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Luminescence Properties of Rare Earth-Doped Thiosilicate Phosphors on Silicon Substrate

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1. Introduction

Crystalline silicon (Si) is a key material in electronics and optelectronics devices. However, Si has no light emission at room temperature because of its indirect band gap. To develop silicon photonics and future optoelectoronics devices, the realization of efficient silicon-based light sources at room temperature remains an important challenge.

Phosphor materials including Si and rare earth ions have been studied for various light sources and displays. Up to now, silicate, silicon nitride, silicon oxynitride and thiosilicate materials were reported [1-5]. Especially, thiosilicate phosphors have advantages that relatively low temperature is necessary for fabrication and various luminescence wavelengths from blue to infrared region are reported [4-9]. From this viewpoint, the application of thiosilicate phosphors for light emitter on Si substrate should be examined.

In this paper, photoluminescence (PL) properties of rare earth-doped thiosilicate phosphors are reported. The materials are fabricated in powder, and on silicon or silicon-on-insulator (SOI) substrates. Efficient visible and infrared luminescence from thiosilicate phosphor on Si substrates is observed. In addition, electroluminescence (EL) from $BaSi_2S_5:Eu^{2+}$ on SOI substrates is realized. The result indicates that thiosilicate phosphor materials can be a light source on silicon-based substrates.

2. Thiosilicate phosphor powders

For the fabrication of polycrystalline thiosilicate powders, the solid-state reaction in a vacuum-sealed silica-glass ampoule was used. As starting materials, alkaline-earth sulfides (BaS, CaS), rare-earth sulfides (EuS, Er_2S_3), Si and S were used and mixed.

Table 1 shows PL properties of thiosilicate phosphors. Luminescence bands in table 1 originate from the $4f^6 5d$-$4f^7$ transition of Eu^{2+} or the $4f^{11}$-$4f^{11}$ transitions of Er^{3+}. Eu_2SiS_4 has the low quantum efficiency because of concentration quenching. $Ba_2SiS_4:Eu^{2+}$, $BaSi_2S_5:Eu^{2+}$ and $Ca_2SiS_4:Eu^{2+}$ have high quantum efficiency because the distance among Eu^{2+} ions is large. $Eu_2SiS_4:Er^{3+}$ has efficient luminescence of Er^{3+}. The reason is intense indirect excitation coming from energy transfer from Eu^{2+} to Er^{3+}.

Table 1 : PL properties of thiosilicate phosphors. PL efficiency was measured using an integrating sphere. Excitation wavelength was 325 nm.

Materials	PL peak (nm)	PL efficiency (%)
$Ba_2SiS_4:Eu^{2+}$	495	42
$BaSi_2S_5:Eu^{2+}$	510	52
Eu_2SiS_4	570	1
$Ca_2SiS_4:Eu^{2+}$	560, 650	30
$Eu_2SiS_4:Er^{3+}$	660, 980, 1540	28 (660 nm)

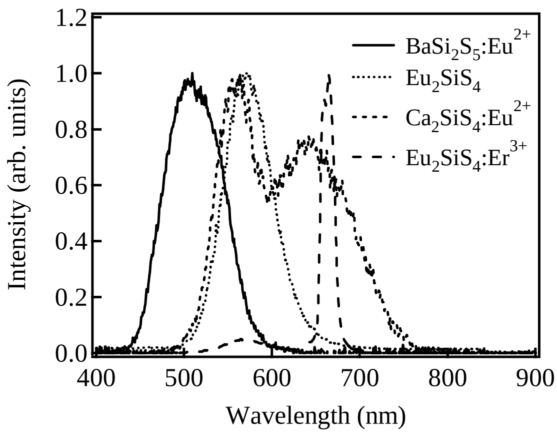

Figure 1 : PL spectra of thiosilicate phosphors on Si substrate. Excitation wavelength was 325 nm.

3. Thiosilicate phosphor on Si substrates

For the fabrication of thiosilicate phosphors on Si substrate, thermal evaporation and annealing were used. After sulfides (EuS, BaS, CaS, Er_2S_3) were deposited on Si substrate, the substrate and S powder were sealed in a silica-glass ampoule in a vacuum of 10^{-2} Pa. The ampoule was heated to 650-800 °C. From the measurement of x-ray diffraction, it was found that Eu_2SiS_4, $Eu_2SiS_4:Er^{3+}$, $Ca_2SiS_4:Eu^{2+}$ or $BaSi_2S_5:Eu^{2+}$ layer was fabricated on Si substrates. The different compositions ($BaSi_2S_5$, Ba_2SiS_4) are possible for barium thiosilicate. Because Si was supplied sufficiently from Si substrate, $BaSi_2S_5$ structure was preferentially synthesized on Si substrates.

Figure 1 shows PL spectra of thiosilicate phosphors on Si substrate. For each sample, similar spectrum to the powder sample is obtained.

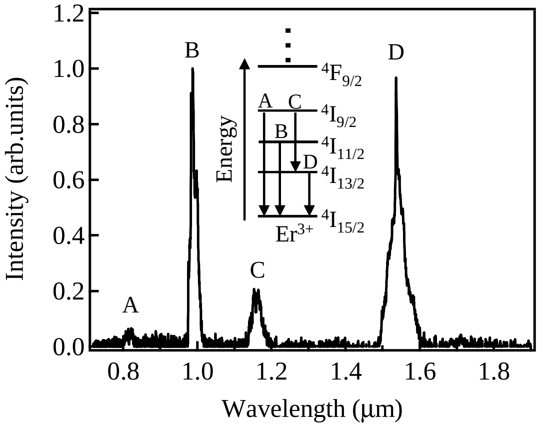

Figure 2 : Infrared PL spectrum of Eu_2SiS_4:Er^{3+}. The excitation source was an Ar ion laser (488 nm, 15mW). In the inset, the energy diagram of Er^{3+} is shown.

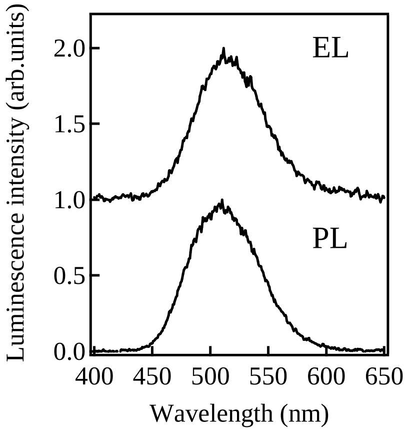

Figure 3 : EL and PL spectra of $BaSi_2S_5$:Eu^{2+} on SOI substrates. The EL spectrum was obtained under the AC voltage of 200 V with the frequency of 1 kHz.

Figure 2 shows infrared PL spectrum of Eu_2SiS_4:Er^{3+}. In the inset of figure 2, the $4f^{11}$ energy levels of Er^{3+} are shown. Each peak index in the PL spectrum is corresponding to the transition in the inset. The intense PL at 1.54 μm of Er^{3+} is observed on Si substrate. Eu_2SiS_4 is useful as a host material for the other luminescence centers.

4. EL of $BaSi_2S_5$:Eu^{2+} on SOI substrates

EL devices were made using $BaSi_2S_5$ on Si. SOI substrates were used to maintain insulation of the devices. On the top of the $BaSi_2S_5$:Eu^{2+} layer, a glass plate having an indium-tin-oxide layer was attached using a transpament polymer (cyanoresin, Shin-Etsu Chemical Co.).

Figure 3 shows EL and PL spectra of $BaSi_2S_5$:Eu^{2+} on SOI substrate. The same spectra are obtained, and the origin of EL is clearly Eu^{2+} in $BaSi_2S_5$. The excitation might be done by hot electrons, as is proposed in inorganic EL devices [10].

5. Conclusions

Rare earth-doped thiosilicate phosphors were fabricated in powder and on Si or SOI substrates. Powder phosphors had various PL bands due to electronic transitions of Eu^{2+} or Er^{3+} ions. Except for Eu_2SiS_4, high quantum efficiencies were obtained decause of the decrease of concentration quenching. For Eu_2SiS_4:Er^{3+}, efficient energy transfer from Eu^{2+} to Er^{3+} was observed. The result indicates that Eu_2SiS_4 is useful as a host material for Er^{3+}. Thiosilicate phosphors were fabricated directly on Si substrates. Intense luminescence from cyan-blue to infrared region was obtained from thiosilicate phosphors on Si substrates. EL device structures were produced by the use of $BaSi_2S_5$:Eu^{2+} on SOI substrates and green luminescence was observed. Phosphor-used devices were realized on silicon-based substrates. These results are believed to be important for applications of silicon photonics and future optoelectronics.

Acknowlegdements

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