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Ionization-Assisted Deposition of SrO_x Thin Films for Electron Injection Layer of Organic Light Emitting Diodes

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SrO_x thin films were prepared by the ionization-assisted deposition as the electron injection layer between the electron transport/emitting layer and the Al cathode of the organic light emitting diode. By inserting an SrO_x layer of a few-nm thick, the luminance increased nearly three orders of magnitudes for the same driving voltage. The device performance was also controlled by the ion acceleration voltage that was applied in the course of SrO_x film deposition. Compared to the simple evaporation, the ionization-assisted deposition improved the luminance and the power efficiency by more than two times. XPS analysis suggested that the ion acceleration leads to two dimensional homogeneous film growth at the initial stage of film deposition.

Keywords organic LED; organic EL; electron injection; strontium oxide; ionization-assisted deposition

INTRODUCTION

Electron injection into organic materials has been one of the key issues in the development of organic light emitting diodes (O-LEDs) due to the incommensurate electron energy levels of organic materials and metallic electrodes. One of the most common methods to solve this problem is to insert a thin electron injection layer, such as LiF, between the organic layer and the metal cathode^[1]. The optimum thickness of such electron injection layer is reported to be a few nanometers or less. Well-controlled deposition of such thin films is not easy because the heterogeneous substrate-film combination often leads to three dimensional island growth rather than uniform layer-by-layer growth.

We have shown that a thin SrO_x film can be an efficient electron injection

layer^[2]. Although the work function of SrO_x is low enough to mediate electron injection, its resistivity is rather high. Therefore, the film thickness should be kept low enough so as not to hinder the electric conduction. With a purpose to control the properties of such a thin film, we have used the ionization-assisted method for the deposition of the SrO_x layer. The ion irradiation in the film formation process can bring about such effects as the creation of nucleation centers, enhancement of adatom surface migration, sputter cleaning and so on^[3]. These factors can be effective to control the growth morphology of very thin films. Therefore, the ionization-assisted deposition method has the possibility of controlling the physical properties of the ultra thin electron injection layer for O-LED.

EXPERIMENT

Figure 1 shows the schematic diagram of the ionization-assisted deposition method. SrO_x films were prepared by evaporating Sr metal from a tantalum boat in the oxygen pressure of 4×10^{-3} Pa. A part of the evaporated Sr was ionized by electron bombardment in the ionizer placed above the evaporator. The ion acceleration voltage was applied between the ionizer and the substrate so as to accelerate the positive ions toward the substrate. The electron energy was 100 eV, and the emission was adjusted to give the ion current of about 2 μA on the substrate holder of about 15 cm^2 wide. Figure 2 shows the structure of O-LED having SrO_x electron injection layer. The LED consists of indium tin oxide (ITO) anode, 60-nm thick spin-coated polyvinylcarbazole (PVCz), 60-nm thick tris(8-hydroxyquinolino)aluminum (Alq_3), the SrO_x layer, and Al cathode. The Alq_3 and Al were prepared by vacuum deposition, and the SrO_x layer either by vacuum deposition or by the ionization-assisted deposition. The O-LED was operated in an air-tight box of acrylic resin evacuated by an oil rotary pump.

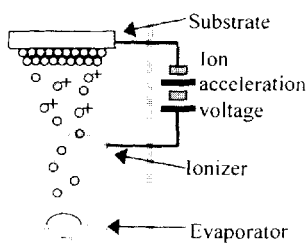


FIGURE 1 Schematic diagram of the ionization-assisted deposition.

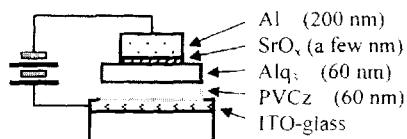


FIGURE 2 The structure of OLED having SrO_x electron injection layer.

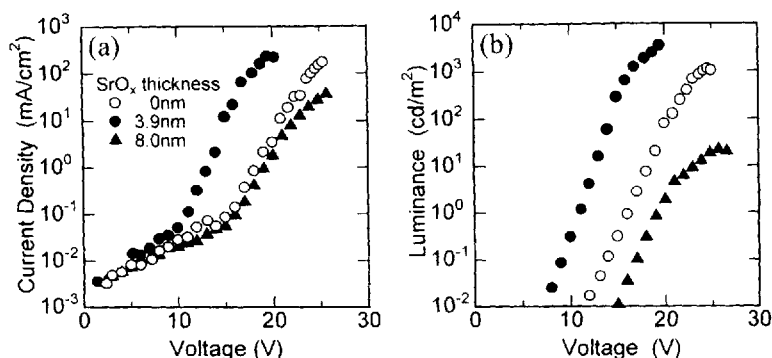


FIGURE 3 The current (a) and luminance (b) characteristics of the O-LEDs having different SrO_x thickness.

RESULTS AND DISCUSSIONS

Figure 3 shows the current and luminance characteristics of the O-LEDs for different SrO_x thicknesses. The SrO_x layers were prepared by vacuum deposition. By inserting a 3.9-nm thick SrO_x layer, the current increased by 140 times and the luminance 920 times at the drive voltage of 15 V, whereas the 8-nm thick SrO_x reduced the device performance. Our detailed experiment has shown that the SrO_x layer works effectively even at a thickness smaller than 1 nm. The luminance decreased slightly with increasing thickness up to 6 nm, and decreased rapidly by further increase of thickness. This is due to the high resistivity (around 10⁸ Ωcm) of the SrO_x film. X-ray photoelectron spectroscopy (XPS) of the SrO_x films on Alq₃ suggested that the films do not have full coverage of Alq₃ surface but assume island structure for thicknesses smaller than 8 nm.

Figure 4 shows the effect of the ion acceleration voltage on the luminance and the power efficiency of the O-LEDs when the SrO_x was deposited by the ionization-assisted method. The devices were operated at 14 V. In this case, the SrO_x thickness was 0.5 nm and the PVCz layer was doped with 50 wt% tetraphenyldiaminobiphenyl (TPD). The ion acceleration voltage significantly influenced the device performance. The highest luminance was obtained at the ion acceleration voltage of 500 V, while the highest efficiency was obtained at 200 V. The improvement of carrier injection can reflect such film properties as higher surface coverage, smaller impurity inclusion at the interface, better adhesion and so on.

XPS spectra of a 3.9-nm thick SrO_x film showed the Al signal from the underlying Alq₃, suggesting the incomplete surface coverage in this thickness range. The intensity ratio of Al 2p to Sr 3d XPS signals was 0.36 for the

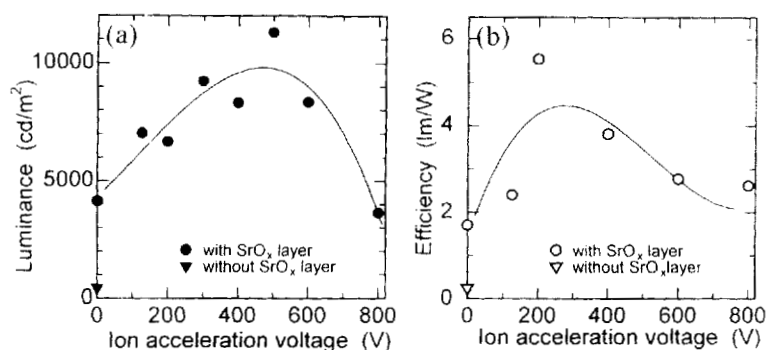


FIGURE 4 Emission intensity (a) and power efficiency (b) at 14 V as a function of the ion acceleration voltage for SrO_x deposition.

film deposited with the ion acceleration voltage of 0 V, 0.22 for 130 V, and 0 for 1000 V. This tendency suggests that the ionization-assisted deposition enhances homogeneous two dimensional film growth and leads to the formation of thin and uniform injection layer, which is effective for making a homogeneous interface. In addition to controlling the growth morphology, the ion acceleration can help to improve the quality of oxide films such as the packing densely^[4]. On the other hand, higher ion acceleration can cause radiation damage on the surface of Alq₃. These competitive effects of the ion irradiation lead to the result shown in Fig. 4.

CONCLUSION

It was found that the SrO_x layer of a few nanometers thick works efficiently as the electron injection layer for the O-LED. Although the conventional evaporation method has little control of the growth morphology for such thin films, the ionization-assisted method was effective in improving the device characteristics possibly through the modification of film microstructure by the ion irradiation effect.

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