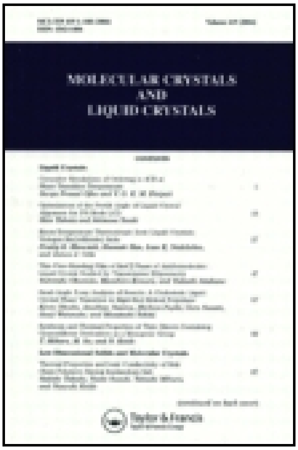

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Growth and Electroluminescence of CaF_2:Mn Thin Films

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We have prepared the CaF_2:Mn thin films on several buffer layer-coated glass substrates by electron beam evaporation method and investigated their structural and electroluminescent characteristics. The experimental results show that the diffraction peaks in the X-ray patterns of CaF_2:Mn thin films correspond to the cubic fluorite phase. In addition, the crystallinity and orientation plane of the films strongly depend on kinds of buffer layer. The CaF_2:Mn thin film electroluminescent devices show the blue emission of the 495 nm peak, originating from the $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}(^6S)$ dipole-dipole transition of Mn^{2+} ions in the O_h crystal field.

Keywords: buffer layer; CaF_2:Mn thin film; crystal structure; thin film electroluminescent device; thin film growth

INTRODUCTION

For the applications of electrooptical devices, interest in CaF_2 thin films doped with impurities such as rare-earth and transition metal has been growing due to the well-known good optical characteristics of the CaF_2 host [1–3]. Up to now, doped CaF_2 thin films have been mainly demonstrated an epitaxial or non-epitaxial growth on semiconductor surfaces [4]. It is well known that the structural properties of thin films are known to be easily affected by not only the deposition method but also kinds of substrates. Nevertheless, to our best knowledge, there have been few reports on the structural properties of CaF_2 thin films grown on buffer layer-coated glass substrate. Thus, finding

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an appropriate buffer layer for the growth of CaF_2 thin films on glass substrate is a major object in this study.

On the other hands, until quite recently, the lack of an efficient blue phosphor precluded inorganic alternating-current thin film electroluminescent (TFEL) device from commercial development of a viable full-color flat panel display. Although a really considerable amount of intensive investigation on the blue-emitting materials, the practical application of TFEL device has not been realized so far. The development of the efficient blue-emitting materials, therefore, should be performed in order to realize the practical application of TFEL device [5].

CaF_2:Mn phosphor is a well-known thermoluminescent materials. In CaF_2:Mn^{2+}, though Mn^{2+} occupies a cubic site with high coordination number, crystal field is not so large because the anion valency of F^- is smaller than that of O^{2-}. In addition, a ratio of Racah parameter is small because of the smaller nephelauxetic effect. Consequently, this material yield the shortest luminescence wavelength observed among Mn^{2+}-doped phosphors [6].

In this study, we have prepared the CaF_2:Mn thin film on different buffer layers and investigated their structural properties. Also, the application possibility of CaF_2:Mn thin film to as the blue phosphor in TFEL devices is discussed.

EXPERIMENTAL

First of all, CaF_2:Mn thin films were deposited on glass substrate (corning #7059) by electron-beam evaporation method with varying substrate temperatures. The evaporation sources of CaF_2:Mn are prepared by a sintering at 800°C for 6 hours in Ar atmosphere. The concentration of MnF_2 is fixed at 1 mol%. The thickness of CaF_2:Mn thin films were fixed at 595 nm. In the experiments, thin films of Al_2O_3, Y_2O_3, and ZnS were used as buffer layer in order to investigate the growth of CaF_2:Mn thin films. All buffer layers were deposited on glass substrate coated with Sn-doped In_2O_3 (ITO) by electron-beam evaporation. The depositions of CaF_2:Mn thin films on several buffer layers were performed at substrate temperature of 300°C by same method.

X-ray diffraction (XRD, Phillips PW3710) studies, using Cu-K_α radiation, were performed to examine the film crystallinity such as the film orientation and grain size. Investigation of electroluminescent characteristics of CaF_2:Mn thin film is carried out in the TFEL device, as in Figure 1. The devices with a structure of Al/Y_2O_3/ZnS/CaF_2:Mn/ZnS/Y_2O_3/ITO/Glass were fabricated by electron beam evaporation except that Al electrode was prepared by thermal

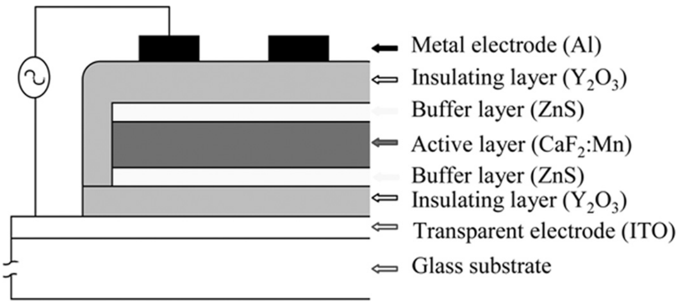

FIGURE 1 The structure of CaF_2:Mn thin film electroluminescent device.

evaporation method. The electroluminescent characteristics of CaF_2:Mn TFEL devices driven by a sinusoidal-wave voltage at 1 kHz were measured using a conventional spectrophotometer.

RESULTS AND DISCUSSION

The XRD patterns of CaF_2:Mn thin films grown on bare glass substrate with varying substrate temperatures are shown in Figure 2.

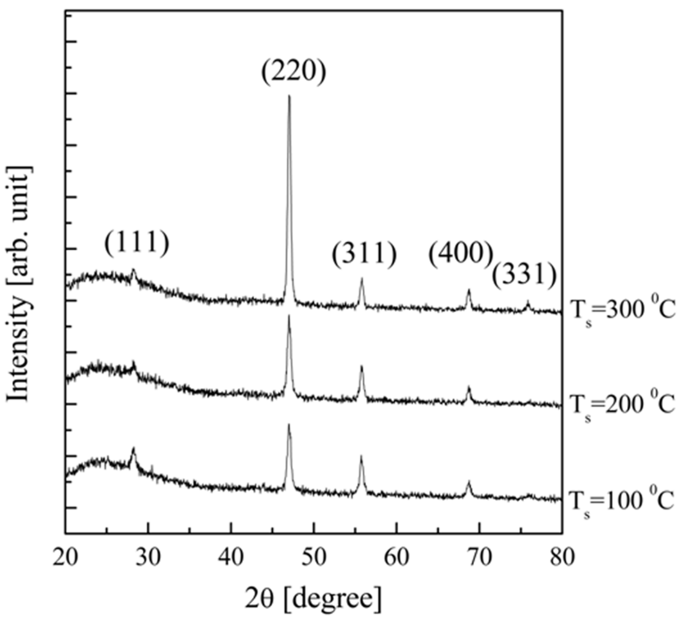

FIGURE 2 X-ray diffraction patterns of CaF_2:Mn thin films grown on glass substrate by varying substrate temperature.

The XRD patterns show that the CaF_2:Mn thin films exhibit cubic fluorite phase with face-centered lattices. As shown in Figure 2, with increase of substrate temperatures, the (220) peak intensity increases, while (111) and (311) peak intensities decrease slightly. Depending of the crystallinity of CaF_2:Mn thin films on substrate temperature may be due to a change in the activation energy of components, which is known to be dependent on the substrate temperatures [7].

Figure 3 shows the XRD patterns of CaF_2:Mn thin films grown on different buffer layers at 300°C. For reference, the XRD pattern of

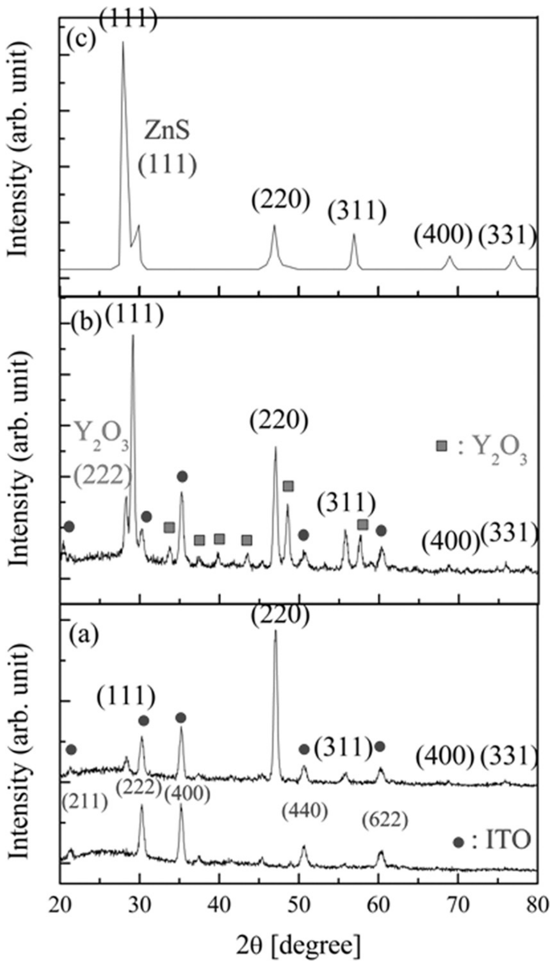

FIGURE 3 X-ray diffraction patterns of CaF_2:Mn thin films grown on different buffer layers; (a) Al_2O_3, (b) Y_2O_3, and (c) ZnS, respectively.

ITO-coated glass is also indicated. The orientation of CaF_2:Mn thin films on Al_2O_3 buffer layer is (220) plane whereas the films on Y_2O_3 and ZnS layers has (111) orientation plane. It is found that the XRD pattern of Al_2O_3 buffer layer does not contain any peaks attributable to crystal, showing an amorphous state. Hence, the structural property of CaF_2:Mn thin film grown on Al_2O_3 buffer layer is similar to that on glass substrate. Contrary to CaF_2:Mn/Al_2O_3, the orientation of CaF_2:Mn on Y_2O_3 and ZnS layer represents the (111) plane. An Y_2O_3 (222) peak can be observed at about $2\Theta = 29°$, and a peak of ZnS (111) at $2\Theta = 29.8°$, which are close to the peak of CaF_2 (111) plane. This may be attributed that the surface energy of CaF_2 (111) plane is quite stable, owing to having the strong ionic bonds. Compared Y_2O_3 with ZnS buffer, XRD diffraction peak of CaF_2:Mn films on ZnS is much stronger than that on Y_2O_3, so the grain size of CaF_2:Mn films on ZnS is larger than that on Y_2O_3, as shown in Figure 3. These results imply that the different buffer layers for the preparation of CaF_2:Mn thin films can be made with varying structural properties. It can be applied to explain the difference of crystalline structures between these thin films deposited on different buffer layers by the theory of crystal growth and migratory diffusion [8]. When thin films are deposited on the different substrates, it is strongly dependent on the migratory diffusion ability and the nucleation work for critical crystal nucleus on the substrates. The Gibbs free energy for transition into crystallite state not only depends on the properties of thin film material itself but also is determined by the properties of the substrate surface. Hence, the diffusion and nucleation of CaF_2:Mn on the surface of ZnS may be easier than on Y_2O_3 at the initial stages of the film deposition.

Figure 4 represent the EL spectrum of CaF_2:Mn TFEL device. The emission displays a characteristic maximum at 495 nm due to the relaxation of an electron from one of the internal ^4G excited states of Mn^{2+} to the ground-state ^6S level. By virtue of the doping of MnF_2 in CaF_2 matrix, Mn^{2+} enters the CaF_2 lattice substitutionally for Ca^{2+}. Its point symmetry is O_h and it possesses eight-fold coordination with the surrounding F^- ions. From analysis of the excitation spectra from CaF_2:Mn [9], it can assign the emission to a transition from the first excited $^4T_{1g}(^4G)$ level to the ground-state $^6A_{1g}(^6S)$ level; the $^4T_{1g}$ and $^6A_{1g}$ terms arise from the cubic crystal field splitting of the original ^4G and ^6S states for the $3d^5$ electrons of the Mn^{2+} ion, associating with a rather low crystal field (10Dq).

Figure 5 shows the effect of ZnS buffer layer thickness on the luminance of CaF_2:Mn TFEL device. In order to investigate the effect of the grain size on the luminance, the grain size of CaF_2:Mn films is plotted

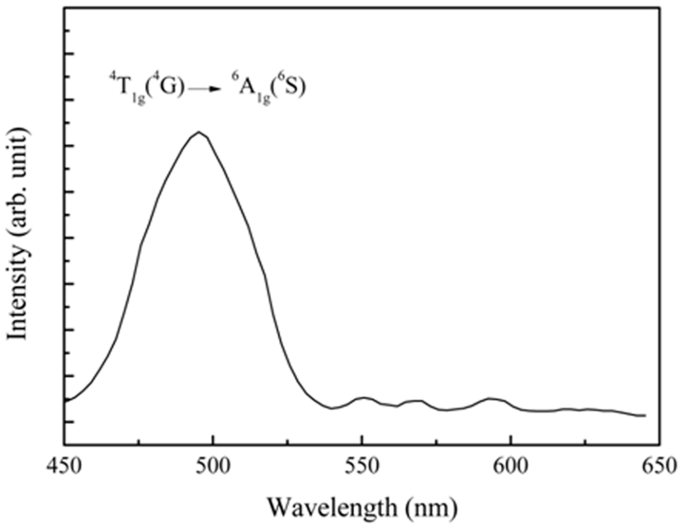

FIGURE 4 Electroluminescent spectrum of CaF_2:Mn thin film electroluminescent device.

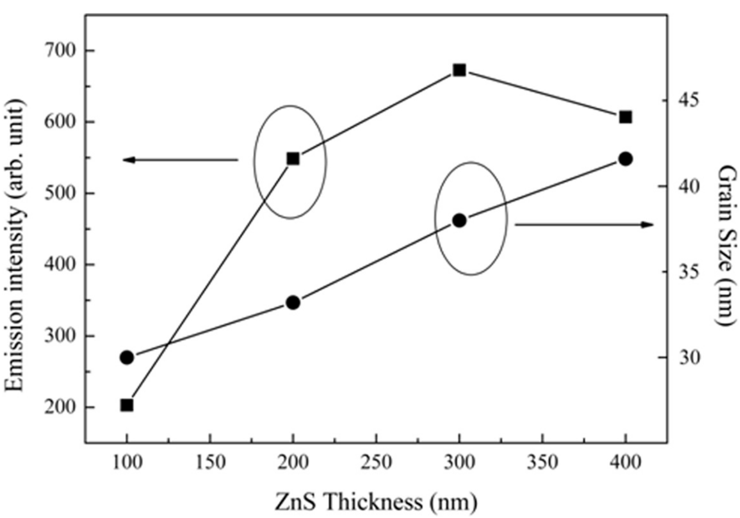

FIGURE 5 Effect of ZnS buffer layer thickness on the luminance of CaF_2:Mn thin film electroluminescent device.

on the right axis. It can be seen that the EL emission intensity and grain size of CaF_2:Mn increase when the thickness of ZnS buffer layer is increased up to 300 nm. In TFEL devices, it is essential to have enough hot electrons to excite the luminescent center Mn^{2+} ion for bright EL. A larger grain size is necessary for the electric field to accelerate the electrons to high enough energy before they are scattered at the grain boundaries [10]. However, when the thickness of ZnS buffer layer is over 400 nm, the luminance slightly decreases although the grain size increases. This may arise from the decrease of effective electric field due to the increasing device thickness.

CONCLUSIONS

In summary, the CaF_2:Mn thin films were prepared by the electron beam evaporation method and their structural and EL characteristics were investigated. The crystallinity and orientation plane of CaF_2:Mn thin films strongly depend on kinds of buffer layer. The CaF_2:Mn TFEL devices show the blue emission of the 495 nm peak, originating from the $^4T_{1g}$ (^4G) $\rightarrow$ $^6A_{1g}$ (^6S) dipole-dipole transition of Mn^{2+} ions in the O_h crystal field. This fact suggests that the CaF_2:Mn luminescent films have the sufficient possibility as the blue phosphor in TFEL device.

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