Study on the Electrical Stability of Al-doped ZnO Thin Films For OLED as an alternative electrode

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Abstract

We investigated the electrical and optical properties of ZnO:Al thin films as a function of the thermal process conditions. The film was prepared by RF magnetron sputtering followed by annealing in a box furnace in air. An ZnO:Al (98:2) alloy with the purity of 99.99% (3 inch diameter) was used as the target material. The electrical properties of the transparent electrode, exhibited surface oxidation as a result of rapid oxygen absorption with increasing annealing temperature. The processed ZnO:Al films and commercial ITO(indium-tin-oxide) were applied to an OLED stack to investigate the current density and luminescence efficiency. The efficiency of the device using the ZnO:Al electrode was higher than that from the device using the ITO electrode.

1. Objectives and Background

Currently, ITO is the most widely used TCO (transparent conducting oxides) on account of its high conductivity, work function, and transparency in the visible spectral range. Although ITO is the most successful TCOs, indium is a relatively scarce and expensive element.[1]

ZnO:Al films were investigated as an alternative to ITO films. ZnO, which is composite semiconductor of the II-Ⅵ group with a wurtzite structure, has many more favorable properties than ITO thin films such as a broader distance between bands, high piezoelectric constant, high transparency, etc.[2,3] However, its commercialization has been delayed by the lack of chemical stability and changes in the electrical characteristics under atmospheric and thermal process conditions.[4]

In this study, ZnO:Al thin films were deposited by RF magnetron sputtering, and the change in the stability of the electrical and optical characteristics were examined according to different heat treatment conditions. SEM, XRD and XPS analysis were used to characterize the films. Some samples were applied to OLED stacks to determine the electro-optical properties of the ZnO:Al films. The feasibility of using ZnO:Al films in SM-OLED devices was examined by comparing the electrical characteristics of commercial ITO and ZnO:Al anodes.

The device structure of the SM-OLEDs grown by vacuum thermal deposition is Anode (300nm ZnO:Al or ITO) /60nm Alq3 /2nm LiF /75nm Al.

2. Results and discussion

High-performance aluminum-doped zinc oxide (ZnO:Al) thin films were deposited on glass by RF magnetron sputtering with a ZnO target containing 2wt.% Al_2O_3 at 200℃. The film thickness was approximately 300nm.

The processed ZnO:Al film was annealed at various temperatures in air, in order to investigate the process compatibility with an OLED. Figure 1 shows the change in the sheet resistance of the ZnO:Al films as a function of temperature.

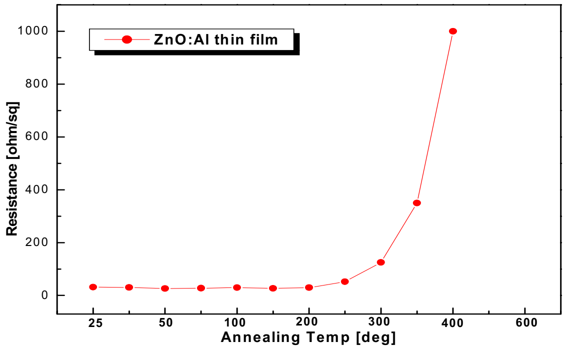

Figure 1. Change in the sheet resistance as a function of the annealing temperature.

As shown in Figure 1. The sheet resistance of the ZnO:Al films was approximately 30-40ohm/sq at annealing temperatures ranging from room temperature to 280℃. However, the sheet resistance increased rapidly with increasing temperature thereafter, reaching 1kohm/sq at approximately 360℃. SEM and EDS analysis were used to examine the composition of the as-deposited sample and the sample annealed at 400℃ in order to explain the changes in sheet resistance. As shown in Figure 2. Even though there was no distinct change in the surface morphology of the ZnO:Al films, EDS analysis result showed a higher oxygen content on the surface of the 400℃ annealed samples. This shows that the rapid increase in sheet resistance of the ZnO:Al films with increasing temperature was due to a change in the chemical stability of the film surface through a reaction with oxygen.[5,6]

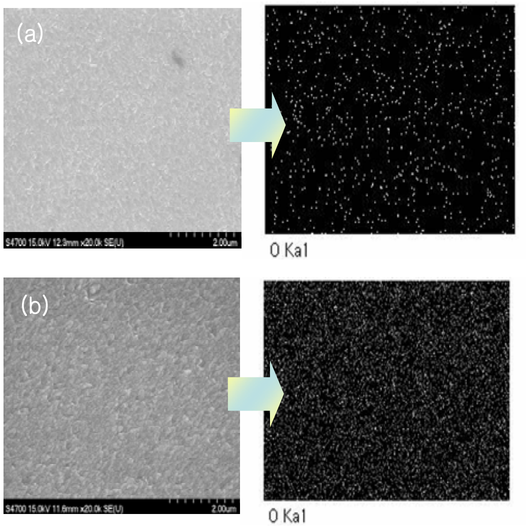

Figure 2. SEM photographs and EDS analysis of the ZnO:Al films (a)RT (b) 400°C

Figure 3 shows the XRD (Rigaku, No. D/Max-2A) patterns of the as deposited sample and the sample annealed at 400℃. The main peak was assigned to the typical Wurtzite (002) plane. There was no peak broadening or other major differences between the two samples.

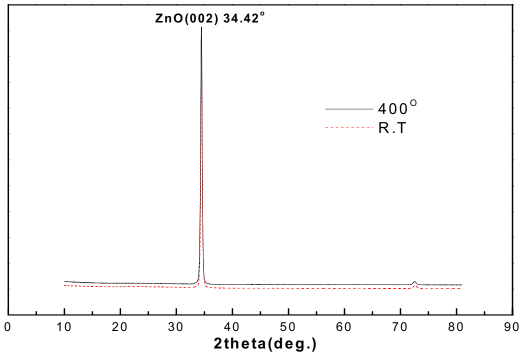

Figure 3. XRD patterns of the ZnO:Al films annealed at different temperatures.

The EDS and XRD results suggest that the change in resistance is due to a change in surface chemistry change as a result of annealing in air. Therefore, an attempt was made to evaluate the quantitative chemical status of surface using XPS. Figure 4 shows the XPS spectra of the ZnO:Al films. The binding energy of Zn2p3 shifted from 1021.38eV (room temperature sample) to 1021.91eV (400C annealed sample). In addition, the O1s binding energy changed from 530.12eV to 529.54eV. A lower binding energy of 532eV was also observed, which was assigned to adsorbed H_2O or adsorbed O_2 on both the as-deposited sample and that annealed at 400℃. The binding energy of Al2pwas 74.2eV peak on the room temperature sample, which was attributed to Al in a ZnO matrix, and 74.6 eV on the 400℃ annealed sample, which was attributed to Al_2O_3 that had precipitated on the film surface. From these results, the change in the sheet resistance can be explained by the weak chemical bond strength of oxygen in the ZnO:Al matrix and the partial precipitation of Al_2O_3 on the film surface.[7]

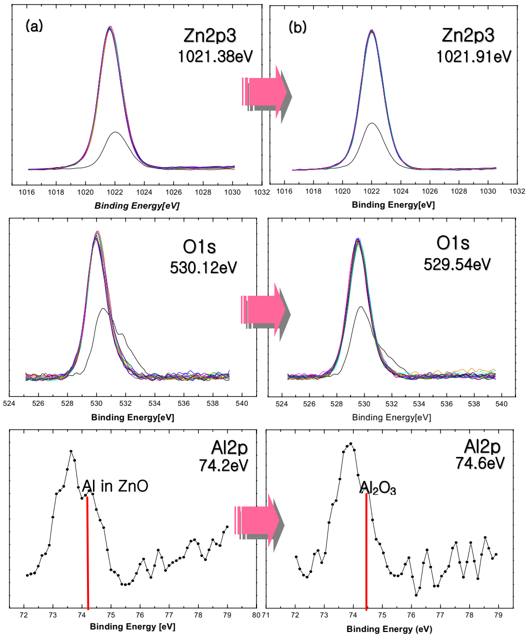

Figure 4. XPS spectra of Zn2p3, O1s and Al2p from ZnO:Al films (a)RT (b) annealed at 400°C

Figure 5 shows the transmission of ZnO:Al films in the UV visible range. The transmittance was > 80% in the visible region. The fluctuations in the spectra over the visible range is typical for ZnO:Al films due to the interference effect of the interface and film surface.

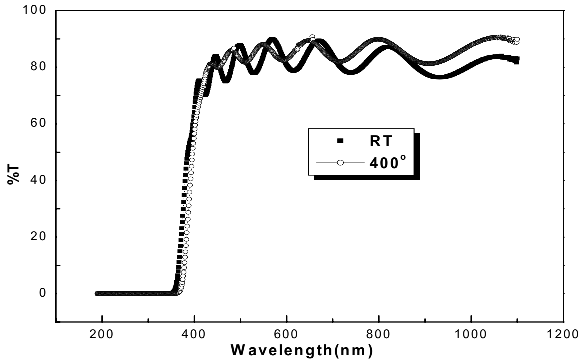

Figure 5. The transmittance in the UV-visible regions of ZnO:Al films (a)RT (b) 400°C

Sample	Work-function (eV)	Sheet Resistance (Ω/sq)	Hall Mobility [㎠/Vs]
ZnO:Al (RT)	4.68	24	22
ZnO:Al (400℃)	5.08	720	4.89
ITO(Commercial)	4.82	23	23

Table 1. Surface work function, elemental composition, and sheet resistance of the ZnO:Al and ITO anode.

Table 1 shows the electrical properties of the ZnO:Al anode and ITO anode, which were used to fabricate the OLED. The structure of the OLED is as follows: ZnO:Al anode or ITO anode/AlQ3/LiF/Al. Among the three types of electrode, the 400℃ annealed sample did not emit light due to its high resistance. Therefore, the device containing the as-deposited ZnO:Al film was compared with the device containing the ITO anode.

The efficiency of the device with ZnO:Al was higher than that of the device with ITO, as shown in figure 6. The lower current density appeared to be due to the lower work function of the ZnO:Al films. The lower work function caused less hole injection from the anode to the organic layers. Therefore, the luminance and current should be lower than those of device with the ITO anode. However, the device with the ZnO:Al anode showed a higher efficiency in all regions of luminance. An increased charge balance might explain some of this higher efficiency but it is not enough to explain this higher efficiency.

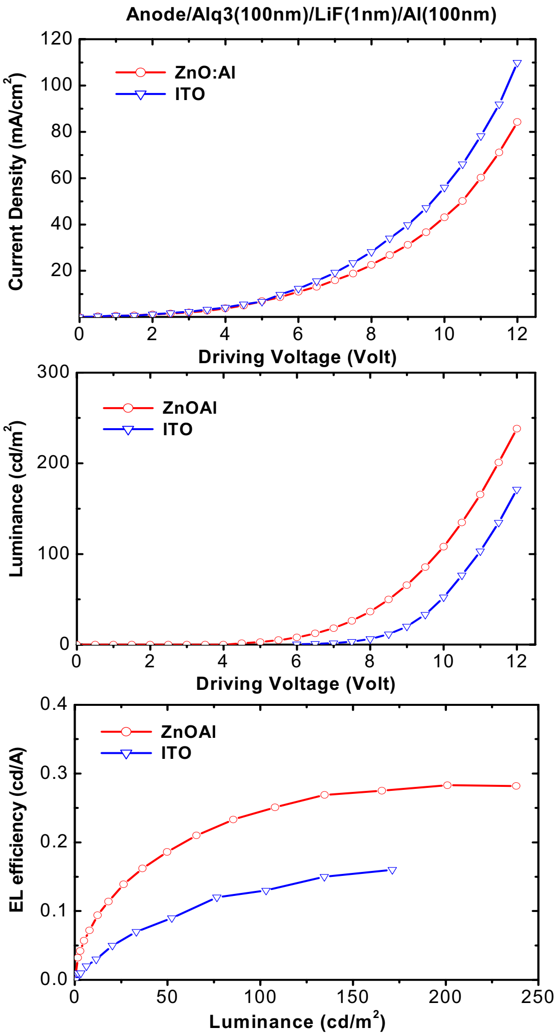

Figure 6. Efficiency characteristic of ITO and ZnO:Al anode using OLED

3. Summary

The thermal stability of a ZnO:Al transparent electrode was investigated as a function of the annealing temperature. The sheet resistance of the ZnO:Al films increased with increasing annealing temperature. XPS showed that high temperature annealing caused more surface oxidation due to rapid oxygen absorption. A comparison of the OLED characteristics of the ZnO:Al with those of the commercial ITO anode with typical SM-OLED stacks showed that the electroluminescence efficiency of the OLED using the ZnO:Al electrode was higher than the ITO device.

4. References

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