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Switchable two-color electroluminescence based on a Si metal-oxide-semiconductor structure doped with Eu

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A Si metal-oxide-semiconductor electroluminescent device structure is reported which emits two colors, while being doped with a single rare-earth element. Thermally grown SiO_2 oxide layers were implanted with Eu and subseqently annealed. Depending on the electrical excitation current, the luminescence is red or blue, which can be ascribed to electronic transitions in tri- and divalent europium (Eu^{3+} and Eu^{2+}), respectively. © *2007 American Institute of Physics*.
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Great efforts are currently undertaken worldwide to achieve efficient light emission from Si based structures and devices with the aim of developing an integrated optoelectronic platform on Si.[1] Such light emitters appear attractive due to their material compatibility with the complementary metal-oxide-semiconductor (MOS) technology and may represent not only the basis for inter-/intrachip optical interconnects but also, e.g., microdisplays, waveguide amplifiers, or biological agent detection. Among the most promising approaches toward this goal are Si nanoclusters,[2,3] often embedded in a SiO_2 matrix and codoped with rare-earth ions.[4–6] Yet also sole doping with rare-earth ions can lead to light emission of different colors,[7] related to their specific energy level structure. Rare earths have also been embedded in other transparent host materials such as the wide-gap semiconductors SiC (Ref. 8) and GaN.[9] Recently, we have demonstrated MOS based light emitting diodes (MOSLEDs) doped with Er^{3+},[10] Tb^{3+},[11] Ce^{3+},[12] or Gd^{3+},[13] emitting in the infrared, green, blue, and ultraviolet spectral ranges, respectively. These MOSLEDs typically reach external quantum efficiencies between 1% and 10%.[7,10–13] In this letter we demonstrate a *switchable two-color* MOSLED doped with Eu, taking advantage of the fact that Eu occurs in the two oxidation states Eu^{3+} and Eu^{2+}. The electroluminescence (EL) can be switched with the excitation current between red (low current) and blue (high current), ascribed to electronic transitions in tri- and divalent Eu ions, respectively.

Most of the rare-earth (RE) elements occur in host materials in their trivalent oxidation state. Their $4f^n$ configuration is relatively isolated and the next excited configuration $4f^{n-1}$ $5d$ is located more than 5 eV above the ground state of the $4f^n$ configuration. The $4f$ electrons of RE^{3+} ions embedded in solids are thus well shielded from external fields, and sharp lines due to intrashell $4f$-$4f$ transitions for both optical absorption and emission spectra are observed. These transitions are dipole forbidden in the free ions and become allowed only due to the reduced symmetry of the host matrix. Eu, Sm, and Yb can also exist in solids as divalent ions containing one more electron. The $4f^{n-1}$ $5d$ states of RE^{2+} ions interact strongly with the matrix and the interconfigurational $4f^n$ to $4f^{n-1}$ $5d$ transitions of divalent rare earths are dipole allowed. They have transition strengths several orders of magnitude higher than $4f$-$4f$ transitions.[14] However, this does not necessarily translate into higher electroluminescence intensity, since the latter also depends on nonradiative relaxation time and the excitation efficiency.

The MOSLED device structures were prepared by standard silicon complementary MOS technology on 4 in. n-type silicon wafers. The structure consists of an active gate oxide area (SiO_2) surrounded by a 1 μm thick field oxide. Thermally grown 100 nm thick SiO_2 layers were implanted by Eu with an energy of 100 keV and subsequently annealed at 900 °C for 40 min. The concentration of Eu was ranging from 0.5% up to 3%. In order to protect the oxide layer against instability breakdown, a 50 nm SiON layer was deposited on it by plasma-enhanced chemical vapor deposition (ratio between O and N was 1:1). The gate electrode consists of a 100 nm thick indium tin oxide (ITO) deposited by rf sputtering. The diameter of the MOS device was between 1 and 500 μm. The EL spectra were measured at room temperature in the region from 350 to 750 nm on MOS structures with a circular ITO electrode of 200 μm diameter at constant current supplied by a source meter (Keithley 2410). The measurements were performed with electron injection from the silicon substrate. The same type of structures was used for the investigation of the EL intensity as function of excitation current. The EL signal was recorded using a monochromator (Jobin Yvon Triax 320) and a photomultiplier (Hamamatsu H7732-10). Photographs were taken by a standard digital camera connected with an optical microscope.

Figure 1 shows the EL spectra of MOSLED device structures implanted with different concentrations of Eu under 10 μA dc current injection. The EL is generated by hot-electron induced impact excitation of RE ions during Fowler-Nordheim tunneling. Peaks at 573, 616, and 655 nm are attributed to the $4f\,^5D_0$-^7F_J ($J=1,2,3$) intrashell transitions of Eu^{3+}, whose spectral positions are known to depend only weakly on the host material. On the other hand, the $5d$ electrons strongly interact with the host crystal field, and therefore the peak position of the lowest transition of Eu^{2+} doped materials varies more strongly with the host material than is the case for RE^{3+} doping.[15] In the case of the SiO_2 matrix, divalent europium exhibits two broad bands with maximum

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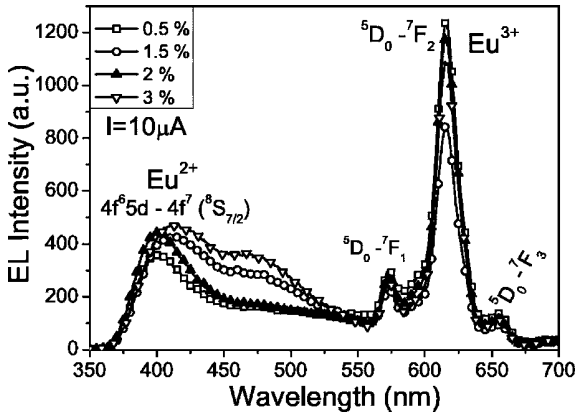

FIG. 1. Electroluminescence spectra of SiO_2:Eu MOSLED devices with different Eu concentrations as indicated. The excitation current is 10 μA and the device diameter is 200 μm.

intensities at 400 and 470 nm, corresponding to the $4f^6$ $5d$-$4f^7$ ($^8S_{7/2}$) transitions. (Note that the peak at 470 nm may also have some contribution from oxygen deficiency centers in SiO_2.[16]). For Eu^{2+} the strongest luminescence was observed for a concentration of 3%, while the trivalent europium shows the highest electroluminescence for the lowest europium concentration (0.5%). At higher concentrations, this intra-4f electroluminescence may undergo concentration quenching,[11] caused by a nonradiative energy transfer between two neighboring Eu atoms.

Figure 2 shows the dependence of the blue and red EL intensities and applied voltage on the current for samples containing 0.5% of Eu. The radiative transition between the $^5D_0$ and $^7F_2$ levels in Eu^{3+} is observed already for a current of 2×10^{-8} A and a voltage of 99 V. With increasing injection current the red light monotonically increases up to the breakdown point. To obtain a population of the first excited level $4f^6$ $5d$ in divalent europium, higher voltages (>105 V) and current ($>4\times10^{-7}$ A) are needed. An increase of the 400 nm emission with current was observed up to 1 mA before it is finally quenched. For a current of up to 90 μA, the red light dominates over the blue one. In the range of 90 mA–1.8 the reverse situation is observed. The

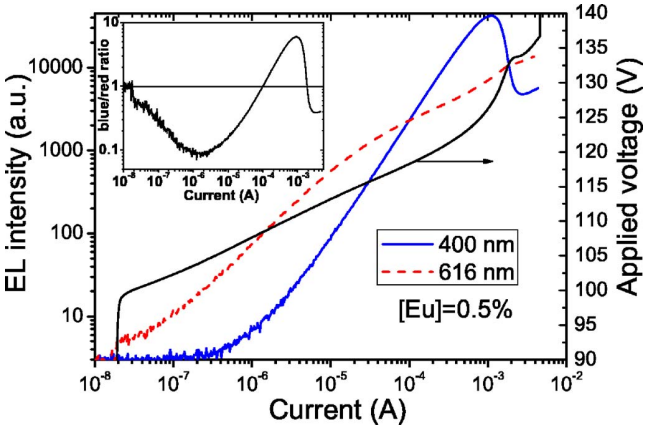

FIG. 2. (Color online) Electroluminescence intensity of a MOSLED device with 0.5% Eu, measured at 400 nm (blue solid curve) and 616 nm (red dashed curve) as a function of the injection current (left scale). The black solid curve shows the applied voltage vs current (right scale). The inset displays the ratio of the blue to the red EL vs injection current. The device was 200 μm in diameter.

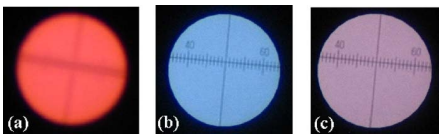

FIG. 3. (Color online) Photographs of SiO_2:Eu MOSLED devices with 200 μm diameter. The excitation currents were 20 μA (a), 1 mA (b), and 2.5 mA (c), respectively.

inset of Fig. 2 shows the blue/red ratio of the EL intensity versus current. It is clearly visible that by a proper choice of the operation current regime it is possible to switch between the two main colors: red and blue. In addition, for a current of around 100 μA as well as higher than 1.8 mA both colors have similar intensity resulting in violet emission [see Fig. 3(c)]. Operating at one of these crossover points, switching can be achieved by superimposing a small ac modulation voltage. Such a switchable two-color behavior has not been reported before for Si based light emitters. We are only aware of GaN based devices, where two colors were generated using two different rare-earth ions (Er and Eu).[17,18] The simplest explanation of the color change with applied voltage can be given considering the hot-electron distribution in the oxide.[19] At lower electric fields the average electron kinetic energy is only sufficient to excite the red transition (transition energy of ~2 eV), whereas at higher fields the electrons are more energetic and can also excite the blue transition (2.5–3 eV). Another possibility is electron capture at high current. A more detailed understanding of the microscopic mechanism will require further experiments.

Figure 3 shows photographs taken from devices of 200 μm diameter by a standard digital camera under an optical microscope. The red-light emission obtained with low-current excitation is presented in Fig. 3(a). Similar results were observed by Heikenfeld *et al.* from a GaN:Eu LED.[20] The blue electroluminescence [see Fig. 3(b)] from any matrix containing Eu^{2+} was not observed up to now. Kim and Holloway have identified both divalent and trivalent europium ions in GaN by x-ray photoelectron spectroscopy, but they observed EL only from Eu^{3+}.[21] Cathodoluminescence from Eu^{2+} doped $BaMg_{(1+x)}Si_xAl_{10}O_y$ has been reported by Studenikin and Cocivera.[22]

In summary, we have presented a switchable two-color MOSLED device structure based on a Eu implanted SiO_2 layer. This shows that photonics based on silicon has still a lot of potential, and even offers interesting optoelectronic functionalities. Future goals will be aimed toward a microscopic understanding of the two-color behavior and a reduction of the operating voltage by using thinner oxides. Combination with a green light emitter such as SiO_2:Tb could result in a Si based full-color microdisplay.

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