Mechanism of formation of light-emitting silicon hexagonal phase 9R-Si

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Abstract. A method of photoluminescence (PL) spectroscopy has been used to study the mechanism of formation of light-emitting hexagonal 9R-Si phase by krypton ion implantation into thermally grown oxide layer on silicon substrate with subsequent annealing. The PL band at ~1246 nm previously assigned to this phase appears at isochronous step-by-step annealing temperatures of 600 °C and higher as well as for one-step annealing. In addition, the PL bands at ~1324 and ~1408 nm previously observed in ion-implanted silicon and assigned to self-interstitial complexes are present in our case. The decrease in their intensities and simultaneous enhancement of the 9R-Si band are observed with increase in annealing temperature. It is concluded that the mechanical stresses arising in SiO$_2$/Si system during implantation are responsible for the formation of the 9R-Si phase.

1. Introduction

Until now, the increase of computing performance has been achieved by reducing the feature size of integrated circuits leading to the increase in transistor number per chip and clock speed. However, we cannot further rely on this trend because of fundamental limitations related to the insufficiently high signal rate transmission over metal interconnections. Active search for alternative approaches is underway now. An approach based on the replacement of electrical interconnections by optical ones, i.e. the creation of optoelectronic integrated circuits, is considered to be very promising. At the same time, the use of silicon as a main active material would be desired. Unfortunately, silicon is poor light emitter due to its indirect band structure. Therefore, it is of great importance to find the ways to improve the luminescent properties compatible with traditional CMOS technologies.

It has been established recently that some non-diamond-like silicon phases possess luminescence, the intensity of which exceeds the luminescence intensity of diamond-like silicon [1, 2]. This is one of the approaches to solve the problem, which consists in the creation on diamond-like silicon surface of a layer or regions of the corresponding allotropic modification of Si, for example hexagonal Si. However, most of the methods for synthesizing hexagonal silicon phases [3, 4, 5] are hardly compatible with modern silicon technology. Ion synthesis does not have this disadvantage. Another benefit of ion synthesis over other synthesis methods is also a high degree of controllability of the concentration of embedded atoms, the possibility of local phase synthesis, in particular by using focused ion beams.

There are few articles on the ion-beam formation of inclusions of hexagonal wurtzite-like (2H) Si phase under ion irradiation of diamond-like (3C) silicon [6, 7, 8], but the studies are not systematic. In
some cases, there are special implantation conditions, for example, the use of sample heating by ion beam [7] or heating of a substrate holder [8], when it is rather difficult to maintain a constant temperature. The luminescent properties of such inclusions are not presented. Thereby, the systematic studies of the Si “hexagonalization” processes under ion implantation and the mechanisms of hexagonal phase formation, as well as the investigation of luminescent properties are very important tasks.

It has been previously shown by us [9, 10, 11] that, at double implantation of Ga⁺ and N⁺ ions as well as at Kr⁺ implantation into silicon or dielectric films on silicon with subsequent annealing, the silicon regions form with another packing of the (111) planes compared to diamond-like silicon. Analysis of electron diffraction patterns shows that these regions are of the 9R-Si hexagonal type (hexagonalization degree is 2/3). Moreover, for the samples, in which this phase was obtained by implantation of krypton ions into SiO₂/Si substrate with subsequent annealing at 800 °C, the photoluminescence (PL) band peaked at 1242 ± 3 nm was found. According to the DFT band structure calculations, this PL emission was related to an indirect optical transition in 9R-Si. It was suggested (for the SiO₂/Si structure) that the formation of 9R phase is due to a relaxation of mechanical stresses at the interface with silicon subsurface layer. These stresses are associated with the action of ion-implanted SiO₂ film. In [11], the annealing was carried out by one step at the temperature of 800 °C. In the present work, for a more reliable judgment about the hexagonalization mechanism, the annealing was performed under different conditions – both one-step and step-by-step (isochronous) mode – combined with PL measurements after each annealing step.

2. Experimental

SiO₂ film with a thickness of 160 nm thermally grown on n-Si (100) wafer was implanted by Kr⁺ ions at the energy of 80 keV and dose of 5·10¹⁶ cm⁻². In accordance with the SRIM calculation [12], the mean projected ion range in SiO₂ was ~ 50 nm. The isochronous post-implantation annealing was carried out in vacuum chamber step-by-step at temperatures ranging from 600 to 950 °C and also at one-step at different temperatures. The time of each step and time of one-step annealing were 30 min. The PL spectra were measured at liquid nitrogen temperature with excitation by light-emitting diode at a wavelength of 530 nm and recorded in a standard lock-in scheme.

3. Results and discussion

PL spectra for the samples annealed in the step-by-step mode are shown in Figure 1. At the annealing temperature of 600 °C, three PL bands with maxima at 1324, 1408 and 1246 nm are observed. The position of the 1246 nm band coincides well with the PL band previously assigned to the emission of 9R-Si phase [11]. Other two bands were not observed in [11]. Their positions are very close to the positions of PL bands reported in [13] for silicon irradiated with Si⁺ ions. These PL bands were identified as related to defect complexes, which include self-interstitiall atoms [13]. In our case, the presence of such complexes is quite possible: according to the SRIM calculation [12] for the SiO₂ thickness of 160 nm, Kr⁺ ion energy of 80 keV and ion dose of 5·10¹⁶ cm⁻², the concentration of Frenkel pairs ~ 10²¹ cm⁻³ is produced in Si substrate near the interface with SiO₂ film, which exceeds significantly the one occurred in [13] (~ 10¹⁷ – 10¹⁹ cm⁻³) under the irradiation of Si with Si⁺ ions at the energy of 145 keV and dose of ~ 1·10¹² – 5·10¹³ cm⁻².

At the annealing temperature of 600 °C, the intensity of PL band related to the 9R-Si phase is significantly weaker than that for the other two temperatures. With increase in temperature of step-by-step annealing, the intensity of defect PL bands decreases with simultaneous enhancement of the 9R-Si PL band. The maximum intensity of the latter band is reached at the annealing temperature of 900 °C. After subsequent annealing at the temperature of 950 °C, this band disappears.

The behavior of PL spectra for the samples with one-step annealing is shown in Figure 2. As mentioned above, for the first annealing at 600 °C, three peaks are observed: two from defects and one from the 9R-Si phase. With increase in annealing temperature, the defect PL bands are weakened or
even disappear. However, the 9R-Si band also disappears at the temperatures higher than 700 °C in contrast to the step-by-step mode.

![PL spectra of silicon samples](image)

**Figure 1.** PL spectra of silicon samples with thermal oxide (160 nm) irradiated with Kr⁺ ions with subsequent step-by-step annealing.

Let’s consider the described regularities of PL behavior from the viewpoint of a hypothesis that the 9R phase forms under the influence of mechanical stresses. From this point of view, the hexagonalization occurs as a kind of relaxation of mechanical stresses localized at the interface layer of silicon. These stresses are created by the action of SiO₂ film implanted with krypton ions. This relaxation process in Si can occur only at sufficiently high temperatures, at which silicon becomes sufficiently plastic. On the other hand, with increase in annealing temperature, the stress relaxation also occurs in the SiO₂ film (viscous flow); therefore, the moving force of phase transition decreases. The resulting final degree of phase transformation is determined by the competition between these two processes, the result of which depends on annealing temperature. The absence or weakly pronounced hexagonalization at high temperatures for one-step annealing apparently indicates that in this case the stress relaxation process in SiO₂ is ahead of the hexagonalization process. (The difference from the result obtained in [11] for one-step annealing at 800 °C is apparently due to the difference in heating and / or cooling rates). On the other hand, in the case of step-by-step annealing, the process of hexagonalization at the second and next steps is promoted by the fact that this process no longer requires the passage of the nucleation stage of a new phase: its volume fraction increases by the growth of inclusions formed at previous steps; therefore, the 9R-Si PL is observed after final annealing at those temperatures, for which such PL is not observed at one-step annealing.

It is not surprising that PL from the 9R-Si phase vanishes at the highest used temperature of step-by-step annealing: the 9R-Si phase, unlike the diamond-like Si, is metastable, and at sufficiently high temperatures it should turn into the diamond-like phase. In general case, in addition to the “impurity” stresses associated with the implantation of krypton, thermal stresses also play a role. Since the atomic
radius of Kr (0.198 nm) exceeds the atomic radius of Si (0.118 nm) and O (0.074 nm), and the
temperature expansion coefficient of SiO$_2$ (6.1·10$^{-6}$ K$^{-1}$ at 400 K) is less than that of Si (3.5·10$^{-6}$ K$^{-1}$ at
400 K) [14], the action of implanted krypton is opposite to the action of thermal stresses.
The thermal desorption or aggregation of Kr atoms may be additional factors determining the final
degree of hexagonalization. The heating and cooling rate can also play important role. The influence
of these and other factors should be a subject of further investigation.

Figure 2. PL spectra of silicon samples with thermal oxide (160 nm) irradiated with Kr$^+$ ions with
subsequent one-step annealing.

4. Conclusions
The obtained results confirm the proposed model, according to which mechanical stresses are the
main moving force for the formation of 9R-Si phase when ions are implanted into SiO$_2$ film on Si. The
formation of a thin strained layer in Si under the action of SiO$_2$ film is consistent with the results of
molecular dynamics calculation for silicon covered with a layer of natural silicon dioxide [15].
Hopefully, the optimization of implantation and annealing conditions will improve the luminescence
intensity during the ion-beam formation of the 9R-Si light-emitting phase. This will create the
background for the application of ion-beam method in the manufacturing technology of silicon
optoelectronic chips. The excellent compatibility of this method with traditional CMOS technology
makes it particularly attractive.

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