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RF plasma treatment of shallow ion-implanted layers of germanium

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ABSTRACT

RF plasma annealing (RFPA) and rapid thermal annealing (RTA) of high-dose implanted n-type and p-type amorphized Ge layers have been studied by Raman scattering spectroscopy and X-ray diffraction techniques. It is shown that recrystallization of n-Ge implanted by BF_2^+ ions requires higher RTA temperatures and power density of RFPA as compared to p-Ge implanted by P^+ ions with the same dose. The RFPA has been performed at considerably lower temperatures than RTA and resulted in the formation of a sharp interface between the implanted and underlying Ge layers both for BF_2^+ ion implantation and P^+ ions implantation.

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1. Introduction

Shallow drain/source p–n junction formation is a key requirement in production of advanced Si and Ge devices. Germanium has considerable advantages in comparison with silicon due to high electron/hole mobility and low temperature activation of implanted impurities [1]. However, diffusion coefficients for donor impurities in germanium, e.g., for phosphorus, are rather high [1], which hampers the formation of super-shallow n^+/p junctions. Therefore in the case of Ge-based devices one should avoid the high-temperature annealings that are traditionally used to eliminate the implantation-induced defects and to activate of implanted impurity [2]. At present, the most widely used methods for annealing of shallow implanted layer in Ge are: low-temperature annealing, such as solid-phase-epitaxial-regrowth (SPER) [3] and microwave annealing (MA) [4]; short time annealing, such as rapid thermal annealing (RTA) [5], flash-lamp annealing (FLA) [6] or laser annealing (LA) [7]. As an alternative the low-temperature RF plasma annealing (RFPA) can be used; this method was employed successfully for the annealing of thin implanted Si layers [8] but up to now it was not applied to implanted Ge layers. It should be noted that in the case of high-dose ion implantation Si layers, when the amorphous subsurface layer is formed, low-temperature RF plasma annealing does not lead to the

recrystallization of the amorphous Si subsurface layer but creates the completely mechanically relaxed amorphous layer [9]. Due to considerably lower recrystallization temperature of amorphous Ge layers as compared to amorphous Si layers [1], and to the fact that RF plasma treatment anneals the defects within a thin surface layer [10], it should be expected that the RFPA could be successfully applied to crystallize shallow amorphous Ge layer and to form shallow p–n junctions. The present paper considers the first fundamental stage of the study of a low-temperature RF plasma treatment associated with a structural transformation of thin amorphous implanted Ge layers and compares with more frequently used method of annealing-RTA.

2. Experimental

The monocrystalline germanium (Ge) wafers with $\langle 100 \rangle$ orientation were fabricated by liquid encapsulated Czochralski (LEC) method and were polished on the front side. The Ge wafers were mechanically relaxed that was confirmed by Raman scattering (RS) spectroscopy measurements (see Fig. 1(b)). The n-type Ge wafer with carriers concentration about 10^{14} cm^{-3} was implanted by BF_2^+ ions with the energy of 20 keV and the dose of $1 \times 10^{15} \text{ ions/cm}^2$. The p-type Ge wafer with carriers concentration about $(7 \pm 2) \times 10^{16} \text{ cm}^{-3}$ was implanted by P^+ ions with the energy 12 keV and the same dose of implantation. Energies of the ions were chosen to obtain equal projected lengths for different implanted ions. In both cases the maximum of ion distribution

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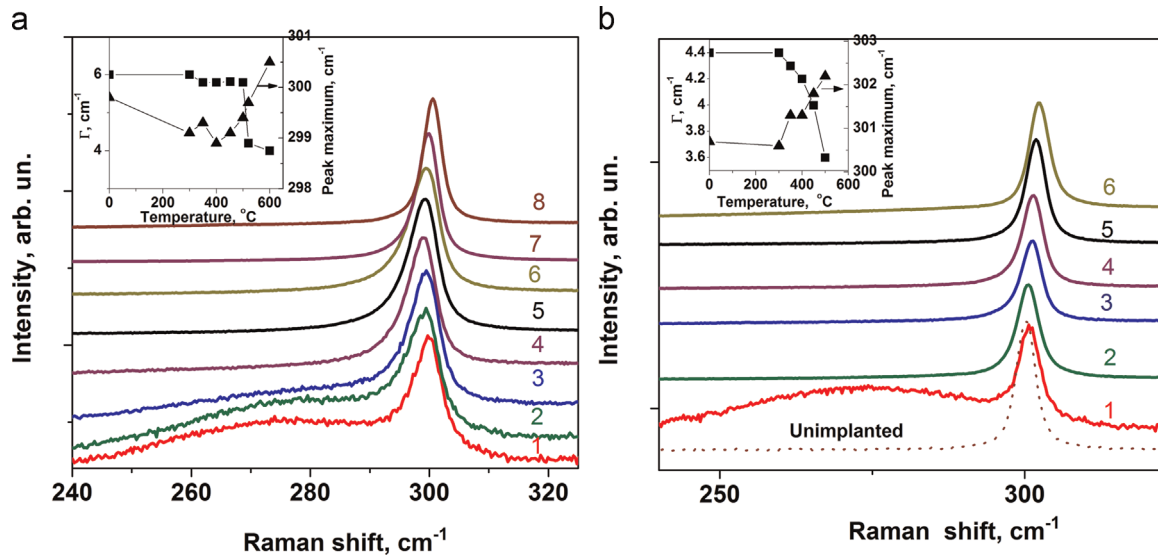


Fig. 1. Normalized RS spectra for n-Ge implanted by BF_2^+ ions (a) and p-Ge implanted by P^+ ions (b). The treatment parameters: 1. As-implanted samples (before RTA); 2. $T=300^\circ\text{C}$; 3. 350°C ; 4. 400°C ; 5. 450°C ; 6. 500°C ; 7. 520°C ; 8. 600°C ($t=15$ s). The insets in figures (a) and (b) show both the half-width, Γ , (■) and the maximum position (▲) of the “crystalline” peak as a function of RTA temperature.

profile was situated about 15 nm from Ge surface. The profiles simulation was performed by SRIM code.

The implanted Ge layer was annealed by RTA methods in nitrogen ambient in temperature range from 300 to 550°C during 15 s. The RF plasma treatment (13.56 MHz) was performed in diode type reactor in the forming gas (90% $\text{N}_2+10\%$ H_2) atmosphere [8]. The samples were located on the heated (up to 200°C) RF electrode. The RF plasma power density was varied from 0.5 to 2.0 W/cm^2 , the treatment duration was 10 min. The sample temperature for plasma treatment was monitored in situ using special calibrated thermal paints that were deposited on the back side of the samples. Calibration of the thermal paint has been done in a standard oven. Results of the measurements are shown in Fig. 5 (c) in the paper [11].

The phase composition of the samples was studied by Raman scattering (RS) spectroscopy at room temperature. The RS spectra were studied using double monochromator DFS-52 equipped with Andor CCD camera. YAG laser ($\lambda=532\text{ nm}$, $P < 10\text{ mW}$) was used for excitation. Information on the deformations distribution near the Ge surface was obtained by the X-ray diffraction (XRD) measurements in the $\omega - 2\theta$ regime using $\text{CuK}\alpha_1$ line (Philips X’Pert-MRD diffractometer was employed). The samples were scanned in the vicinity of (004) Bragg’s reflex with a step of 0.001° . Surface morphology was studied by atomic force microscopy (AFM) using NanoScope IIIa Dimension 3000.

3. Results and discussion

3.1. Raman scattering spectra

The RS spectra of implanted and RTA treated n-Ge and p-Ge samples are presented in Fig. 1(a) and (b), respectively. The spectrum 1 corresponds to the implanted Ge samples and consists of the wide peak with the maximum at 273 cm^{-1} related to the amorphous Ge phase and the narrow asymmetric peak at 300 cm^{-1} which is ascribed to the crystalline Ge phase. In our case when the amorphous Ge layer has a thickness of about 20 nm (according to the SRIM simulation), and the penetration depth for the light with the wavelength of 532 nm is about 25 nm, the crystalline component from the Ge substrate is always present in the Raman spectrum. Asymmetry of the peak can be caused by

additional light scattering by Ge nanocrystals [12] and stretched Ge layer [13].

After RTA of the implanted n-Ge at temperatures from 300 to 350°C the intensity of the wide peak, that corresponds to the amorphous phase, decreases; this peak completely disappears in the spectra of the samples annealed at 400°C and higher (Fig. 1 (a)). It should be noted that the “crystalline” peak in RS spectrum for the RTA at 400°C has considerably larger half-width ($\sim 6.5\text{ cm}^{-1}$) than in the case of initial unimplanted sample (3.3 cm^{-1}) and the maximum is somewhat shifted to lower frequencies (see the inset in Fig. 1(a)). These features can be associated with appearance of Ge nanocrystals in the annealed implanted layer, which results in a low-frequency shift of the Ge crystalline peak [12] and to effect on his broadening.

The smaller the size of Ge nanocrystallites results in more red shift of the Ge “crystalline” peak. When the temperature of RTA is higher than 400°C the size of nanocrystallites in the implanted layer increases, and after the RTA at 600°C the implanted layer is totally transformed into monocrystalline Ge layer. The effect of the increase of nanocrystallites size leads to the blue shift of Ge “crystalline” peak, and after the RTA at 600°C the half-width and position of the crystalline peak is almost the same as in the case of the initial unimplanted n-Ge. However, the effect of tensile stresses in the implanted Ge layer on the RS “crystalline” peak cannot be neglected. It is known, that tensile stress in implanted semiconductor layers varies along the depth of the layer [14] that can cause the “crystalline” peak broadening and red shifting. Relaxation of the tensile stresses during the annealing has to restore the peak position and half-width. In our case we, probably, observe the influence of both factors.

Furthermore, the observed value of crystallization temperature (about 400°C) is considerably higher than the one obtained for the phosphorus-implanted Ge (see Fig. 1(b)). This observation can be attributed to two effects: firstly, implantation with more heavy ions (BF_2^+ regarding to P^+) results in more amorphized (more damaged) layer; secondly, introduction of fluorine into the damaged germanium (dose about $2 \times 10^{15}\text{ cm}^{-2}$) leads to stabilizing of defects and, thus, can also increase the temperature of amorphous layer recrystallization. Moreover, it is known [15] that at the annealing temperature about 500°C fluorine can passivate vacancies in Ge and form the F_nV_m cluster; this process leads to the relaxation of the tensile stresses and enhanced boron diffusion in

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