青色発光 CaS:Cu,F 薄膜の発光特性

中西洋一郎 1,2, 川角明人 1, 青木 徹 2, 立岡浩一 2,3, 桑原 弘 2,3, 畑中義式 1,2

静岡大学

1電子工学研究所, 2電子科学研究所, 〒432-8011 静岡県浜松市北3-5-1
2工学部 〒432-8561 静岡県浜松市北3-5-1
TEL & FAX : 053-478-1346
E-mail : nakanishi@rie.shizuoka.ac.jp

あらまし 電子ビーム蒸着法を用いて CaS:Cu,F 薄膜を作製し、アニールを行った。750℃以上のアニールによって[110]配向した膜が得られ、その結晶性はアニール温度の上昇とともに向上した。アニールにより薄膜は435から450 nmにかけての青色の発光と長波長側のブロードな発光を示し、750℃以上のアニールにより、435 nmにピークを持つ青色の発光が支配的となった。また、時間分解発光スペクトラル測定の結果から CaS:Cu,F 薄膜の発光機構も蛍光体と同様D-Aペア発光ではなく、Cu+イオン内の電子遷移によることが示された。

キーワード CaS:Cu,F, 薄膜, 電子ビーム蒸着法, 青色発光, E L, P L

Luminescent Properties of Blue-Emitting CaS:Cu,F Thin Films

Y.Nakanishi 1,2, A.Kawasumi 1, T.Aoki 2, H.Tatsuoka 2,3, H.Kuwabara 2,3 and Y.Hatanaka 1,2

1Research Institute of Electronics, Shizuoka University
2Graduate School of Electronic Science and Technology, Shizuoka University
3Faculty of Engineering, Shizuoka University
3-5-1 Johoku, Hamamatsu 432-8011, Japan
TEL & FAX : +81-53-478-1346
E-mail : nakanishi@rie.shizuoka.ac.jp

Abstract Structural and luminescent properties of CaS:Cu,F thin films prepared by the electron beam evaporation have been investigated. The film annealed at higher than 750℃ showed [110] orientation and the crystallinity of the film was improved with increasing annealing temperature. The annealed films showed spectra with peaks at 435 and 450 nm and broad emission at longer wavelength at room temperature, and the 435 nm emission became dominant by the annealing at temperatures higher than 750℃. It was suggested from the measurement of the time-resolved emission spectra that the blue luminescence of not only the phosphor but also the film is not due to D-A pair recombination but due to the intraionic transition in the Cu ion.

Key words CaS:Cu,F, thin film, electron beam evaporation technique, blue emission, EL, PL
1. Introduction

Recently, Cu-doped alkaline earth sulfide thin films such as CaS:Cu and SrS:Cu are attracting strong attention for full color thin-film electroluminescent (TFEL) displays, because they show strong blue emission with better chromaticity than SrS:Ce [1]. However, the luminescent spectra of these phosphors change depending on Cu and coactivator concentration, and kind of coactivator which are added together into a bulk material. Therefore, it is thought that the mechanism of the luminescence from Cu in CaS or SrS is different from ZnS:Cu,X (X:coactivator), but due to the transition in Cu$^{+}$ ion [2] or between the conduction band and Cu acceptor level [3]. Moreover, the high luminance of blue EL of SrS:Cu,X TFEL is obtained by annealing after the deposition [1]. Therefore, in this study, the structural and luminescent properties of the CaS:Cu,F thin films with respect to annealing temperature and atmospheric gas were investigated, aiming at the preparation of blue-emitting CaS:Cu,F TFEL device showing high luminance.

2. Experimental

The CaS:Cu,F phosphor, which was used as a source material for the deposition, was synthesized by firing a mixture of luminescent grade CaS, CuS and CaF$_2$ powders at 900°C for 3 h in active carbon. The contents of Cu and F were 0.5 and 10 at%, respectively.

The CaS:Cu,F thin films were deposited on a quartz glass substrate at a substrate temperature of 500°C by the electron beam evaporation. After the deposition, the films were annealed at several temperatures higher than 600°C for 30 min in Ar or H$_2$S flow.

The structural and optical properties were characterized by X-ray diffraction (XRD) and spectral transmittance measurements, respectively. Luminescent properties were characterized by PL measurements under excitation with a peak at 325 nm of He-Cd laser. The time-resolved PL spectra was also measured for the analysis of the luminescent mechanism.

3. Results and discussion

3.1 Structural and luminescent properties

Figure 1 shows XRD curves of CaS:Cu,F films annealed at several temperatures in Ar. Two diffraction peaks from (200) and (220) planes are obtained at the annealing temperature lower than 750°C. It can be seen from this result that [110]-oriented CaS:Cu,F film can be obtained by the annealing at higher than 750°C. The same result was obtained in the case of the annealing in H$_2$S.

Figure 2 shows PL spectrum of CaS:Cu,F phosphor used as the evaporation source in this experiment. A blue emission peaking at about 430 nm is based on the Cu luminescence center.
incorporated into CaS during the firing.

Figure 3 shows normalized PL spectra of CaS:Cu,F films annealed at several temperatures in Ar. It is seen from this figure that the spectra consist of blue emission and broad band ranging from green to red. The peak position of the blue emission shifts from about 460 nm at 600°C to about 435 nm at 800°C and the intensity of the blue emission increases compared with the broad emission with increasing the annealing temperature. The origin of the blue emission is based on the Cu center, whereas the broad band is thought to be due to the defects such as sulfur vacancy. Nearly the same result was obtained for the samples annealed in H₂S.

![Fig.3 PL spectra of the CaS:Cu,F films annealed at several temperatures in Ar.](image)

Figure 4 shows the blue emission intensity of the CaS:Cu,F films as a function of the annealing temperature in Ar and H₂S. The intensity decreases at the annealing temperature higher than 750°C in Ar and 700°C in H₂S.

![Fig.4 Blue emission intensity of the CaS:Cu,F films as a function of annealing temperature.](image)

Figure 5 shows the dependence of spectral transmittance of the films annealed in Ar on annealing temperature. Strong absorption at around 250 nm is due to absorption edge of CaS. The increase of the transmittance at longer wavelength than the absorption edge suggests the improvement of the crystallinity of the CaS:Cu,F film when the annealing temperature is elevated up to 750°C. On the other hand, the decrease of the amplitude of the oscillation due to interference effects in the spectra at the annealing higher than 700°C means that the flatness of the film surface decreases. The cause of the decrease of the flatness might be due to the growth of crystallite in the film. The significant decrease of the transmittance at 800°C-annealing suggests that the film consists of large crystallities grown during the annealing, and as a result incident light is scattered. Moreover, the decrease of the blue emission intensity of 800°C annealed film as shown in Fig.4 also seems to be due to the scattering of excitation light of 325 nm at the film surface.

3.2 Emission mechanism of CaS:Cu,F

It has been reported [2,3] that the emission mechanism in CaS:Cu and SrS:Cu is different from
The Institute of Image Information and Television Engineers
NII-Electronic Library Service

ZnS:Cu,X. The time-resolved PL spectra of the CaS:Cu,F phosphor powder and thin film were measured in order to confirm the emission mechanism in this study. The measurement was carried out under excitation at 325 nm and at 20 K.

Figure 6 shows the time-resolved PL spectra of the CaS:Cu,F phosphor used as the evaporation source. Emission peak at about 415 nm is shifting to shorter wavelength compared with the samples measured at room temperature. Moreover, it can be seen that the peak position does not shift at the decay time up to 250 μs. This result suggests that the emission is not originated from the recombination of an electron at donor state due to F and a hole at acceptor state due to Cu⁺, but due to the inner shell transition of 3Eg → 1A₁s in Cu⁺ ion under O₆ symmetry [2].

Figure 7 shows the time-resolved PL spectra of the CaS:Cu,F film prepared using the phosphor shown in Fig.6. The film was annealed at 800°C in H₂S. The spectra and their dependence on decay time are almost the same as the case of the phosphor. Therefore, it is concluded that the luminescence mechanism of CaS:Cu,F film prepared in this experiment is the same as the powder phosphor.

4. Summary

In this experiment, the CaS:Cu,F thin films were deposited on quartz glass substrates at a substrate temperature of 500°C by the electron beam evaporation, and then annealed in Ar or H₂S atmosphere.

Those films showed [110] orientation at annealing temperatures higher than 750°C, and their crystallinity was improved with increasing annealing temperature.

The films annealed at temperatures higher than 750°C showed blue emission with a peak at about 435 nm in both annealing atmosphere.

It was concluded from the measurement of the time-resolved PL spectra that the emission mechanism in the CaS:Cu,F thin film is also based on the inner shell transition of electrons in Cu⁺ ion in the same way as the CaS:Cu,F phosphor.

References