Direct Al cathode layer sputtering on LiF/Alq3 using facing target sputtering with a mixture of Ar and Kr

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Using facing target sputtering (FTS) with a mixture of Ar and Kr, direct Al cathode sputtering on LiF/Alq3 layers was accomplished without the need for a protective layer against plasma damage. Organic light emitting diodes (OLEDs) with a directly sputtered Al cathode in a mixture of Ar and Kr showed a much lower leakage current density (~1 × 10^{-3} mA/cm^2 at ~6 V) than those (~1 × 10^{-1} mA/cm^2 at ~6 V) of OLEDs with an Al cathode prepared by FTS or dc sputtering in a pure Ar ambient. This indicates that the bombardment of energetic particles is effectively restricted by mixing a heavy noble gas. Based on the current-voltage curve for the OLED, a possible mechanism is proposed to explain the effect of a heavy noble gas mixture on electrical properties of OLEDs for direct Al cathode sputtering by FTS. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178483]

Organic light emitting diodes (OLEDs) are attracting considerable attention because of their potential applications in flat panel displays, flexible displays and thin-paper displays. To fabricate high-performance OLEDs, acquiring high-quality cathode contacts to the organic layer is essential. Al, Ag, Pt, and Mg–Ag alloys have been widely investigated so far for cathode material on OLEDs, in addition to low work function metal (Mg, Ca, or Li). In preparing a cathode layer, resistive heating-induced thermal evaporation is mainly employed for depositing the cathode layers because the organic layer is extremely sensitive to radiation during sputtering or electron-beam evaporation. However, thermal evaporation methods have critical drawbacks, such as the serious undesirable reaction of Al with the ceramic crucible, creeping up of Al on the crucible wall, and difficulty in achieving a stable rate control and a large-area deposition. For these reasons, sputtering has been considered as a possible solution for preparing a cathode layer. Sputtering is a commonly used deposition method because of its simplicity, high throughput, and improved adhesion. However, the bombardment of energetic particles during the sputtering process can result in damage to the underlying organic layers, in an investigation of an direct cathode sputtering on organic layer, reported that a careful adjustment of rf sputtering conditions makes it possible to prepare a cathode electrode of Al, Mg:Ag, and Mg/Ag without any noticeable degradation. However, the performance of their devices with such electrodes was so poor that the effect of plasma damage was hardly detectable. Therefore, the development of a direct sputtering method for an Al cathode layer on organic layer without a buffer or protective layer is imperative in finding a solution of the problems of Al thermal evaporation and applying a sputtering process to the fabrication of organic-based optoelectronic devices.

In this letter, we report on the successful fabrication of OLEDs with an Al cathode layer directly sputtered by a facing target sputtering (FTS) technique in a mixture gas of Ar and Kr. The OLEDs fabricated using this method exhibited a much lower leakage current density than OLEDs fabricated by dc sputtering and FTS in pure Ar gas. It was found that the bombardment of energetic particles was effectively restricted when a noble gas heavier than Ar was employed in the FTS process.

All organic layers were deposited by thermal evaporation on glass substrates coated with an indium tin oxide anode in the following order: Hole transporting layer (HTL)/electron transporting layer (ETL) and emission layer (EL). α-naphthphenylphenlbenzphen, and tris-(8-hydroxyquinoline) aluminum (Alq3) were used as the HTL and ETL (EL) layers, respectively. A 5 Å thick LiF layer was then thermally evaporated on the Alq3 layer. After the LiF deposition, Al cathode layers were directly sputtered on the LiF/Alq3 layer using the FTS system. The FTS system was specially designed for the plasma damage-free deposition of an Al cathode. Al layer (~50 nm thick) was directly sputtered on the LiF/Alq3 layer in a diffused plasma mode in a mixture of Ar and Kr without a buffer layer. Both the dc power and Ar/Kr flow ratio were maintained constant at 50 W and 15/5 sccm. The diffused plasma mode was generated by inserting of a cast iron yoke plate between the Al target and the ring-type gun magnet. Two 4 in. Al targets were placed face-to-face at a distance of 70 mm, generating magnetic fields that ideally entered and left the targets perpendicularly. The substrate was located at a distance of 100 mm from the common axis of the targets. For comparison, Al cathode layers were directly sputtered on the same test sample by FTS and dc sputtering in a pure Ar ambient, respectively. The
specific conditions of the Al layers deposition by the dc sputter and the FTS in the different ambient are given in Table I. After depositing the Al cathode layer, all of the OLEDs samples were glass encapsulated for protection against moisture and oxygen in the air. The current-voltage (I-V)-luminescence characteristics of the OLEDs were examined using a Photo Research PR-650 spectrophotometer driven by a programmable dc source.

Figure 1 shows the I-V characteristics of the OLEDs with directly sputtered Al cathodes without a buffer layer by dc sputtering in a pure Ar ambient as a function of working pressure and low dc power. All samples show a very high leakage current density at a reverse bias, e.g., leakage current density between $10^{-1}$ and $10^{-3}$ mA cm$^{-2}$ at $-6$ V regardless of the working pressure and dc power. This leakage current density is much higher than that of OLEDs prepared by thermal evaporation (reference sample), in Fig. 1. In addition, OLEDs exhibit a high leakage current density at a forward bias before the turn on of OLEDs due to a large shunt resistance, which is indicative of leaky interfaces between the Al and LiF/Alq3 layers. The high leakage current density of OLEDs prepared by dc sputtering is believed to be caused by the bombardment of energetic particles during the dc sputtering process. Liao et al.,$^{11}$ in an investigation of surface damage in Alq3 layers, reported that high-energy ion irradiation resulted in a change in the band structure of the Alq3, especially highest occupied molecular orbital and as a result influenced the performance of OLEDs. Gu et al.,$^{5}$ also reported that top-emitting OLEDs fabricated by radiofrequency (rf) sputtering at a low rf power have a large leakage current due to the conducting paths resulting from local damage at the interface between the metal and organic layer, which occurs during the sputtering. Therefore, it is believed that the large leakage current density of OLEDs with a dc sputtered Al cathode is related to the conducting paths resulting from plasma-induced local damage. The EL image of the OLED with directly sputtered Al prepared by dc sputtering is shown in the inset of Fig. 1. Numerous dark spots, caused by the bombardment of energetic particles and the presence of large sputtered particles on the LiF/Alq3 surface, are evident.$^{12}$

Figure 2 shows the I-V characteristics of OLEDs with Al cathodes deposited by FTS in a pure Ar ambient on a LiF/Alq3 layer without a buffer layer as a function of working pressure at a constant dc power of 50 W. The I-V curve shows improved electrical characteristics with a leakage current density at a reverse bias lower than that of OLEDs prepared by dc sputtering. All samples show a leakage current density between $10^{-1}$ and $10^{-3}$ mA cm$^{-2}$ at $-6$ V. However, they still exhibit leakage current at the initial forward bias, which is caused by shunt resistance at the interface between Al and LiF/Alq3. In a previous study, we reported that top-emitting OLEDs fabricated by radiofrequency (rf) sputtering at a low rf power have a large leakage current due to the conducting paths resulting from local damage at the interface between the metal and organic layer, which occurs during the sputtering. Therefore, it is believed that the large leakage current density of OLEDs with a dc sputtered Al cathode is related to the conducting paths resulting from plasma-induced local damage. The EL image of the OLED with directly sputtered Al prepared by dc sputtering is shown in the inset of Fig. 1. Numerous dark spots, caused by the bombardment of energetic particles and the presence of large sputtered particles on the LiF/Alq3 surface, are evident.$^{12}$

Figure 3 shows the relationships between the discharge voltage and the working pressure in pure Ar and a mixture of Ar and Kr. It was clearly shown that the addition of Kr to the Ar ambient resulted in an increase in the discharge voltage. Matsushita et al.$^{17}$ reported that the discharge voltage and floating voltage increased linearly with an increase in Xe partial pressure in a Xe and Ar mixture in the FTS process.

![Figure 1](image1.png)  
**FIG. 1.** I-V characteristics of an OLED with a directly sputtered Al cathode by dc sputtering in a pure Ar ambient as a function of working pressure and dc power with inset of EL image.

![Figure 2](image2.png)  
**FIG. 2.** I-V characteristics of OLED with a directly sputtered Al cathode by FTS in a pure Ar ambient as a function of working pressure with inset of EL image. It is noteworthy that the size and number of dark spots in EL image were remarkably reduced when the FTS was used.

![Figure 3](image3.png)  
**FIG. 3.** I-V characteristics of OLEDs with Al cathodes deposited by FTS in a pure Ar ambient on a LiF/Alq3 layer without a buffer layer as a function of working pressure at a constant dc power of 50 W. The I-V curve shows improved electrical characteristics with a leakage current density at a reverse bias lower than that of OLEDs prepared by dc sputtering. All samples show a leakage current density between $10^{-1}$ and $10^{-3}$ mA cm$^{-2}$ at $-6$ V. However, they still exhibit leakage current at the initial forward bias, which is caused by shunt resistance at the interface between Al and LiF/Alq3.
They concluded that the decrease in electron confinement resulting from the plasma extension was the main reason for the increase in discharge voltage in Ar and Xe mixture gas.

Figure 4 shows the I-V characteristics of OLEDs with directly sputtered Al cathodes prepared by FTS in a mixture of Ar and Kr (25% Kr) at different growth conditions without a buffer layer. It can be clearly seen that the leakage current density of the OLEDs was remarkably reduced, e.g., to between 10^{-4} and 10^{-5} mA cm^{-2} at -6 V, similar to the data of the reference sample. In addition, the I-V curves of OLEDs fabricated by directly sputtered Al cathode layers with different thicknesses (50 nm, 75 nm, and 100 nm) in a mixture of Ar and Kr exhibit a low leakage current density. Even without a buffer or protective layer between the Al cathode and the LiF/AIq3 layer against plasma damage, the I-V curve with a very low leakage current density at the reverse and forward bias was obtained. The EL image of an OLED prepared in a mixture of Ar and Kr in the inset of Fig. 4 reveals a uniform contrast without any dark spots, indicating that no plasma damage occurred during the FTS process.

The effects of Ar and Kr mixing during the Al sputtering process on the electrical properties of top-emitting OLEDs can be related to the effective energy dispersion by the added Kr with a large collision cross section. From the kinetics gas theory, the mean free path (\lambda) of sputtered atoms traveling through a gas is

\[ \lambda^{-1} = 8.34 \times 10^{14} \frac{(\sigma_r + \sigma_g)^2}{4} (1 + M_r/M_g)^{1/2}, \]

where \rho is the pressure of the sputtering gas, \sigma_r, \sigma_g are the sputtered and gas atom diameters, and \( M_r, M_g \) are the mass of the sputtered and gas atoms. This equation shows that an increase in gas atom diameter leads to a decrease in the mean-free path of a sputtered atom. Therefore, most of the energy of the sputtered particles, or recoiled particles, was effectively dispersed in a mixture gas of Ar and Kr. Noma et al., investigating Ba ferrite films grown by FTS in a mixture of Xe, Kr, Ar, and O2, reported that the energy of the recoiled Kr atoms was smaller than Ar atoms, due to severe scattering with the Kr gas species. Because Kr (atomic weight: 83.8 g/mol) is heavier than Ar (39.94 g/mol) and Al (26.98 g/mol), the recoiled particles in the Ar and Kr mixture gas were suppressed to a greater extent than that in a pure Ar ambient.

In summary, we successfully achieved direct Al cathode sputtering on organic layers without the need for a protective layer against plasma damage in a mixture of Ar and Kr. The effective energy dispersion of the energetic particles and the more random scattering of sputtering atoms in a mixture of Ar and Kr permitted the preparation of OLEDs with a directly sputtered Al cathode.

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