Structure and Optical Properties of the Ca/Ag Double Layer for Transparent Cathode in TEOLED

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Abstract

Ca/Ag double layer which is fabricated by thermal evaporation exists as the double layer of (Ca+O)/(Ag+Ca). In Ca layer, are crystalline Ca(OH)2 and amorphous Ca and in Ag layer, are crystalline Ag and amorphous Ca. And for the certain thickness of Ag, in the Ca/Ag double layer, the thicker Ca is, the higher transmittance is.

1. Introduction

As a representative of flat panel display(FPD). the liquid crystal display (LCD) is currently the dominant technology due to its light weight, low power consumption and easy operation. But LCD still has drawbacks in view angle, response time and brightness. As a result, the organic light-emitting diode (OLED) which has solutions for the drawbacks of LCD has come into the spotlight as an alternative for LCD. For the OLED to replace the LCD, AMOLED should be realized. AMOLED needs more TFTs compared to LCD due to its driving method and it reduces aperture ratio. As a result, to enhance an aperture ratio, top emission type that has nothing to do with the number of TFTs needs to be applied to AMOLED. For that, the technology on stable reflective anode, transparent cathode and transparent encapsulation should be guaranteed.[1-4]

Basically, for cathode, it is desirable to use metals having a low-work function for the easy electron-injection. These include Al, Mg, Ca, Ag, Mg:Ag, and LiF:Al. However, because metals with a low-work function are always susceptible to atmospheric oxidation, alloys with stable metals having relatively high-work function or low-work function metals with a protective layer are used for cathode. And to be transparent in visible light, to have a thickness of less than optical skin depth and not to destroy the

underlying organic layer, cathode is fabricated by a thermal evaporation method.

In this study, Ca/Ag double layers have been fabricated for the transparent cathode in top emission OLED by thermal evaporation without vacuum breaking to a thickness of less than optical skin depth. Ca is suitable for easy electron-injection due to its low work function (2.9~3.0 eV) and Ag is suitable for the protective layer of reactive Ca due to its high stability and easy deposition. Besides its relatively low resistivity(1.6 $\mu\Omega$ cm) is a help to high electrical conductivity for an electrode. The structure and optical properties of the Ca/Ag double layer are studied.[5]

2. Results

The structure and optical properties are studied. The Ca single layer has an infinite sheet resistance and is transparent. Even though it is too thick to be transparent, it becomes transparent, after all(fig. 1 (a)). And Ca exists as a form of Ca(OH)₂. When the Ag single layer is continuous film on glass, the transmittance of the Ag single layer has the regular pattern which is decreased by increasing a wavelength.

The transmittance of the Ca/Ag double layer has two tendencies(fig.2). Above a critical thickness of Ag layer(that means the Ag layer is a continuous film on glass), the transmittance of the Ca/Ag double layer is reduced as the thickness of Ca layer increases. On the other hand, below a certain thickness of Ag layer(that means the Ag layer is a discontinuous film on glass), the transmittance of the Ca/Ag double layer is enhanced as the thickness of Ca layer increases. But in latter case, from the SEM image, the Ag layer on Ca layer is almost a continuous film even though the Ag layer on glass is a discontinuous film(fig.2). When the Ca/Ag double layer is too thick(especially Ag

layer on Ca layer), after all, the transmittance of the Ca/Ag double layer also becomes enhanced like Ca single layer(fig.1 (b)).

The structure of the Ca/Ag double layer is studied. The existence of Ag and Ca(OH)₂(fig. 3) and the fact that the Ca/Ag double layer is actually the (Ca+O)/(Ag+Ca) double layer are confirmed(fig. 4). An amount of Ca exists uniformly throughout the upper layer and also an amount of oxygen exists uniformly throughout the lower layer.

From the result of XPS, the Ca 2p peak at 346.5 eV is for metallic Ca, CaO, or CaH₂ and there is no way to figure out what it is for exactly. But the O 1s peak at 531.7 eV is for hydroxide and the O 1s peak at 528.5 eV is for metal oxide. As a result, even though there is no reference of Ca 2p peak of Ca(OH)2, it can be known that there are metallic Ca and CaO, and Ca(OH)₂ in lower layer(fig. 5). From the facts that an amount of extra Ca exists throughout the whole layer(fig. 4) and no Ca peak is detected(fig. 3), it is concluded that Ca is intermixed with Ag in amorphous state in upper layer, and Ca exists in amorphous state in lower layer. In other words, the upper layer consists of Ag crystalline state and Ag-Ca intermixing of Ag amorphous state. And the lower layer consists of Ca(OH)₂ crystalline state, Ca amorphous state and CaO amorphous state.

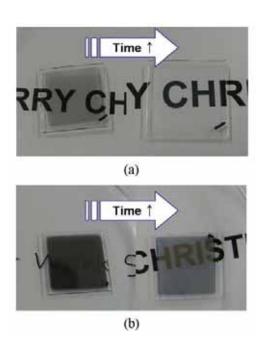


Figure 1 (a) Ca single layer (b) Ca/Ag double layer after time passes

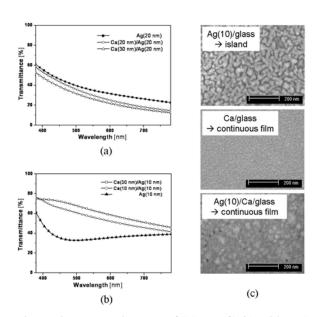


Figure 2 Transmittance of (a) the Ca/Ag(20 nm) double layer and (b) the Ca/Ag(10 nm) double layer, (c) SEM image of Ag, Ca and Ca/Ag layer

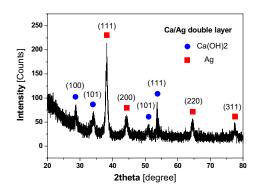


Figure 3 XRD of the Ca/Ag double lay

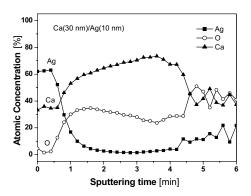


Figure 4 AES of Ca/Ag double layer

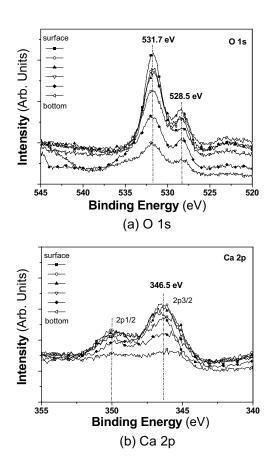


Figure 5 XPS of Ca(20 nm)/Ag(7 nm) double layer (a) O 1s peak (b) Ca 2p peak

This structure is formed as follows: in vacuum, the Ca/Ag double layer is formed. After the sample is exposed to air, H₂O in air is reacted with Ca through Ag layer. And then Ca is changed to Ca(OH)₂ accompanying the volume expansion. At this time, a small amount of Ca is changed to CaO and large amount of Ca is remained untouched. By the volume expansion in this change, the remaining Ca is pushed into the Ag layer(fig.6). At first, from the facts that thick Ca layer becomes transparent after time passes and compared with discontinuous Ag film on glass, Ag on Ca layer is formed as a continuous film, metallic Ca and Ag are deposited in turn and then, Ca is changed to Ca(OH)₂ in air. Secondly, from the fact that as the thickness of Ag layer in Ca/Ag double layer increases, the time for saturation transmittance is increases, the change of Ca is under way through Ag layer. Thirdly, volume expansion by adding oxygen is easily expected

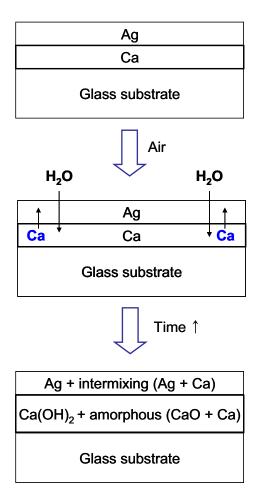


Figure 6 Model of formation of Ca/Ag double layer

Because the composition ratio of Ag and Ca is constant and no oxygen is detected in the upper layer, (fig. 4), the solubility of Ca in Ag is about 35 % and Ca is intermixed with Ag in an amorphous state.

Especially when the Ag film does not fully cover the Ca layer, high transmittance(average over the 70 % in visible light) and reasonably low sheet resistance(8.5 Ω/\Box) are acquired. In this case, O is detected and Ca is much more than Ag in upper layer, compared to other cases in which Ag film fully covers the Ca layer. And according to XPS, Ca(OH)₂ and CaO exists in the Ag layer. Thanks to Ca(OH)₂, CaO and the holes in the Ag layer, large aperture is acquired and this leads to high transparency. Also the Ag film that is not fully covered but continuous leads to good electrical conductance(fig. 7).

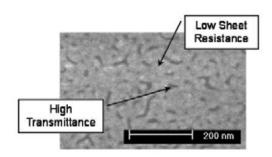


Figure 7 SEM image of Ca/Ag double layer

3. Conclusion

The Ca/Ag double layer has been fabricated for the transparent cathode in TEOLED and the optical properties and structure of that has been studied for the first time. Above a certain thickness of Ag layer, transmittance of the Ca/Ag double layer is reduced as the thickness of Ca layer increases. On the other hand, below a certain thickness of Ag layer, transmittance of the Ca/Ag double layer is enhanced as the thickness of Ca layer increases. Actually the Ca/Ag double layer exists as the (Ca+O)/(Ag+Ca) double layer. The structure of this layer is as follows: (1) the upper layer(Ca+O) consists of a crystalline Ag and a

mixture of Ag and Ca. (2) lower layer(Ag+Ca) consists of crystalline Ca(OH)₂ and amorphous Ca and CaO.

In case that Ag film does not fully cover the Ca layer, Ca(OH)₂ and CaO also exist in the upper layer. This leads to better transmittance same as holes in upper layer and holds low sheet resistance. Still the sheet resistance is low enough for this layer to be applied as the transparent cathode for TEOLED.

4. Acknowledgements

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5. References

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