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Electroluminescence induced by Ge nanocrystals obtained by hot ion implantation into SiO_2

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Commonly, electroluminescence (EL) from Ge nanocrystals (Ge NCs) has been obtained by room temperature (RT) Ge implantation into a SiO_2 matrix followed by a high temperature anneal. In the present work, we have used a novel experimental approach: we have performed the Ge implantation at high temperature (T_i) and subsequently a high temperature anneal at 900 °C in order to grow the Ge NCs. By performing the implantation at $T_i = 350$ °C, the electrical stability of the MOSLEDs were enhanced, as compared to the ones obtained from RT implantation. Moreover, by changing the implantation fluence from $\Phi = 0.5 \times 10^{16}$ and 1.0×10^{16} Ge/cm^2 we have observed a blueshift in the EL emission peak. The results show that the electrical stability of the hot implanted devices is higher than the ones obtained by RT implantation. © *2009 American Institute of Physics*. [doi:10.1063/1.3262627]

I. INTRODUCTION

Since the discovery of photoluminescence (PL) in porous Si,[1] a large number of studies concerning the properties of Si or Ge nanoclusters (NCs) have been reported. Several techniques have been used in order to produce the NCs embedded in the matrix. Among them, the ion implantation technique has shown to be a very reliable tool because it offers several advantages.[2–4] In addition to the compatibility with the microelectronic technology, it is very precise in controlling the amount and depth of the excess ions introduced in the matrix, thus presenting great reproducibility.

First experiments using ion implantation as a technique to produce Si or Ge NCs were already reported in the early 1990s[2–4] and their promising results were followed by an intense research activity, as illustrated by the review of Rebohle *et al.*[5] However, in all the cases, the Ge implantation was performed at room temperature (RT), followed by a high temperature anneal.

Recently we have used a different experimental approach. Instead of performing Ge implantation into the SiO_2 layer at RT, we have done it keeping the substrate at 350 °C and then anneal the samples at 900 °C. As consequence, the 390 nm band increased its PL yield by a factor of almost 4 as compared with the RT implantation. Moreover, by finding the proper Ge implanted concentration we were able to further increase the PL yield of the 390 nm band by another factor of 3.[6]

The main goal of the present paper is to study the electroluminescence (EL) emitted by metal-oxide-semiconductor (MOS) devices made with the Ge NCs obtained by hot implantation and compare the results with those produced by RT implantation.

II. EXPERIMENTAL PROCEDURE

A 195-nm-thick SiO_2 layer, thermally grown onto a n-type Si ⟨100⟩ wafer by dry oxidation at 1050 °C, was implanted with 120 keV Ge ions keeping constant the substrate temperature at RT and 350 °C, respectively. The implantations were done at fluences of 0.5 and 1.0×10^{16} Ge/cm^2, corresponding to a Gaussian-like depth profile with a peak concentration of about 1.5 and 3 at. %, respectively, 90 nm far from the SiO_2 surface. Subsequently, the as-implanted samples were submitted to a furnace anneal at 900 °C for 30 min in flowing N_2. Then, a SiON layer with a thickness of 100 nm was deposited onto the SiO_2 layer by plasma-enhanced chemical vapor deposition in order to enhance the electrical stability of the device,[7] followed by the same annealing process. MOS dot structures for EL studies were prepared using sputtered layers of indium tin oxide and Al as front and rear electrodes, with a thickness of 100 and 150 nm, respectively. Photolithography was used to make a dot matrix pattern with a dot diameter of 200 μm. Finally, an annealing procedure of 400 °C for 30 min was performed to improve the Ohmic behavior of the contacts. A sketch of the device is shown in Fig. 1.

The EL measurements were performed at RT utilizing a Triax 320 spectrometer with a R928 Hamamatsu photomultiplier. Current injection was done by a Keithley 2410 sourcemeter with a positive voltage applied to the gate. This feature corresponds to an electron injection from the Si substrate into the SiO_2 layer.

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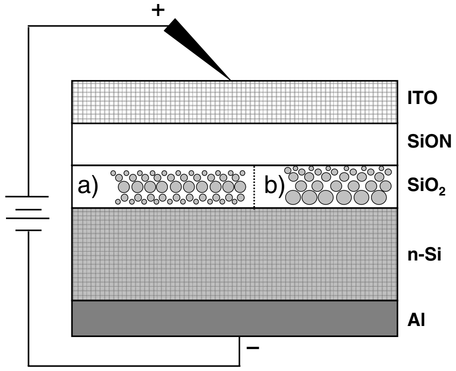

FIG. 1. Schematic diagram of the MOSLED (not drawn to scale). In detail: representation of the Ge NCs for (a) RT implantation and (b) high temperature implantation.

Structural characterization of the samples were performed by transmission electron microscopy (TEM), using a 200 keV JEOL microscope with the samples prepared in a cross sectional mode by mechanical polishing and ion milling techniques.

III. RESULTS

A. TEM Results

The TEM measurements reveal the formation of crystalline Ge NCs in both RT and hot implanted samples after the 900 °C anneal, as shown in Figs. 2(a) and 2(b), respectively. For the RT implanted sample [Fig. 2(a)] we have found a Gaussian-like NCs size distribution with a mean diameter size of 4.2 nm.

Concerning the hot implantation [Fig. 2(b)], the mean size and size distribution differ significantly from the one observed when the Ge implantation is done at RT. In fact, the Ge NCs distribution presents a positive gradient profile of crystal sizes along depth. The shallow region shows quite small nanocrystals having about 2 to 3 nm in diameter. The intermediate one contains medium size Ge NCs of around 3 to 5 nm and in the deepest region, it is possible to observe larger NCs ranging from 5 to even 9 nm in diameter.

B. Electroluminescence measurements

In this set of experiments, the electrical properties of the MOS light emitting devices (MOSLEDs) were analyzed. Figure 3 shows the EL spectra of the devices, under a constant current injection density (J) of 320 $\mu A/cm^2$, for the hot and RT samples implanted at the two different fluences. The first observed feature is that the intensities of the EL peaks of the hot implanted samples are around 30% lower than the ones corresponding to the RT implanted ones. Another characteristic present in this spectra is the blueshift in the EL peak position, of 8 nm, in the devices implanted with the higher fluence (1×10^{16} Ge/cm^2), as compared to the ones implanted with the lower fluence (0.5×10^{16} Ge/cm^2). It should be mentioned that the 310 nm band seen in Ref. 6 could not be detected in the present experiment because non UV-transparent optics were utilized.

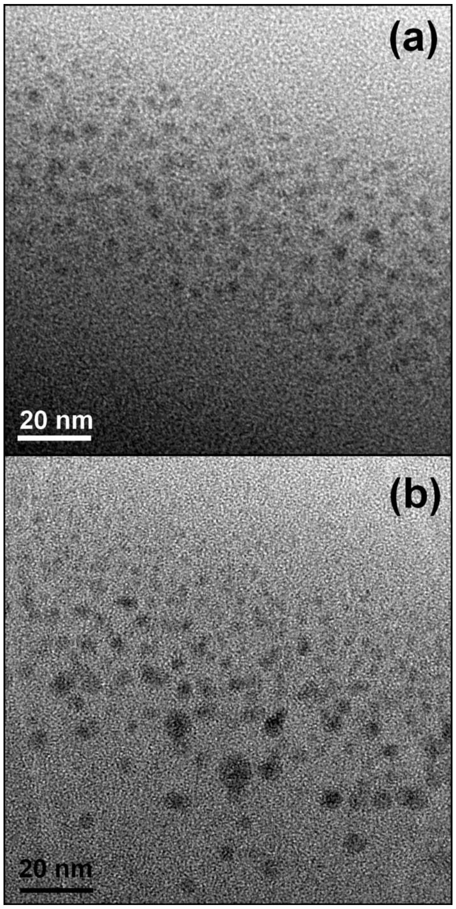

FIG. 2. Detailed TEM view showing the NCs size distribution for (a) RT implantation (b) high temperature implantation (samples implanted to $\Phi = 1.0\times10^{16}$ Ge/cm^2 and annealed at 900 °C for 1 h).

Figure 4 displays the EL intensity as a function of the injected carriers under constant current density of 320 $\mu A/cm^2$ with the spectrometer centered on the wavelength of the EL peak of each device. The experiments were done for the hot and the RT implanted samples, and for both implanted fluences. It was verified that the hot implanted samples show an electrical stability that is around three times larger than the one obtained by the RT implants.

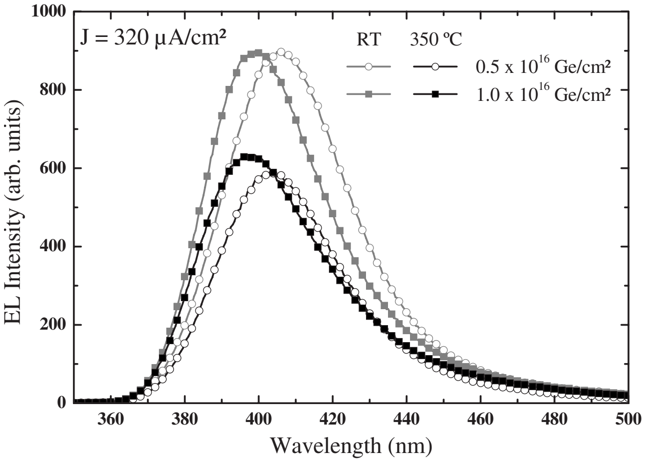

FIG. 3. EL spectra from the MOS devices, implanted at different temperatures (gray lines: RT, black lines: 350 °C), and fluences (open circles: $\Phi = 0.5\times10^{16}$ Ge/cm^2 and solid squares: $\Phi = 1.0\times10^{16}$ Ge/cm^2).

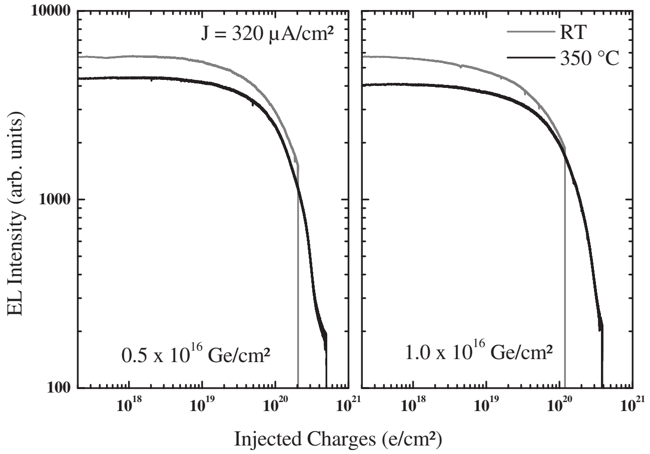

FIG. 4. EL peak intensity over injected charges, implanted at different temperatures (gray lines: RT and black lines: 350 °C) and fluences (left: $\Phi = 0.5 \times 10^{16}$ Ge/cm^2 and right: $\Phi = 1.0 \times 10^{16}$ Ge/cm^2).

IV. DISCUSSION AND CONCLUSIONS

As mentioned before, in previous works[4–6] the Ge NCs embedded in SiO_2 matrix were obtained by RT implantation followed by a high temperature anneal. When excited at 5.1 eV, two PL bands were obtained, one at 310 nm and the other, with much higher yield, at 390 nm. The origin of the PL bands was attributed to radiative defects present at the Ge NCs/matrix interface, specifically, neutral oxygen vacancies (NOVs) such as $\equiv$Ge–Si$\equiv$ and/or $\equiv$Ge–Ge$\equiv$ defects generated by the local deficiency of oxygen and the incorporation of Ge into the SiO_2 network surrounding the NCs.[5,8,9]

Related to the EL measurements, the lower EL intensity of the hot implanted samples—see Fig. 3—can be explained based on the results of the TEM observations. The hot implanted samples have significant larger NCs at the deepest region of the implantation profile, as compared to the RT implanted ones. These larger NCs act as scattering centers for the electrons during the injection process as illustrated by Fig. 1 causing a kinetic energy loss and thus decreasing the corresponding EL cross section, producing a less intense emission.

The blueshift in the EL spectra observed for the highest implantation fluence (see Fig. 3) can qualitatively be explained as follows: The EL induced by the Ge NCs is due to NOV-type radiative defects, such as $\equiv$Ge–Si$\equiv$ and/or $\equiv$Ge–Ge$\equiv$, with emission energies of 2.92 and 3.1 eV, respectively.[7] Both of them are among the ones that contribute the most to the observed EL band. A higher Ge implantation fluence produces larger NCs, after the thermal anneal, due to the higher Ge concentration in the matrix. Consequently, the $\equiv$Ge–Ge$\equiv$ to $\equiv$Ge–Si$\equiv$ ratio increases, producing a more intense emission of the 3.1 eV component and a corresponding reduction of the 2.92 eV component of the EL band, resulting in a slight blueshift, as observed in Fig. 3.

Figure 4 indicates that the hot implanted samples can sustain an approximately three times larger number of injected charges before the breakdown device (Q_{BD}) occurs, as compared with the RT implanted ones. Since the Q_{BD} is depending, among other factors, on the injected current density and operation time, this means that a MOSLED made utilizing hot implantation can sustain a current density three times higher, giving a higher EL intensity, or, for the same current density, results in a three times higher operation time. As the breakdown is a statistical event, the improvement factor may vary, however the general tendency is clear.

The above feature in principle can be attributed to the fact that the hot implantation produces less damage in the SiO_2 layer during the implantation process and a higher quality of the SiO_2/Si interface, thus resulting in lower number of nonradiative defects present in the oxide and in the interface.

In order to compare the PL and EL emissions, all the implantation and annealing parameters were the same ones reported in Ref. 6, which gave place to the maximum PL emission. It is possible that the optimal conditions for the EL emission are not the same as the PL ones.

In summary, in the present communication we have found that devices based on Ge NCs produced by hot implantation have greater electrical stability, as compared with the ones produced by RT implantation. Concerning the EL yield, as mentioned above, it is possible that the best conditions for the EL emission are not the same as compared with the PL ones. It is necessary to perform further optimizations aiming to increase the EL emission of the MOS devices. In this sense, work is on the way.

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