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We report an electroluminescent device fabricated by a europium silicate layer on a silicon substrate. The device exhibits uniform-intense white color electroluminescence with an external quantum efficiency about 0.1% at room temperature, a low operating threshold voltage (about 6 V) and a fast response to the modulation signal at the frequency of 1 MHz. © *1999 American Institute of Physics.* [S0003-6951(99)00621-X]

III-V semiconductors and organic materials are extensively studied for electroluminescent (EL) devices. However, the device made from these materials lacks of long-term stability and/or large area uniform emission. Furthermore, the large-scale integrated circuit fabrication processes for these devices are not so highly implemented as those for Si devices. Therefore, the EL device which can offer large-area uniform emission, possibly to a Si substrate, is demanded for attaining various applications such as the flat panel displays and Si based optoelectronic integrated circuits (OEIC).

Europium compounds are known as an intense and stable luminescent materials in the visible region. They have been applied to many practical devices, such as the fluorescent lamps, the cathode-ray tube and the x-ray recording devices. These studies suggested that the europium compounds seem to be a candidate of luminescent materials for the flat panel displays and Si based OEIC. To achieve the above purposes, there are some works of forming a luminescent layer on Si,[1,2] such as Eu doped CaF_2/Si system. However, the fabrication methods in these works require costly epitaxial and doping techniques. On the other hand, though the photoluminescence from europium silicates has been studied for decades,[3,4] until now, no EL investigation of europium silicates to the Si substrate has been reported to our knowledge.

In this letter, we report an EL device, which has a thin europium silicate layer deposited on a Si substrate. The device shows uniform-intense white-color EL, with the external quantum efficiency of the order of 0.1%, a low operating threshold voltage less than 6 V, and a high-speed modulation at the frequency of 1 MHz. The obtained large-area uniform EL appears promising for the fabrication of flat panel displays and OEIC on the Si substrate.

The sputtering targets were a 99.99% Si disk (10 cm in diameter) and 99.9% $EuSi_2$ powder. The substrate was p-Si (100), of which surface was cleaned by dilute HF ethanol solution to remove the oxide layer. The sputtering was performed in the atmosphere of 0.5 Pa Ar gas (99.999%). The rf power was 100 W and the substrate temperature was 300 °C. The deposited film thickness was about 2 μm. After sputtering, the films were annealed in vacuum at the temperature of 1000 °C for 15 min. The films were characterized by the x-ray photoelectron spectroscopy, x-ray diffraction, and transmission electron microscopy. The transmission electron microscopy observations showed that the film was uniformly formed from the nanocrystals, with the average size of about 9 nm in diameter. The x-ray photoelectron spectroscopy and x-ray diffraction results demonstrated that $EuSiO_3$ and Eu_2SiO_4 were formed in the samples with the relative concentrations of Eu:0.24, Si:0.15, and O:0.61 (the film is denoted as EuSiO for simplification). The reason why oxygen atoms are contained in the samples is not clear. However, it is considered that the oxygen atoms adsorbed at the nanocrystal surfaces after sputtering and that they reacted with the surface atoms during the annealing process. An indium–tin–oxide (ITO) layer about 100 nm thick was deposited on the luminescent layer by the rf sputtering method.

A schematic of the ITO/EuSiO/Si EL device structure is shown in Fig. 1(a). The luminescence spectra were measured by a monochromator equipped with a liquid nitrogen cooled charge coupled device (CCD) system, and the external quantum efficiency was measured by a photodiode detector. Figure 1(b) shows a photograph of the white EL from the EL device at the driving voltage of 30 V. The luminence is about 130 Cd/m^2 at 30 V bias voltage. The external quantum efficiency (η_{ext}, photons per electron) was evaluated to be about 0.1% by

$$\eta_{\text{ext}}=\frac{L/h\nu}{I/q}, \tag{1}$$

where the light power output L is 12 μW when the injection current I is 10 mA, h, ν, and q denote the Planck constant, the frequency of the emitted light, and the elemental electric charge, respectively.

Figure 2 shows the EL spectrum obtained at 30 V bias voltage. The EL spectrum shows a broad spectral structure ranging from 400 to 800 nm, which covers almost whole

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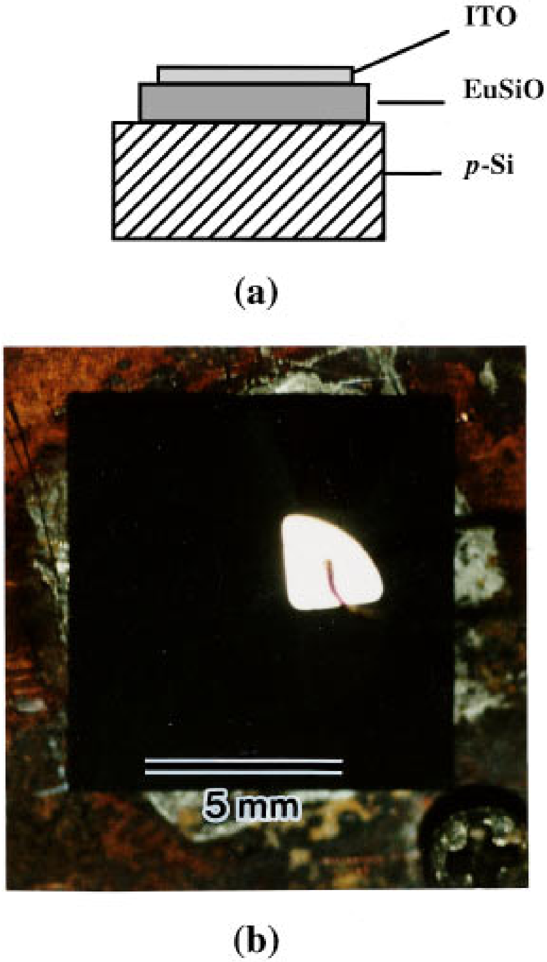

FIG. 1. (a) A scheme of the europium silicate EL device structure. The luminescent europium silicate layer and the ITO transparent electric cathode layer are about 2 μm thick and 100 nm thick, respectively. (b) A photograph of the uniform white light emission from the device. The applied bias voltage is 30 V, and the luminescent area is 4.9 mm^2. The wire in the luminescent zone is the electrode attached to the ITO film.

visible wavelength range. This broad spectrum can be assigned to the $(4f)^6(5d)-(4f)^7$ transition of the divalent europium ions. A series of relatively narrow spectral structures denoted by the arrows are also observed on the broad spectrum, as shown in Fig. 2. These structures are likely to originate from the small trace of trivalent europium ions in the sample, as their peak energies agree well with the $^5D_j-{}^7F_{j'}$ transition energies of Eu^{3+} ions in the solid matrices.[5]

Figure 3(a) shows a logarithmic current density (J) versus voltage (V) characteristic of the europium silicate EL device. From the lower current density region, around 10^{-6} A/cm^2, we estimated the resistivity of the layer to be on the order of $10^{10}\Omega$ cm. This value suggests that the europium silicate layer can be regarded as an insulator. As shown in Fig. 3(a), the $J-V$ characteristic exhibits a power-law relationship, $J=\kappa V^{\nu}$ (κ is a proportionality factor), where ν increases from 1 to 3 with increasing applied bias voltage. This $J-V$ characteristic behavior is similar to that of the space-charge-limited current with traps observed for the carriers injection into the insulator, where the injected current flowing is strongly influenced by the localized defect states in the forbidden gap in response to the applied voltage.[6,7]

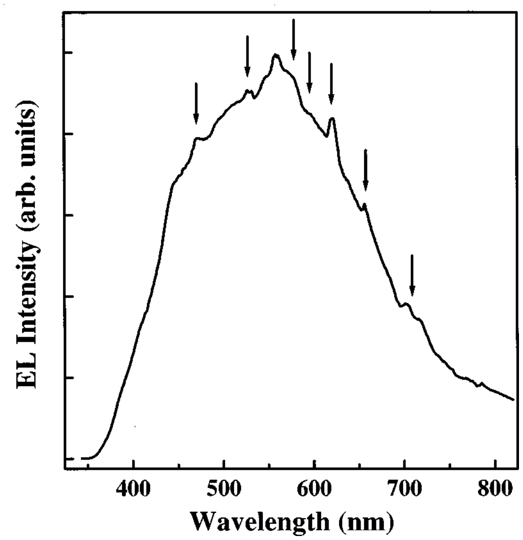

FIG. 2. The EL spectrum obtained at the bias voltage of 30 V. Arrows show the luminescence energy positions of trivalent europium ions in the sample.

Figure 3(b) shows a logarithmic plot of the integrated EL intensity as a function of the injection current density. The dashed curve represents the experimental result. The onset of EL was seen at the injection current density of about 0.4 mA/cm^2. This means that the EL starts at a low bias voltage of about 6 V. The EL intensity increases with the increase of the forward current density. On the other hand, we could not observe any light emission in the reverse cur-

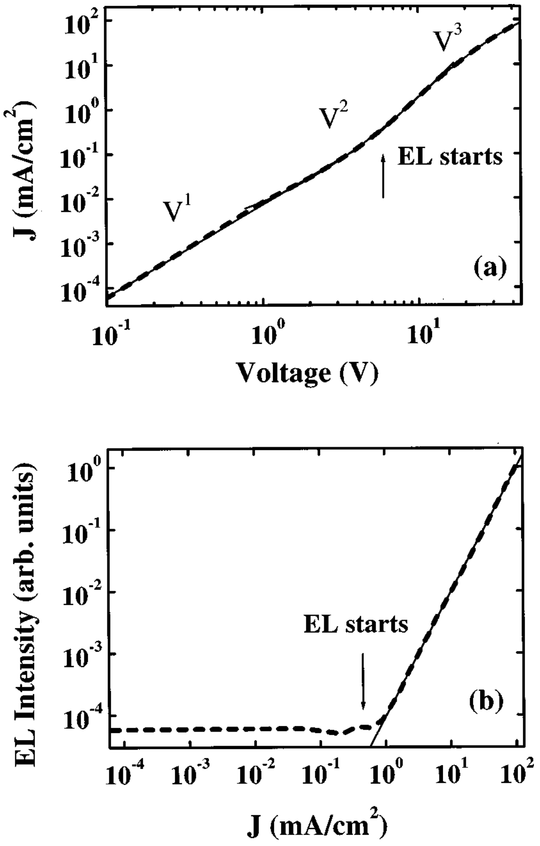

FIG. 3. (a) Logarithmic plot of current density versus driving voltage. (b) Integrated EL intensity vs injection current density. The dashed and the solid curves represent the experimental results and the fitted ones, respectively.

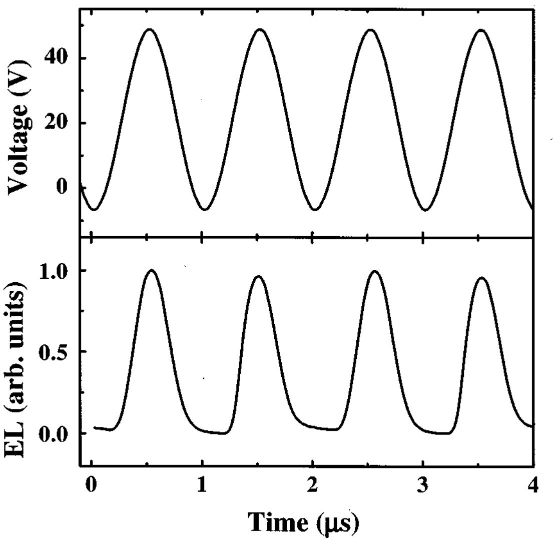

FIG. 4. Temporal behavior of integrated EL intensity from the device modulated by sine-wave bias voltage. The amplitude and the frequency of the modulation sine-wave signal are 27.5 V and 1 MHz, respectively. The additional forward bias voltage is 20 V.

rent direction even at the breakdown voltage of around 90 V. The solid line in Fig. 3(b) gives the result fitted by the square dependent function $I_{\mathrm{EL}}\sim J^2$. The square dependence of EL as a function of the injection current density suggests that both holes and electrons are injected into the luminescent layer from the $p-$Si substrate and the ITO electrode layer. These injected carriers can be trapped at the Eu^{2+} ion centers and other defects, where the current flow is strongly influenced by these localized centers, showing the power-law relationship of the $J-V$ characteristic, as observed in Fig. 3(a). Subsequently, the electron-hole pairs bound at europium centers recombine, and the energy transfer to the Eu^{2+} ions occurs. As a result, the Eu^{2+} ions emit light through the $(4f)^6(5d)-(4f)^7$ transition.

Figure 4 shows a temporal behavior of the integrated EL intensity from the europium silicate EL device modulated by a sine-wave bias voltage. For the modulation, a sine wave signal with the amplitude of 27.5 V and frequency of 1 MHz, was applied in addition to the forward bias voltage of 20 V. The EL was found when the sine-wave modulation signal voltage is above 8 V in the rising side. A tail of EL was observed in the fall side, which results in the asymmetry of EL in the rising side and the fall side. Even so, the EL intensity follows the forward modulation sine wave signal with little distortion in shape. It suggests that the signal processing speed of the device can be as fast as 1 MHz. From the tail in the fall side, we can estimate the EL decay time of about 0.5 μs. It agrees with the fluorescent decay time of Eu^{2+} ions of sub-μs order.[8] It is likely that the speed of EL modulation of the device is limited by the fluorescent decay time of Eu^{2+} ions.

In summary, we have shown an EL device having a europium silicate layer on the silicon substrate. The EL device exhibits the characteristics of broad spectral band, large-area uniform emission, high external quantum efficiency, fast response, low threshold, and simplicity in fabrication. This work has demonstrated that europium silicate appears a promising candidate material for the fabrication of flat panel displays and OEIC on the Si substrate.

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