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Fabrication of Molybdenum Trioxide Thin Films Using Precursors by Wet Process and Examination of Annealing Conditions

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ABSTRACT

Molybdenum trioxide (MoO_3) thin films were prepared by a spin-coating method using ammonium molybdate tetrahydrate (AMT, $(NH_4)_6Mo_7O_{24}4H_2O$) as a precursor. In particular, the annealing condition was strictly evaluated. For example, some samples were annealed twice; the first annealing was in vacuum, and the second was in air. The transmission spectra and surface roughness strictly depended on the annealing condition. We also evaluated the electroluminescence (EL) properties of organic light-emitting diodes (OLEDs) that contained the fabricated MoO_3 thin films as a hole-transporting layer.

I. INTRODUCTION

Molybdenum trioxide (MoO_3) is a wide-gap material that has been used as both the hole transporting layer and the buffer layer of photonic and electric devices. MoO_3 thin films are usually fabricated using RF magnetron sputtering [1, 2]. In this research, we fabricated MoO_3 thin films by a spin-coating method using ammonium molybdate tetrahydrate (AMT, $(NH_4)_6Mo_7O_{24}4H_2O$) as a precursor [3, 4] because a wet process enables low-cost production. Moreover, some samples were annealed twice; the first annealing was in vacuum, and the second was in air. Finally, organic light-emitting diodes (OLEDs) were fabricated that contain an MoO_3 layer as a hole-transporting layer.

II. EXPERIMENTAL

Fabrication of MoO_3 films. As a precursor solution, we mixed an AMT solution with pure water. The thin films of the precursor solution were formed by a spin-coating method on a substrate. Then the samples were annealed in air at various temperatures ranging from 340 to 500°C. Some samples were annealed twice; the first annealing was in vacuum, and the second was in air. This is because the first annealing in vacuum reduces the oxygen atoms.
Fabrication of OLEDs. We fabricated the following five kinds of OLEDs:

G1 & G2: ITO / MoO_3 / MDMO-PPV / Al

Annealing at 360°C in air. The AMT densities are 1wt% (G1) and 0.5wt% (G2).

H1 & H2: ITO / MoO_3 / MDMO-PPV / Al

First annealing at 340°C in vacuum and second annealing at 360°C in air. The AMT densities are 1wt% (H1) and 0.5wt% (H2).

I: ITO / PEDOT:PSS / MDMO-PPV / Al

Measurement setup. The surface roughness of the MoO_3 thin film was evaluated using an atomic force microscope (AFM, FS-150N, SII Nanotechnology). The transmission spectra were evaluated using a spectrophotometer (UV-2450, SHIMAZDU). The current-voltage characteristics and the electroluminescence (EL) spectra were measured using a combination system of a source meter (2400, Keithley), an integrating sphere, and a multichannel monochrometer (PMA-12, Hamamatsu). FT-IR spectroscopy was performed using an FT/IR-4100 (Jasco).

III. RESULTS AND DISCUSSION

The precursor thin films became MoO_3 films by annealing at over 340ºC because the FT-IR signals, which originated from the stretching and bending vibration of the N-H of the NH_4^+ groups at around 3200 and 1400 cm^{-1}, disappeared after the annealing at over 340°C. In addition, the surface roughness increased by annealing at over 380°C (Fig. 1). The transmittance in the visible light regime was also reduced by annealing over 380°C due to light scattering by the surface roughness. Thus, we concluded that the optimum annealing temperature ranges from 340 to 360ºC.

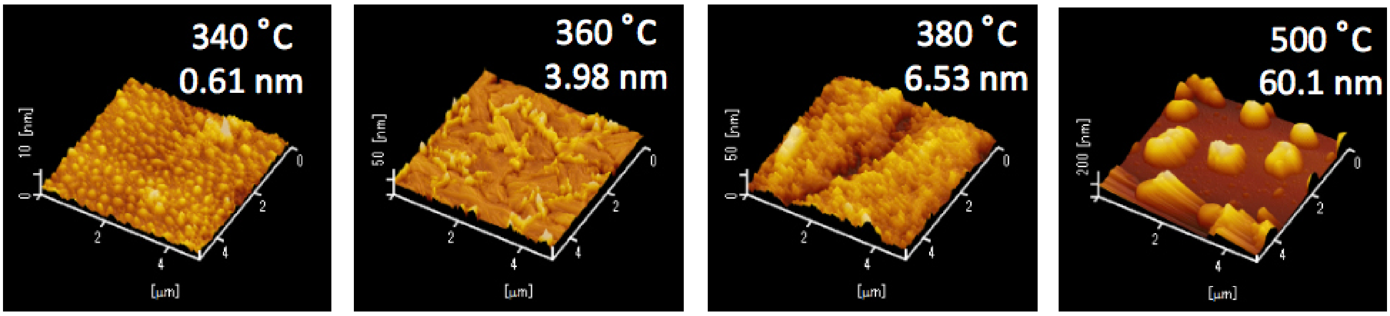

Figure 1 Surface of MoO_3 films annealed at different four temperatures. Annealing temperatures and averaged surface roughnesses are denoted in the figures.

To improve the surface roughness, we annealed two samples (A and B) in vacuum at different temperatures. A second annealing was also attempted for three samples (C, D, and E). The annealing conditions are listed in Table 1. The surface roughnesses of the samples from A to E are 1.00, 9.11, 0.398, 26.9, and 12.0 nm. Consequently, the best annealing condition is sample C. Figure 2 shows the transmission spectra of the three samples. Sample C reveals fine transmittance due to very small surface roughness. On the other hand, sample A reveals smaller transmittance in the visible light regime. In addition, it looks blue, which is most likely caused by the lack of oxygen atoms due to the annealing in vacuum.

Table 1 Annealing condition of five samples.

Sample	1st annealing (temp.)	Atmosphere	2nd annealing (temp.)	Atmosphere
A	340	vacuum	-	-
B	500	vacuum	-	-
C	340	vacuum	360	air
D	360	vacuum	500	air
E	500	vacuum	360	air

Figure 3 shows both the current-voltage and voltage-luminance characteristics of the five OLEDs. The driving voltage of the OLEDs containing MoO_3, which was annealed at 360ºC in air (sample G1), was reduced by about 44% compared to an OLED containing a PEDOT:PSS layer as a hole-transporting layer (sample I). The power efficiency at the maximum emission voltage also improved by about 2.17 times (sample G2). Thus, sample G2 outperformed sample G1. Sample H2's driving voltage is lower than sample I. However, its maximum luminance is much smaller than that of sample I. The driving voltage of sample H1 almost equals sample I. In addition, its maximum luminance is much smaller than sample I. Thus, the performance of samples H1 and H2 must be improved.

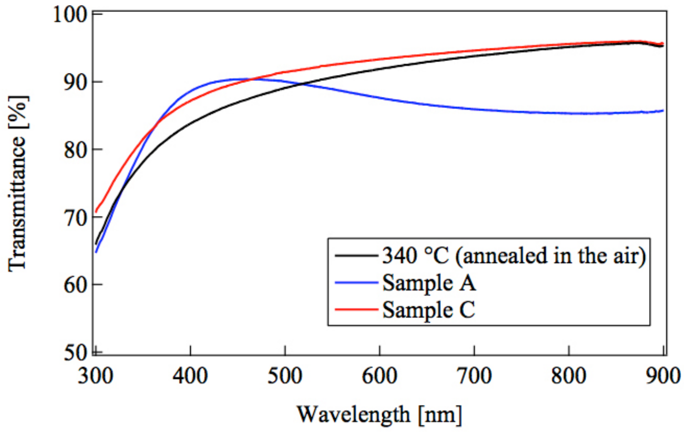

Figure 2 Transmission spectra of three samples. Sample A looks blue, resulting in smaller transmittance in visible light regime.

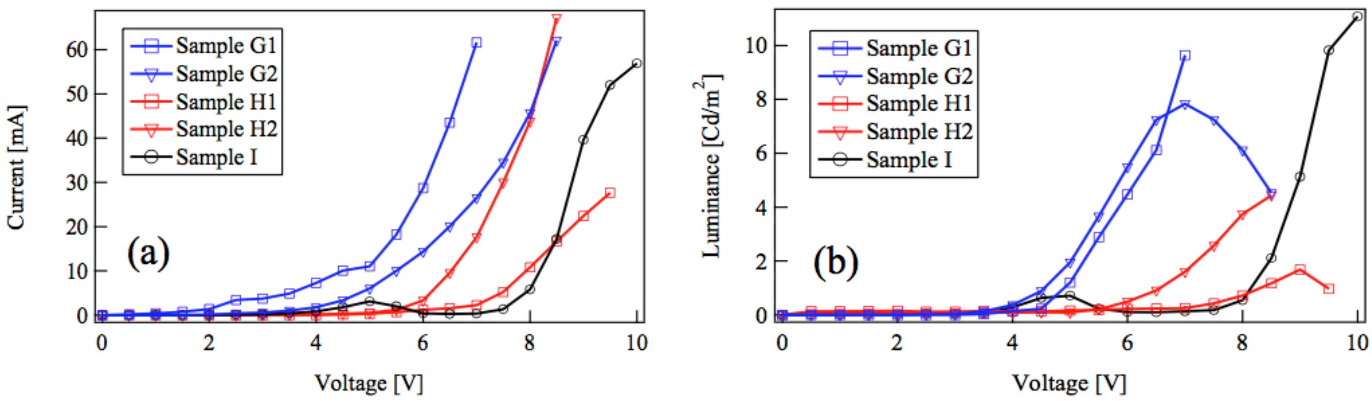

Figure 3 (a) current-voltage characteristics and (b) voltage-luminance characteristics of five OLEDs.

IV. SUMMARY

The annealing conditions of wet-processed MoO_3 films were evaluated. MoO_3 film that was annealed at 360°C in air reveals good performance as a hole-transporting layer in OLEDs. The surface roughness was clearly improved by double annealing in vacuum and air (sample C). However, the EL properties that contain the double annealed MoO_3 layer must be optimized.

V. REFERENCES

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