Diffusion of ZnS:Mn Active Layer to Plasma Polymerized p-xylene Thin Film

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Synopsis

As a preliminary work to fabricate an organic and inorganic compound EL device, we investigated diffusion across two layers by annealing. p-xylene was plasma polymerized on ZnS:Mn film deposited by the sputtering method. The diffusion is enhanced as the annealing time and temperature increases. And the previous annealing effectively suppresses the diffusion of inorganic material afterward.

KEYWORDS: Plasma polymerization, p-xylene, ZnS:Mn

1. Introduction

Organic electroluminescent (EL) and inorganic EL devices, which are expected as new generation flat display device, have many advantages such as high brightness, thinness and self emitting. However inorganic EL device has high operating voltage and organic EL device has short life time. The organic and inorganic compound EL is expected to resolve these disadvantages. We prepared an organic and inorganic compound thin film. The organic layer is plasma polymerized p-xylene (PPPX) with high durability and less pinholes. However it is easily deteriorated after deposition due to its active radicals. Inorganic layer is ZnS:Mn layer which is often used as an active layer of inorganic EL devices. We investigated depth profile of atomic composition with ESCA (Electron Spectroscopy for Chemical Analysis, SHIMADZU INC. ESCA-750).

2. Experimental

ZnS:Mn thin film was prepared by RF magnetron sputtering method on the cleaned indium-tin oxide (ITO) coated glass substrate (MATSUNAMI GLASS IND., LTD., Corning #7059 25 x 25 x 0.6 mm). Then plasma polymerized p-xylene thin film was deposited using p-xylene monomer. Fig.1 and Fig.2 show capacitively coupled glow discharge system for plasma polymerization (SAMCO ENGINEERING INC. PD-2) and RF magnetron sputtering equipment (TOKKI INC. SPK-301) respectively. Deposition conditions are shown in Table 1, Table 2.

Table 1: ZnS:Mn sputtering conditions

<table>
<thead>
<tr>
<th>Target</th>
<th>ZnS:Mn (Mn = 0.5 wt.%)</th>
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<tbody>
<tr>
<td>Base pressure</td>
<td>1.2 ~ 1.4 x 10^{-6} Torr</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>2 x 10^{-3} Torr</td>
</tr>
<tr>
<td>RF power</td>
<td>50 W</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Deposition time</td>
<td>50 min</td>
</tr>
<tr>
<td>Sputtering gas flow rate</td>
<td>Ar:10 ccm + He:10 ccm</td>
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</tbody>
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Table 2: Deposition conditions of PPPX

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<table>
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<tbody>
<tr>
<td>Base pressure</td>
<td>0.02</td>
</tr>
<tr>
<td>Discharge pressure</td>
<td>0.3</td>
</tr>
<tr>
<td>RF power</td>
<td>19.6</td>
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<tr>
<td>Substrate temperature</td>
<td>40 °C</td>
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<tr>
<td>Deposition time</td>
<td>15 min</td>
</tr>
<tr>
<td>Bubbling gas (Ar) flow rate</td>
<td>50 ccm</td>
</tr>
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</table>

Depth profile of Zn(2p 3/2) and S(2p) were investigated. Etching was performed under the conditions of Ar pressure of $5 \times 10^{-4}$ Torr, acceleration voltage of 2 kV and ion beam current of 10 μA. Etching speed of all PPPX layer was about 6 nm/min. Any PPPX thin films are about 150 nm in thickness. After deposition of PPPX, samples were annealed by heat-treatment equipment (KOYO LINDBERG INC.) under several different conditions.

![Fig. 1: Capacitively Coupled Glow Discharge System for Plasma Polymerization](image1)

![Fig. 2: RF Magnetron Sputtering Equipment](image2)

3. Experimental results and discussions

3.1 Temporal change after annealing and effect of annealing temperature

Fig. 3 shows the effect of annealing on depth profile of Zn(2p 3/2) peak and S(2p) peak and the temporal change after annealing. The time of annealing was 1 hour. As PPPX layer thickness and etching speed are known, we can easily estimate that 25 min etching reaches the boundary between the PPPX layer and the ZnS:Mn layer. Fig.3(a) and Fig.3(d) show that, when the sample was not annealed, the peak of Zn(2p 3/2) of the sample one week after deposition is observed at the shallower position than that in the as deposited sample. Concerning S atom, Fig.4(a) and Fig.4(d) show the similar result. Therefore it is clear that the diffusion of Zn atoms and S atoms to PPPX layer occur one week after deposition. Fig.3(a) through Fig.3(c) and Fig.4(a) through Fig.4(c) show that the higher annealing temperature causes enhanced diffusion. Comparing between Fig.3(a) and Fig.3(d), Fig.3(b) and Fig.3(e), Fig.3(c) and Fig.3(f), it is found that the annealing at higher temperature brings less change in the depth profile after one week. It suggests that annealing at higher temperature promotes more crosslinking reaction and the tightly crosslinked structure would suppress diffusions of Zn and S atoms.
Fig. 3: Effect of annealing on depth profile of Zn(2p 3/2) and temporal change after annealing
Fig. 4: Effect of annealing on depth profile of S(2p) and temporal change after annealing
3.2 Annealing time dependence of diffusion

Fig. 5 and Fig. 6 show depth profile of Zn(2p 3/2) and S(2p) peak of the samples annealed at 200 °C for 0~3 hour. These figures show that the boundary between ZnS:Mn and PPPX moves up to the surface as the annealing time is increased.

![Graphs showing depth profile of Zn(2p 3/2) and S(2p) peak](image)

(a) as deposited  (b) soon after annealing at 200 °C for one hour  (c) soon after annealing at 200 °C for two hours  (d) soon after annealing at 200 °C for three hours

Fig. 5: Depth profile of Zn(2p 3/2) in the sample after annealing

![Graphs showing depth profile of S(2p)](image)

(a) as deposited  (b) soon after annealing at 200 °C for one hour  (c) soon after annealing at 200 °C for two hours  (d) soon after annealing at 200 °C for three hours

Fig. 6: Depth profile of S(2p) in the sample after annealing

4. Conclusion

The conclusions can be summarized as follows:

1. Annealing at higher temperature enhanced the diffusion of ZnS:Mn into the PPPX thin film.

2. Previous annealing of the sample suppresses diffusion of inorganic material into organic material afterward.

3. Annealing temperature and annealing time have to be optimized for the effective elimination of radicals and effective suppression of inorganic material diffusion.

Acknowledgement

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