Efficient electroluminescence from rare-earth implanted SiO₂ metal-oxide-semiconductor structures

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Abstract

The IR, green, and UV electroluminescence from rare-earth (Er, Tb, and Gd) implanted SiO₂ MOS devices is studied, exhibiting quantum efficiencies comparable to III-V light emitting diodes.

Recently, several approaches for gaining light from silicon-based systems have been reported with the prospect of sufficient electroluminescence (EL) efficiency. The most prominent systems are porous silicon,¹ silicon nanocrystals in SiO₂,² pn diodes,³ and Er-doped SiO₂.^{4,5} The latter ones, realized as MOS light emitting devices (MOSLED), are especially attractive, since they have high efficiency and tunable emission wavelength by implantation of different rare-earth luminescent centers; also the processing is fully compatible with silicon complementary MOS technology.

Here we use an alternative solution for improving the stability and EL efficiency of rare-earth implanted SiO₂ MOS light emitting devices (MOSLED). Efficient and stable electroluminescence from Er, Tb, Gd-doped MOSLEDs are reported emitting light in the IR, green, and deep UV with high external quantum efficiency above 14% (IR), 16 % (green)⁶ and 1 % (UV).⁷

The MOS structures were fabricated by local oxidation of silicon (LOCOS) with gate oxide and a field oxide thickness of 1 μ m. The active layer in the gate oxide is a 100 nm thermally grown SiO₂ implanted with different rare-earth ions at 100 keV,

or using double energy of 50 and 110 keV. The implantation was followed by furnace annealing at 800°C-1000°C in flowing N₂ for 1 hour. The gate electrode is a 100 nm transparent indium-tin-oxide layer deposited by RF sputtering.

The rare-earth ions Er, Tb, and Gd give strong EL due to their large excitation cross-sections. Fig.1 shows the EL spectra of Er, Tb, and Gd-implanted MOSLEDs at an injection current of 10 μ A on 0.5 mm diameter devices. The electronic transition from ⁴I_{13/2} → ⁴I_{15/2} of Er³⁺ gives rise to an IR peak at 1535 nm; Tb³⁺ yields two groups of peaks from the ⁵D₃ and ⁵D₄ to ⁷F_j (j=3-6) levels, the latter one in the green at 541 nm. The ⁶P_{7/2} to ⁸S_{7/2} transition of Gd³⁺ generates a sharp peak in the UV at 316 nm.

The external quantum efficiency of Er, Tb, and Gd-implanted MOSLEDs was calibrated as a function of the implanted concentrations, as shown in Fig.2. The Er-implanted sample has an efficiency of up to 14% after annealing at 900°C

Fig.1 EL spectra from Gd, Tb, and Er-implanted MOSLED, normalized to the same peak value.

Fig.2. External quantum efficiency of the EL from Gd, Tb, and Er-implanted MOSLEDs. The internal quantum efficiency of SiO₂ device is above 5 % due to the strong absorption at UV range by the top ITO electrode.

for one hour. The Tb-implanted samples show a maximum EL efficiency up to 16% when annealed at 800°C, and the efficiency drops down to 11% at higher annealing temperature of 900°C. The Gd exhibits an external quantum efficiency of 1%, but taking account the strong absorption of the top ITO electrode in the UV region, the internal quantum efficiency of the Gd implanted UV MOSLED should be above 5%. The three rare earth elements show nearly the same optimum concentration of 2% in SiO₂ for generation of efficient electroluminescence.

It has been shown that Si nanoclusters in SiO₂ can act as sensitizers for the Er photoluminescence (PL).⁸ However, EL and PL of Er³⁺ in Si-rich SiO₂ behave differently, as summarized in Fig. 3. There the PL and EL intensity of the 1.54 μ m line of Er³⁺ are plotted as a function of the density and the average distance between silicon nanoclusters. The PL intensity increases with increasing the density of the silicon nanoclusters. On the contrary, the EL is strongly quenched, when the average distance between the silicon clusters drops below the mean free path of the hot electrons (or the heat-up distance of $\sim$ 3 nm) in SiO₂ as determined by different methods.⁹ The electrons, which travel between two silicon clusters with a distance below such a heat-up distance, will not gain sufficient

Fig.3. EL and PL intensity from the different peaks of Er³⁺ and Si nanoclusters as a function of the density of the silicon clusters. The average diameter of the Si nanoclusters is taken as 2 nm for estimating the average distance between Si clusters.

energy from the electric field to overcome the losses due to scattering processes. The average energy of the electrons will decrease with an increase of the fraction of direct tunneling between the silicon clusters. These results reveal that introducing silicon clusters into SiO₂, while improving the device stability, strongly reduces the efficiency of EL in Er-MOSLEDs. Therefore, for making efficient MOSLEDs, we use a dry thermal SiO₂ layer and follow other routes to improving the high-field stability of both the gate oxide layer and the structure of MOSLEDs.

The EL and PL properties of the Tb-doped SiO₂ active layers are studied concerning variations of the Tb concentration and the annealing temperature. Fig.4 (a) compares the concentration dependence of the EL peak intensity of the ⁵D₃-⁷F₅ (blue peak at 413 nm) and ⁵D₄-⁷F₅ (green peak at 541 nm) transitions for the samples annealed at 800°C for 1 hour. The green peak increases linearly with increasing the Tb concentration up to 2% and then saturates, while the blue peak shows a strong concentration quenching after increasing the Tb concentration above 0.15 %. Fig.4 (b) shows the peak intensity ratio of the blue divided by the green peak (B/G ratio) as a function of the Tb concentration. The B/G ratio decreases with increasing Tb

Fig.4. Concentration dependencies of the EL intensity (a), the blue/green ratio (B/G ratio) (b), and the lifetime (c) of the two transitions from ⁵D₃-⁷F₅ (blue peak at 413 nm) and ⁵D₄-⁷F₅ (green peak at 541 nm).

concentration, which indicates a more effective population of the ⁵D₄ levels. To trace back the origin of this behavior, we have measured the EL decay time of the blue (⁵D₃) and green (⁵D₄) lines in Fig.4 (c). The decay time of the ⁵D₃ level decreases with increasing Tb concentration, while the decay time of the ⁵D₄ level slightly increases. This indicates a faster non-radiative decay of ⁵D₃, leading to a higher average population of ⁵D₄. We ascribe this behavior to the cross-relaxation from the ⁵D₃ to the ⁵D₄ level in adjacent Tb³⁺ ions, made possible through the very small energy mismatch of 11 meV for (⁵D₃-⁵D₄)≡(⁷F₀-⁷F₆). The cross-relaxation enhances the green light emission at high Tb concentration.

The EL excitation mechanism is ascribed to direct impact excitation of rare earth ions by hot electrons in the conduction band of SiO₂. The change of the ratio between two peaks from a high and a low excited level of rare earth ions reflects a shift of the average energy of hot electrons. The ratio of blue/green (B/G) peaks of the Tb³⁺ and the ratio of green/infrared (G/I) peaks of Er³⁺ in the EL

spectra are measured versus the average electric field. An increase of the (B/G) and (G/I) ratio of the EL spectra (prior to the saturation of excitation) was observed with increasing electric field from Tb and Er doped MOSLEDs, respectively. This gives strong evidence that the EL excitation of rare-earth doped SiO₂ is related to the electron heating after F-N tunneling injection of electrons into the conduction band of SiO₂.

In summary, we reported a comprehensive study of MOSLEDs fabricated by rare-earth implantation. Insight into the physical mechanism is gained by studying the concentration quenching, cross-relaxation, electronic heating. The Er, Tb and Gd implanted MOSLEDs exhibit high EL efficiency compared to other silicon-based LEDs and could have high potential for various applications in silicon photonics.

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