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Light Emitting Device of Organic-Inorganic Layered Perovskite Prepared by Dual- Source Vapor Deposition

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1. Introduction

The organic-inorganic layered perovskite compounds, with the general formula $(R\text{-}NH_3)_2MX_4$ (R: organic group, M: metal, X: halogen), self-organized quantum well structures where MX_4 semiconductor layers and $R\text{-}NH_3$ dielectric layers are piled up alternately[1-7]. These quantum well structures can stabilize excitons having large binding energy (>300meV) and oscillator strength, which exhibits attractive optical properties: a strong absorption at room temperature and photoluminescense (PL)[1-3], nonlinear optical effect[4], and polariton absorption[5]. These attributes make them potentially attractive as emitter materials in the light emitting devices (LEDs). Previously, the LED of the perovskite using a simple spin-coating as an emissive layer exhibited a strong electroluminescence at liquid nitrogen temperatures[6].

Solution-based techniques can be adopted for their preparation owing to the self-organization nature. For example, a spin-coating from a solution containing an organic ammonium compound and an inorganic salt is the most frequently used process. However, the solution-based techniques have significant disadvantages when we try to apply them for optical or electrical devices. It is quite difficult to control the film thickness and structure precisely. It is, furthermore, almost impossible to deposit them onto another layers of organic semiconductor materials. Therefore, we aim at developing vapor phase deposition techniques, such as vacuum deposition[7] as a device fabrication process for the organic-inorganic layered perovskite to solve the above-mentioned problems.

In this study, we investigated the organic-inorganic light emitting devices (OILEDs) which have the emissive layers of $(C_6H_5C_2H_4NH_3)_2PbI_4$ (PhE-PbI_4) prepared by dual-source vapor deposition.

2. Experimentals

Fig.1 shows the structures of the fabricated OILEDs. The phthalocyanine copper (CuPc) layer, deposited by vacuum vapor deposition, or the octadecyltrichlorosilane (OTS) monolayer, prepared by soaking a substrate in the OTS/ toluene solution (0.1 mol%) for two hours at room temperature, was formed on an indium-tin-oxide (ITO) as a buffer layer. The PhE-PbI_4 was deposited by dual-source vapor deposition of lead iodide PbI_2 and 2-phenylethylammonium iodide $C_6H_5C_2H_4NH_3I$ (PhEI) to be an emmisive and hole transport layer followed by annealing at 100°C for 20min under nitrogen atmosphere. After annealing, 2,9-dimethyl-4,7-diphenyl-1,10- phenanthroline (BCP), 2,4-pentanedionato lithium (Liacac), and Al were deposited successively on the PhE-PbI_4 films as an electron transport layer, an electron injection layer, and a cathode, respectively. All materials were deposited by vacuum vapor deposition at the background pressure of about 10^{-4}Pa. The deposition rate and the deposition amount and the stoichiometric ratio (PbI_2:PhEI=1:2)of the PhE-PbI_4 films were monitored with a quartz oscillator balance. All OILED characteristics were measured at liquid nitrogen temperatures.

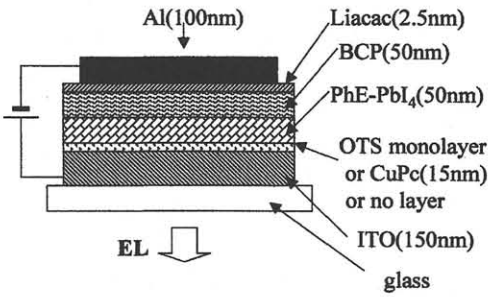


Fig.1 OILED structures

3.Results and Discussion

Fig.2 shows the temperature dependences (300K-60K) of the integrated PL intensities in the PhE-PbI_4 films. The integrated PL intensity was normalized by the absorbed photon. Accordingly, it indicates the relative PL quantum efficiency. The integrated PL intensity of PhE-PbI_4 on the ITO substrate treated with CuPc was doubled compared with that on a non-treated ITO. The OTS treatment also enhanced it in five times. This photoluminescence enhancement owing to the hydrophobic treatment indicates that an optically high-quality film[8], i.e. with stronger exciton absorption and photoluminescence, can be formed on a hydrophobic surface than on a hydrophilic one probably because the mass-ratio of both components was improved on the substrate

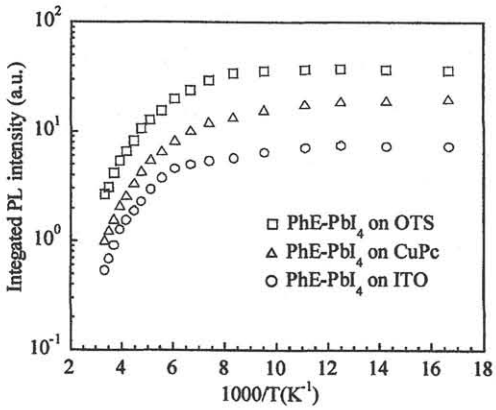
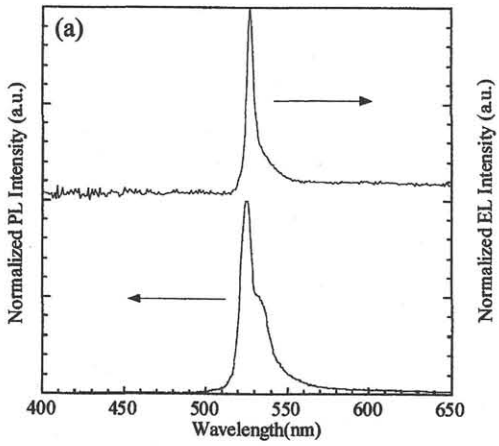


Fig.2 The temperature dependences (300K-60K) of the integrated PL intensities in the PhE-PbI4 films



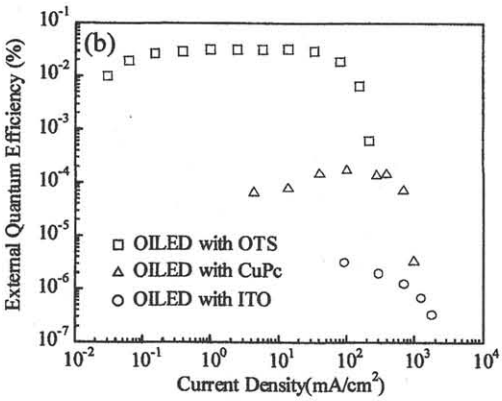


Fig.3 (a) The representative PL spectrum of the PhE-PbI4 films at liquid nitrogen temperature, and the representative EL spectrum of the OILEDs at liquid nitrogen temperatures.
(b) The external quantum efficiency-current density characteristics f the OILEDs at liquid nitrogen temperatures.

with a lower surface energy or because the molecular orientation of the firstly absorbed material was changed to a more favorable way.

Every OILED fabricated on the ITO substrate non-treated or treated with the hydrophobic reagent, showed EL in driven at liquid nitrogen temperatures. A representative EL spectrum is shown in Fig.3(a.). The sharp and greenish EL spectra corresponding to the PL spectra of the PhE-PbI$_4$ films at same temperatures were obtained for all OILEDs. Fig.3(b) shows the external quantum efficiency-current density characteristics for the OILEDs performed at liquid nitrogen temperature. The OILED with CuPc exhibit the highest external quantum efficiency, though the integrated PL intensity of PhE-PbI$_4$ on CuPc was lower than that on OTS. Since CuPc can act as a material for an efficient hole injection layer of EL devices, holes are injected into the PhE-PbI$_4$ emissive layer more easily, resulting a well-balanced carrier injection and an efficient carrier recombination. On the other hand, the OTS layer acts as an insulator, resulting lower EL efficiency.

4. Conclusion

In this paper, we demonstrated the organic-inorganic light emitting devices (OILEDs) which have the emissive layers of PhE-PbI$_4$ prepared by dual- source vacuum deposition, and the electroluminescence enhancements, from the PhE-PbI4 emissive layers, have been observed by the effect of hydrophobic treatment. It has been found that light-emitting devices with a high efficiency can be fabricated with the vapor deposition technique.

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