thickness of the deposited layer was controlled using a quartz crystal microbalance. The thickness of the Ag layers was also confirmed using X-ray fluorescence spectrometry.

To fabricate the IAM structures, the bottom IZO layer was deposited via sputtering onto a glass substrate. The deposition of a 30-nm-thick IZO layer onto a glass substrate was performed by RF sputtering using a 2-inch diameter IZO (10 wt% ZnO) target under an O$_2$ atmosphere, as previously reported [8]. The sample was then transferred into the vacuum evaporation chamber in which the Ag and top MoO$_3$ layers were deposited exactly as conditions as they were in the MAM structure.

The sheet resistance ($R_s$) of the samples was measured using a four-point-probe method, and transmittance was measured in the wavelength region of 200–800 nm using a spectrophotometer. The figure of merit (FOM) is expressed as $T^{10}/R_s$ [11], where $T$ is the transmittance of the films and $R_s$ is the sheet resistance. We used two values for transmittance in this calculation: the first was that at a wavelength of 550 nm because it is the approximate maximum human visual sensitivity; the second was the average transmittance value in the visible range because the use of this average is also practiced in other reports. The surface morphology was observed using an atomic force microscope (AFM).

3. Results and discussion

3.1. MoO$_3$/Ag/MoO$_3$ (MAM) multilayer

The thicknesses of the top and bottom MoO$_3$ layers were optimized, whereas that of the Ag layer was fixed to 14 nm. The optimum IAM structure has been shown to be 30/14/30-nm thick [8]; therefore, we attempted to explore the thickness of each layer in a similar range. First, the transmission spectra of MAM, in which the top layer was fixed to 30 nm, whereas the bottom layer was varied from 15 to 30 nm were measured. As a result, all the spectra were similar, but the structure with a 20-nm-thick bottom layer could have the highest transmittance. The sheet resistance ($R_s$) of the structures was consistently low, with values of 3.4–3.8 Ω/sq., because it mostly depends on the sheet resistance of the Ag layer.

![Figure 1](image-url). The properties of MoO$_3$(20 nm)/Ag(14 nm)/MoO$_3$(x nm) multilayer samples, where x is varied from 25 to 45 nm. a) the transmission spectra and b) the FOM calculated using two different transmittance values.
Figure 1(a) shows the transmission spectra of MAM, in which the bottom layer was fixed to 20 nm, whereas the top layer was varied from 25 to 45 nm. A larger change was observed in these spectra, and 30 nm could afford the highest transmittance at $\lambda = 550$ nm. The $R_s$ of the structures was again consistently low, being in the range of 3.2 to 3.8 $\Omega$/sq. Figure 1(b) shows the FOM values of the MAM structures as a function of the thickness of the top MoO$_3$ layer. Transmittances at both the 550 nm and average visible range wavelengths (380 to 780 nm) were used, and in both cases, our results show that a 30-nm-thick top layer affords the highest FOM value.

Figure 2. The properties of MoO$_3$(20 nm)/Ag(x nm)/MoO$_3$(30 nm) multilayer samples, where x is varied from 10 to 16 nm. a) the sheet resistance, b) the transmission spectra, c) the FOM calculated using two different transmittance values, and d) AFM image and roughness values of MoO$_3$(20 nm)/Ag(14 nm)/MoO$_3$(30 nm) multilayer (scanning area: 10×10$\mu$m$^2$).

The effect of the thickness of the Ag layer was also confirmed; by increasing the thickness from 10 to 16 nm, the sheet resistance decreased from 4.5 to 2.8 $\Omega$/sq., as shown in Fig. 2(a). However, transmittance was considerably lower for the thicker Ag layer, and a high transmission was only obtained in a narrow region, as shown in Fig. 2(b). Consequently, the highest FOM value was obtained with 14 nm thickness when the transmittance at $\lambda = 550$ nm is used, as shown in Fig. 2(c). In conclusion, the optimum MAM structure is observed to be MAM (20/14/30 nm). This structure shows a high transmittance (at $\lambda = 550$ nm) of 67.9%, a low sheet resistance (3.4 $\Omega$/sq). When the average transmittance (60.8%) was used, FOM was decreased slightly to 2.0 $\times$ $10^{-3}$ $\Omega^{-1}$. We observed that the optimum structure in our results exhibit a thickness range similar to those of the optimum MAM structures in literatures. Nguyen et al. reported that an MAM structure with a 35-nm-thick top MoO$_3$ layer, a 20-nm-thick bottom MoO$_3$ layer, and a 10-nm-thick middle Ag layer afforded an average transmittance of 70% [10], which is higher than our average transmittance. However, the $R_s$ and FOM of this optimum structure were not shown. Naka et al. reported that a combination of MoO$_3$ layers between 20 and 50 nm and an Ag layer between 5 and 15 nm led to high transmittance (70% at
\( \lambda = 550 \text{ nm} \) and low sheet resistance (5.8 Ω/sq.) [9]; therefore, we obtained similar FOM values in this study.

Finally, the surface morphology of the MAM multilayer was also investigated. AFM image and root mean square roughness and height difference values of the MAM (20/14/30 nm) are shown in Fig. 3(d). It is found that the surface roughness is very small, however, some spikes are also observed therefore relatively large \( R_y \) value is measured.

### 3.2. IZO/Ag/MoO\(_3\) (IAM) multilayer

The FOM value of MAM is found to be much lower than that of the IAI multilayer [8]. We attempted to improve the FOM by combining a MoO\(_3\) layer and an IZO layer in the structure. A 14-nm-thick Ag layer and a MoO\(_3\) top layer (with thicknesses between 20 and 60 nm) were deposited onto a 30-nm-thick sputtered IZO film. Figure 3(a) shows the transmittance spectra of all the samples. The different MoO\(_3\) layer thicknesses resulted in varying positions of the peaks, but apparently the sample consisting of a 50-nm-thick MoO\(_3\) layer shows a transmittance (at \( \lambda = 550 \text{ nm} \)) of 79.2%, which is high. The sheet resistance of all the samples remained constant because the thickness of the Ag layer remained constant. Figure 3(b) shows the FOM of all the samples based on the two transmittance values. In both cases, the IAM(30/14/50 nm) sample showed the highest values, and a value of \( 32 \times 10^{-3} \Omega^{-1} \) was achieved. We expect that the IAM electrode could be successfully used as an anode in OLEDs.

![Figure 3](image)

**Figure 3.** The properties of IZO(30 nm)/Ag(14 nm)/MoO\(_3\)(x nm) multilayer samples, where x is varied from 20 to 60 nm. a) the transmission spectra and b) the FOM calculated using two different transmittance values.

Table 1 summarizes results of representative film structures concerning about FOM values and thicknesses of IZO layer. A higher FOM value can be obtained by using the IAM structure instead of the MAM structure, although the FOM value is still lower than that of the IAI structures [8]. On the other hand, the MAM is indium-free and the IAM consisting of hybrid oxides could reduce the thickness of the IZO layer, which implies significantly less indium is used, compared to IAI. Both MAM and IAM are superior to a 70-nm-thick IZO single film which has a low FOM value due to its high electrical resistivity (3.0 \( \times \) 10\(^{-4} \) Ωcm) and sheet resistance (42 Ω/sq.).

There is a report describing a hybrid structure of MoO\(_3\) and In\(_2\)O\(_3\) [12], where post-annealing of the multilayers was required to obtain a low sheet resistance. The as-deposited film exhibited a high sheet resistance of approximately 50 Ω/sq.; then, annealing at 120 °C lowered the value to 8.2 Ω/sq. The transmittance at 550 nm in the study was stated to be 85%; therefore, its FOM was estimated as 24 \( \times \) 10\(^{-3} \) Ω\(^{-1}\). However, our IAM multilayer achieved a higher FOM without any annealing, with a similar indium-saving level.
Table 1. The FOM values and IZO layer thicknesses of representative samples.

| Structures       | FOM (x 10^{-3} \Omega^{-1}) | Thickness of IZO layer (nm) |
|------------------|--------------------------------|-----------------------------|
| MAM(20/14/30)    | 6.2                           | 0                           |
| IAM(30/14/50)    | 32                            | 30                          |
| IAI(30/14/30) [8]| 56                            | 60                          |
| IZO single film  | 2.3                           | 70                          |

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4. Conclusion
Indium-free, transparent conductive multilayers are fabricated, and the optimum structure is found to be MAM (20/14/30 nm). The FOM value is observed to be lower than that for a previously studied IAI multilayer; therefore, the fabrication of a hybrid oxide multilayer consisting of MoO_3 and IZO is attempted for the first time. Following this, IAM (30/14/50 nm) structure exhibits the highest FOM value, which is still lower than that of the IAI multilayer, but it is important because less indium can be used in display devices.

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