Formation of hexagonal silicon regions in silicon

A A Nikolskaya, D S Korolev, A N Mikhaylov, A I Belov, A A Sushkov, D A Pavlov and D I Tetelbaum

Lobachevsky University, 23/3 Gagarin prospect, Nizhny Novgorod, 603950, Russia

E-mail: alena.nikolskaya.1994@mail.ru

Abstract. The synthesis of hexagonal phase of silicon (9R polytype) by ion implantation has been studied. Transmission electron microscopy reveals the 9R regions in a subsurface layer of silicon substrate after ion implantation and subsequent heat treatment. The results are discussed from the viewpoint of the effect of mechanical stresses on the hexagonal phase formation.

1. Introduction

Silicon is still the main material of semiconductor electronics. However, due to its indirect band structure, diamond-like silicon has a significant drawback – low efficiency of light emission, which prevents its use in new generations of devices based on optical and electro-optical phenomena. The main ways of solving this problem are the formation of regions of another phase with better luminescent properties (Ge, iron silicide, GaAs, GaN, silicon quantum dots in a dielectric matrix, etc.) on the silicon substrate, doping of silicon with a rare-earth impurity (Er), or a change of the silicon structure by external impact [1].

Despite a great amount of research carried out within the mentioned approaches, none of them have still found wide practical application. Another way is to create nanoregions with hexagonal structure within the ordinary silicon. The change of the symmetry type (transition to a new syngony) creates the prerequisites for a radical change in the band structure and improvement of the luminescence efficiency. Indeed, it has been shown theoretically and experimentally [2, 3] that hexagonal silicon has higher photoluminescence intensity than the usual diamond-like phase. However, there is still no method for synthesis of bulk crystals of hexagonal silicon, which are stable under normal conditions. Therefore, the existing methods for creating thin layers of this modification are of little use for practical purposes. Thus, the development of methods compatible with silicon technology for the production of sufficiently stable inclusions of hexagonal silicon and the study of their properties are relevant both from a fundamental point of view and in connection with the problem of overcoming the pointed disadvantages of silicon. Ion-beam treatment method is most compatible with the traditional methods of silicon technology. In [4], a method for synthesis of the hexagonal (2H) phase of Si by ion implantation in cubic silicon using the high-current irradiation with As’ ions under conditions of poor thermal contact of the sample with the holder for the realization of heating by ion beam was suggested. However, this method is not quite appropriate for practical usage.

In this work, the formation of hexagonal 9R-Si phase in the subsurface region of silicon after implantation of gallium and nitrogen ions followed by annealing has been for the first time revealed by the transmission electron microscopy (TEM).
2. Experimental

The silicon samples were cut from (100) n-Si wafers with the thickness of 380 μm. First, the sample was implanted by N$_2^+$ (20 keV, 2.6·10$^{17}$ at/cm$^2$) with 1100 °C post-implantation annealing. Then N$_2^+$ (5·10$^{16}$ at/cm$^2$) and Ga$^+$ (5·10$^{16}$ at/cm$^2$) ions were co-implanted with energies of 40 keV and 80 keV, respectively. The final annealing was performed at 800 °C (30 min) in a dry nitrogen atmosphere.

The {110} cross-sections of the synthesized samples were studied by TEM using the JEOL JEM-2100F microscope.

3. Results and discussion

A cross-sectional transmission electron microscopy image of the silicon sample is shown in Figure 1a. The preliminary 20 keV nitrogen implantation followed by annealing at 1100 °C was used to synthesize a layer of silicon nitride, which prevents the out-diffusion of implanted gallium from the sample during annealing [5]. The corresponding layers are seen on the microscopic image. The topmost layer is the epoxy which used for preparation. Beneath it, a layer with lighter contrast is seen, which is an ion-synthesized silicon nitride. Inside the latter (in its lower part) dark inclusions are visible, which are identified as inclusions of a gallium-containing phase. The silicon nitride film is separated from the modified silicon substrate by a wavy boundary. Below it, a relatively thick (> 100 nm) layer with a non-uniform contrast is located. The main attention was devoted to studying the structure of this layer. Note that the boundary between this layer and an unmodified substrate is at a depth substantially exceeding the projected ranges of Ga$^+$ and N$^+$ ions ($R_p = 60$ nm). The analysis of the images shows that, within this layer, there are some regions with the structure different from diamond-like silicon. An image obtained with atomic resolution (Figure 1b) allows us to identify the structure of the regions. Simulation of the diffraction pattern by Fourier transform is shown in Figure 1c.

The interpretation of such structure, which often arises in the case of heteroepitaxial growth of silicon on sapphire, is described in some detail in [6]. In Figure 1a, upon closer examination, an ordered arrays of twinning defects are observed in silicon structure, which on the (110) cross section are represented by two series of (111) planes with an angle of 70° 32’ to each other. There are four such series in the diamond structure, but only two of them can be seen on the (110) cross section.

The alternation of the (111) layers in the structure of diamond-like Si can be written as ...ABCABCABC... (or ...ccc...). In the presence of a twinning boundary, the alternation of layers looks like: ...ABCABCBCABC... (or ...ehc...), where Č points out the position of the twin boundary (stacking fault). If another twin boundary arises after a certain number of layers, the order of alternation of close-packed layers becomes the original one, and then a twin lamel (twin pair) appears. It is assumed that, at the rearrangement of a three-layer diamond packing within the regions, the lattice of which remains conjugate to the "defect-free" region of silicon substrate, an energy-optimal number of built-in twin pairs should be multiplied by three.

The main polytypes of diamond, containing simultaneously fragments of hexagonal and cubic packages are described in [7]. The primitive unit cell of one of these polytypes – 9R includes three periods in one direction, each of which in turn includes one fragment of the cubic packing ...ABCABCABC... and two fragments of the hexagonal packing (hhc). The stacking sequence in the 9R phase can be described as ... ABACACBCB ... The degree of hexagonality of this polytype is 2/3. The change in the periodicity of the packing in the direction perpendicular to the close-packed planes is confirmed by the fact that in the simulated diffraction pattern (Figure 1c) between the central reflection and the reflection, which corresponds to the interplanar distance $d_{111} = 0.313$ nm in diamond-like 3C-Si, there are two additional reflections (tripling the packing period). Since in this case a structure with hexagonal syngony is considered [8], these reflections can be assigned with four-digit indices, the respective values at interplanar distances (d) of which are $d_{0003} = 0.943$ nm; $d_{0006} = 0.471$ nm; $d_{0009} = 0.313$ nm (Figure 1c).
**Figure 1(a,b,c).** (a) High-resolution cross-sectional TEM image of silicon with pre-synthesized silicon nitride layer irradiated with Ga$^+$ and N$_2^+$ ions and annealed at 800°C; (b) enlarged image of the indicated square region; (c) Fourier-transform pattern for this image.

Figure 2 shows an image of the “hexagonalized” region, in which two orientations of the 9R phase are clearly visible with the angle between the respective arrays of planes of 70° 32’. This is also revealed on the picture of microdiffraction (Figure 2b), in which two additional reflections are observed along with the main reflections of 3C-Si.

The possible mechanism for the formation of the 9R-Si phase is as follows. First, a layer of silicon nitride is formed on the surface of substrate by ion-beam synthesis and high-temperature annealing (1100 °C). This layer, as shown by the XPS method [5], prevents gallium from leaving the sample due to out-diffusion. It is known that silicon nitride, in comparison with silicon, has a higher limit of plastic deformation. With ion implantation of nitrogen and gallium, a high level of elastic stress arises in this and underlying implanted layer, which exert a strong elastic influence on the underlying layers of the substrate. This creates a high level of stress in it. Then, annealing is carried out at a temperature of 800 °C. It is known that at such temperatures silicon becomes a plastic material, however, the mobility of dislocations (which plastic deformation is usually associated with) at such temperatures is very low. Therefore, the relaxation of elastic deformation occurs not by sliding dislocations, but by
shifting the atomic planes (111), leading to multiple twinning, and, as described above, “hexagonalization” with the formation of the 9R-Si phase. Since the elastic deformation decreases with depth, the formation of the 9R phase is limited by a boundary layer with a thickness of \( \sim 100-200 \) nm (see Figure 1a). In the absence of a Si\(_3\)N\(_4\) film, the stress needed for the formation of hexagonal phase is achieved only locally, so the transformation occurs, but the volume fraction of the 9R phase is low.

4. Conclusions
The work demonstrates for the first time the formation of hexagonal phase of 9R-Si upon ion implantation in silicon with thermal treatment. It is shown that a continuous layer of silicon nitride is formed by implantation of nitrogen ions in silicon and post-implantation annealing. During the subsequent double implantation of gallium and nitrogen ions, the hexagonal phase formation process

**Figure 2(a,b).** (a) High-resolution TEM image of a silicon region, which covers several adjoining hexagonalized regions with different orientations; (b) picture of microdiffraction for this region.
occurs in the silicon at the interface with the ion-synthesized Si₃N₄ film. A mechanism for the formation of hexagonal regions is proposed that includes the relaxation of mechanical stresses induced by ion implantation.

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