Light-emitting hexagonal 9R-Si phase obtained by implantation of Kr$^+$ ions in Si and SiO$_2$/Si

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Abstract. To study the mechanism of a 9R-Si hexagonal phase formation upon ion irradiation of the SiO$_2$/Si system, three types of experimental samples have been investigated by photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM): SiO$_2$/Si system irradiated by Kr$^+$, silicon irradiated by Kr$^+$ and silicon irradiated by (Kr$^+$ + O$^-$) ions. All the samples were annealed after irradiation. The first type sample shows the presence of the 9R-Si phase and PL band at ~ 1240 nm; the third type sample shows the same PL band and twin defects; for the second type sample, the PL at 1240 nm is not detected. Based on the results, the role of mechanical stresses, radiation defects and oxygen in the formation of the hexagonal silicon phase is discussed.

1. Introduction

Almost all modern scientific tasks are based on the implementation of high performance computing and big data processing. For these purposes, laboratories equipped with supercomputing systems are created. The use of electronic circuits in supercomputers leads to an increase in the size and the cost of such devices. Therefore, the main task of modern electronics is to find the ways to raise the rate of signal transmission without increasing the number of elements and the cost of electronic components. The idea of using optical signals instead of electrical ones was offered. But silicon, being a traditional material of microelectronics, cannot be used as light emitter in its conventional cubic phase due to the peculiarities of its electronic band structure. Therefore, there is a demand in the silicon processing methods which would allow improving its optical properties.

It has been already found [1-4] that the band structure of some hexagonal silicon modifications changes in such a way that the probability of interband radiative transition increases more than several hundred times compared with cubic silicon. However, the creation of stable forms of hexagonal silicon is a difficult and poorly controlled process [5, 6], since it is necessary to produce non-equilibrium conditions for the phase transition [7, 8]. The ion irradiation of silicon or silicon substrates covered with dielectric films by heavy ions can be a promising solution to the problem, since it produces a significant level of mechanical stress [9, 10], which in principle can stimulate the transition to hexagonal phase.

As it was shown previously [11, 12], the inclusions of hexagonal silicon of the 9R-Si phase were formed in silicon substrate at the interface with thin SiO$_2$ film upon irradiation of the SiO$_2$/Si system by Kr$^+$ ions followed by annealing at 800 °C. The average projected range ($R_p$) of Kr$^+$ ions was less than the film thickness. For such samples, a photoluminescence (PL) band was detected at ~ 1235 nm (~ 1.004 eV) at helium temperature with a shift to ~ 1240 nm at nitrogen temperature, which was assigned to the light emission of the 9R-Si phase. It was supposed that the formation of this phase
occurred under the action of mechanical stresses arising in a dielectric film during implantation and/or thermal annealing.

To check this interpretation, in the present work, we have carried out additional experiments on the irradiation of silicon without a dielectric film and SiO$_2$/Si system with Kr$^+$ and (Kr$^+$ + O$_2^+$) ions, followed by annealing. The structural and optical properties of the synthesized samples are considered.

2. Experimental

Three types of samples were investigated. The first type was the SiO$_2$(140 nm)/Si system irradiated by Kr$^+$ ions (80 keV, 5·10$^{16}$ cm$^{-2}$) with $R_p$ ~ 50 nm in SiO$_2$. The second type was silicon substrate (without SiO$_2$ film) irradiated by Kr$^+$ ions with such values of energy (9 keV) and dose (2.5·10$^{16}$ cm$^{-2}$), at which, according to the SRIM code [13], the atomic displacement profile was close in shape and height to that in silicon substrate for the first type sample (Figure 1). The third type was the same as the second one but additionally irradiated by O$_2^+$ ions (6 keV). The O$_2^+$ implantation dose was selected to be 1·10$^{15}$ cm$^{-2}$, since the number of oxygen atoms implanted per unit area was approximately equal to the number of oxygen recoil atoms when the SiO$_2$/Si system was irradiated by Kr$^+$ ions (for the first type sample) (Figure 1). After irradiation, all the samples were annealed at 800 °C (30 min) in a dried nitrogen atmosphere. The PL spectra were measured at liquid nitrogen temperature upon laser excitation at 405 nm with a power of 10 mW. The cross-sections of the samples were studied by high-resolution transmission electron microscopy (TEM) using the JEOL JEM-2100F microscope.

![Figure 1. SRIM-calculated profile of Si vacancies and O recoil atoms in Si substrate after irradiation of SiO$_2$/Si system by Kr$^+$: left and bottom scales are for the red curve, right and top scales are for the blue curve.](image_url)

3. Results and discussion

The PL spectra for the experimental samples are shown in Figure 2. A PL band at ~ 1240 nm is revealed for the first and third type samples, which was previously observed by us for the samples with ion-irradiation-induced 9R-Si phase [11, 12, 14]. The PL intensity is higher for the first type sample compared to the third one. No PL bands were observed for the second type sample.
Figure 2. PL spectra of the first and third type samples.

To explain the results, structural studies were performed using the TEM method. For the first type sample, the hexagonal inclusions of the 9R-Si phase were detected in silicon substrate at the interface with SiO$_2$ film (Figure 3). The formation of the 9R-Si phase is proved by the period of atomic planes which is practically equal to the tripled (111) interplanar distance of the cubic silicon, as well as by the presence of two additional reflections on the diffraction pattern obtained by the Fourier transform of the selected region (inset in Figure 3) [4, 15].

Figure 3. High-resolution TEM image of the SiO$_2$(140 nm)/Si sample irradiated with Kr$^+$ ions and subsequently annealed at 800 °C for 30 min; (inset) the Fourier transform pattern of the selected areas of the image.
A cross-sectional TEM image of the third type sample is shown in Figure 4 (a). The topmost layer is the epoxy glue used for the preparation. Below it, the silicon layer ~20 nm thick with a non-uniform contrast is located; the thickness of this layer approximately corresponds to the calculated range of Kr\(^+\) ions in silicon. The presence of twin defects is observed in this layer (Figure 4 (b, c)), which can be considered as the nucleation centers of the 9R-Si phase.

**Figure 4.** (a) High-resolution TEM image of the Si sample irradiated with Kr\(^+\) and O\(^+\) ions, subsequently annealed at 800 °C for 30 min; (b, c) HRTEM images of the twin defects in the sample.

The results can be explained as follows. Kr\(^+\) ions implanted into the SiO\(_2\)/Si system introduce additional mechanical stresses in the film whose relaxation upon annealing causes the phase transformation in the silicon substrate. In addition, some of the implanted ions penetrate into the substrate from the SiO\(_2\) film, creating defects and mechanical stresses in it. These factors together can synergistically contribute to the 9R-Si phase formation.

Our assumptions are confirmed by the experiments with irradiation of silicon substrate without SiO\(_2\) film (the third type sample). Since only the second factor (penetration of ions into substrate) takes place in this case, the process of hexagonal phase formation is not so strongly expressed. Nevertheless, the PL data speak in favor of the formation of 9R-Si inclusions in the third type sample, but with sufficiently lower concentration according to much lower intensity of the ~1240 nm PL line. So, the TEM method, which probes only small parts of the sample, cannot in principle reveal local inclusions of the new phase. Since no PL band at ~1240 nm is found for the second type sample, we can also draw a conclusion about the role of oxygen in the 9R-Si phase formation, including the influence of oxygen recoil atoms in the irradiated SiO\(_2\)/Si system. Probably, the introduced oxygen atoms stabilize the defects in the Si substrate during annealing. These defects then induce stresses required for the new phase formation.

4. Conclusions

In the present work, the mechanism of the 9R-Si hexagonal phase formation in the cubic silicon substrate upon Kr\(^+\) ion irradiation of the SiO\(_2\)/Si system with subsequent thermal annealing has been studied. It is assumed that the formation of a new phase occurs under the action of mechanical stresses, whose relaxation upon annealing causes the phase transformation in the silicon substrate. The experiments on the irradiation of a silicon substrate without SiO\(_2\) film show that the generation of mechanical stresses occurs under the influence of two factors: the stresses associated with the incorporation of massive krypton ions into the SiO\(_2\) film and stresses caused by the defects arising...
from the penetration of recoil ions to the substrate. The role of the oxygen ions in the formation of the hexagonal phase has been demonstrated.

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