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Structural Peculiarities of A_3B_5 Nanocrystals Created in Si by Ion-Beam Synthesis

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We reported the structure peculiarities of nanocrystals formed in Si by means of high-fluence implantation at 25 and 500 °C followed by rapid thermal annealing (RTA). The structure of implanted samples has been investigated by means of transmission electron microscopy (TEM). The crystalline nature of the precipitates is proved by the Moiré fringe patterns presence in the TEM images. The Moiré fringe distance (Moiré period) is equal of 1.8 nm for small precipitates. This experimental value coincides with the calculated one for crystalline InAs. It is noted a Moiré period increasing in the case of large precipitates. We suppose that this feature is a result of surplus As or In atoms embedded in precipitates. One can see an interesting effect – "glowng" of nanocrystal/Si interfaces at the dark-field images of implanted and annealed samples. We ascribe this effect to a presence of misfit dislocation networks at the InAs/Si interfaces generated as a result of strain relaxation in highly mismatched InAs/Si system.

Keywords: Crystalline silicon, InAs nanocrystals, High-fluence implantation, Thermal treatment

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1. INTRODUCTION

With the increasing of miniaturization current Si technology approaches more and more the physical limits drawn by the material properties of Si. Currently used metal interconnections will cause serious problems in future such as heat penalty, nonacceptable delay and complexity, crosstalk. On-chip optical interconnections are believed to be able to overcome these problems. The quest is for an efficient light source operating at room temperature and preferably emitting in a narrow wavelength range. Red or near-infrared light would be very suitable for communication purposes. A light-emitting source based on silicon would be a radical solution. Unfortunately, Si is inapplicable to operate as a light emitter due to its indirect band gap of about 1.1 eV. This has motivated an intense research for light emitting materials which can replace Si but can be integrates well in the current Si technology. Light-emitting diodes and lasers based on A^3B^5 semiconductors show excellent technical qualities, but their integration into a silicon chip is problematical. Furthermore, it is impossible to grow direct band gap A^3B^5 materials epitaxially on Si wafers because of the large lattice misfit. A direct creation of narrow-gap A^3B^5 quantum dots (QDs) in crystalline silicon by ion implantation followed by thermal annealing is a promising approach to overcome this difficulty. Density and size of nanocrystals can be controlled by varying implantation and annealing conditions [1]. The advantage of ion implantation is its compatibility with industrial Si device production lines. In this technique, high-fluence ion implantation produces a supersaturation of one or more implanted species in the near-surface of crystalline or amorphous matrix. The embedded impurities then form precipitates within the host during thermal processing at elevated temperatures. Unfortunately, thermal processing of implanted crystals results not only in precipitation and radiation damage recovery. Negative consequences of thermal processing exist, too. High-fluence implantation of heavy ions results in a significant damage of Si crystalline lattice. Partly, a damaged crystal structure recovers during post-implantation annealing. At the same time a "secondary" defect formation (dislocation loops, microtwins) takes place after high temperature treatment. Thus, on the one hand complex defect structures are formed during implantation and annealing at elevated temperatures, which significantly influence the formation, the size, and the depth distribution of the precipitates. On the other hand, the existence of the precipitates has also a strong effect on the quality of the surrounding crystalline host after the post-implantation annealing. The aim of this work is to present our results on structural characterization of "Si - InAs nanocrystals" system.

2. EXPERIMENTAL

(100) Si wafers were implanted at 25 and 500°C subsequently with As (170 keV, 3.2×10^{16} cm^{-2}) and In (250 keV, 2.8×10^{16} cm^{-2}). After that, the implanted samples were annealed at 950 and 1050°C for 3 minutes using RTA in an inert ambient. A part of the samples implanted at the room temperature was additionally exposed to H_2^+ ions (100 keV, 1.2×10^{16} cm^{-2} in terms of atomic hydrogen). This procedure was performed to obtain an internal getter at a depth of about 500 nm during post-implantation annealing. A structure of the implanted samples was studied by means of TEM in plan-view geometry. The TEM investigations were performed using a Hitachi H-800 instrument operating at 200 keV. The samples prepared for the TEM measurements have to be transparent for probe electron beam. It is possible if this thickness does not exceed 150 - 200 nm. For this reason for detailed investigations of more deep regions into crystal bulk we combined PV-TEM preparation with the precise removal of thin layers from the surface of the sample.

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3. RESULTS AND DISCUSSION

Figure 1 depicts TEM-images of the samples after room temperature implantation and RTA.

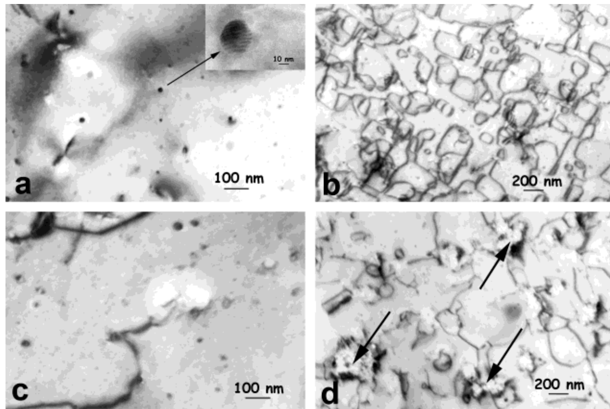

Fig. 1 – TEM images of the samples implanted at 25°C and annealed at 1050°C for 3 min. The samples with getter layer (a, b) and without getter layer (c, d)

On the plan-view images of the subsurface region up to depth of about 150 – 200 nm one can see precipitates. The size of ones varies in the range about of (5 – 40) nm). The crystalline nature of the precipitates is proved via the presence of Moiré fringe patterns in the nanocluster TEM images (inset in Fig. 1a). The Moiré fringes at precipitates are caused by the overlap of two crystalline lattices with closed parameters. In our experimental conditions it is possible a formation of In, As, and InAs crystallites. We have calculated Moiré fringe distance for the In, As, and InAs crystallites in Si matrix. The following equation has been used:

$$D = \frac{d_1 d_2}{|d_1 - d_2|},$$

where D is the distance between the Moiré fringes, and d_1 and d_2 are the first and the second interplanar distances of the lattice, respectively.

We have compared the calculated quantities with the values measured from the bright-field TEM images. The experimental value of 1.8 nm is in a good agreement with the calculated one of 1.818 nm for the {220} planes of crystalline InAs.

The layer of secondary defects is situated at the depths of 300 - 400 nm (b, d). The getter layer introduction does not affect the size and density of the nanocrystals. Though, the structure of the layer with secondary defects is different for samples with and without the getter. Thus, for the sample without the getter (d) elongated curved defects of dislocation type and the disordered region are observed at the depths of 300 - 400 nm (marked with arrows). The size of the disordered regions gets up to 500 nm. The layer with secondary defects for the sample with the getter consists of densely packed small dislocation loops (b). Figures 2 and 3 present TEM-images of the samples after "hot" implantation and RTA. One can see from Figure 2 that the "hot" implantation leads to a significant increase of the size and density of clusters in comparison with the room temperature one.

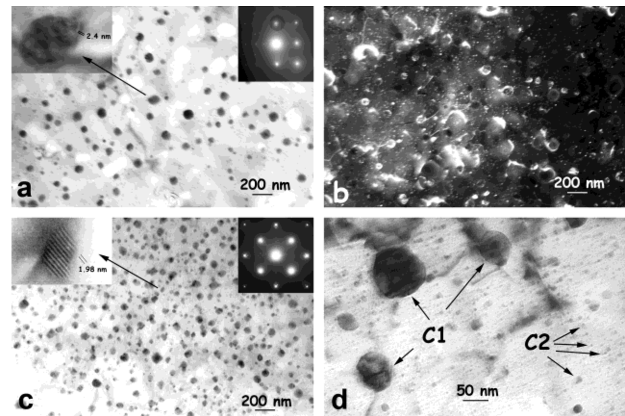

Fig. 2 – Bright-field (a, c, d) and dark-field (b) images of the samples implanted at 500 ºC and annealed for 3 minutes at 1050°C (a, b) and at 950°C (c, d). Right top insets are diffraction patterns and left top insets are precipitate images taken at high magnification (a, c)

The largest precipitates have a size of ~ 100 nm. In microdiffraction patterns (insets in a, c) reflections from microtwins are clearly visible. The density of precipitates in the samples after RTA at 950°C is higher in comparison with the samples annealed at 1050°C. The characteristic Moiré fringes are observed at the precipitates, too. However, for large inclusions the Moiré fringe period are larger than for small ones in the samples implanted at room temperature (Fig.1a, c). A tendency of Moiré period increasing is also observed with increasing sizes of incorporations.

In order to interpret the obtained Moiré patterns let us consider the results reported in [2]. In this paper the dependence of the Moiré fringe period on the quantum dot size, the presence of stress and the atoms of another sort was investigated for quantum dots InSb grown on a substrate InAs by liquid phase epitaxy. In particular, it was shown that for small QDs (less than 17 nm) the Moiré period corresponded to the calculated value for a pure material InSb. For larger ones (30 - 45 nm) the Moiré period was significantly larger than for a pure material. The authors showed that the increase of the Moiré period was observed due to the presence of arsenic atoms in QDs. In our case the increase of the Moiré fringe distance can also be associated with the presence of excessive amounts of As or In inside precipitates. In addition, the increase of the Moiré period can be caused by a partial loss of coherence and the presence of stresses inside large inclusions.

It should be noted that precipitates seem larger on the dark-field image because of "glow" of the boundaries between nanocrystals and the silicon matrix (Fig. 2b). A large number of small (2 to 5 nm) clusters are also present on the dark-field image. A bimodal distribution of cluster sizes is observed for samples annealed at 950°C, too (d). Figure 3 illustrates a structure difference for samples implanted in "hot" conditions and annealed at 950 and 1050°C.

One can see dislocations connected with large precipitates in the annealed samples. In addition, there are dislocations - precipitates conglomerates in the samples annealed at 950°C. Separate dislocations connected with precipitates and chains of precipitates connected with lines of dislocations form a cellular structure (*c, d*).

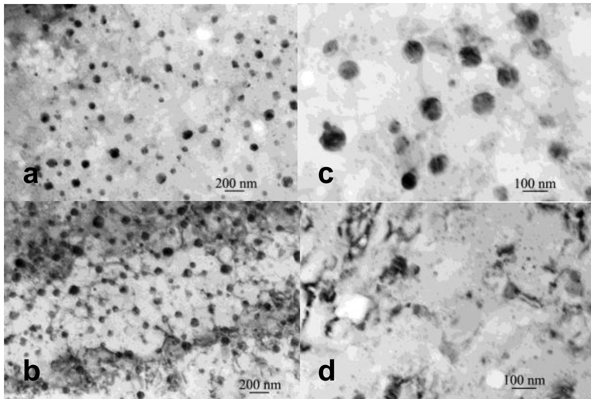

Fig. 3 – TEM images of the samples implanted at 500 °C and annealed at 1050 °C (a, b) and at 950 °C (c, d)

In order to explain an appearance of cellular structure let us discuss the data presented at [3]. The authors of [3] have been studied a strain relief of InN quantum dots grown on GaN/sapphire wafers. An average InN island diameter was equal to 73±12 nm, an average height - 12±2 nm. This values and large precipitate size from our experiment are similar. In highly mismatched heterosystems, it is well-known that the strain is relieved by the generation of an array of geometrical misfit dislocations at the interface between the two materials [4, 5]. The authors of [3] have been carried out an analysis of Moiré fringe patterns on InN QDs and a computer processing of high-resolution TEM images. It has been shown that a strain relief at InN QDs is accomplished due to the generation of a 60°-misfit dislocation network at the InN/GaN interface. When they are close to the boundary of the quantum dot, the dislocations bend due to the free surface forces, thus forming a network of threading dislocations surrounding the QD. Threading dislocations do not appear to be present inside the dots. Though, it has been found separate dislocations propagated into GaN matrix.

A lattice mismatch for InAs/Si system is equal of 11.5%. The formation of large InAs precipitates should be result in an appearance of significant mechanical strains at «InAs nanocrystal/Si» interfaces. In our case the same strain relief mechanism can act as for the InN/GaN system that discussed above. Probably, an effect of «glowing" nanocrystal/Si interfaces (Fig. 2b) is due to dislocation networks formation close the precipitates. It is very likely, the dislocation in silicon matrix beside the nanocrystals (Fig. *3c, d*) are created because of strain relief at InAs/Si interface. If a large precipitate density is high enough the dislocations at high temperature can interact and create conglomerates like cellular structures.

4. CONCLUSIONS

The structural characteristics of the precipitates created in silicon matrix by means of (As + In) ion implantation followed by RTA have been studied using TEM.

It has been shown that small inclusions with size from 5 to 40 nm are formed in the samples implanted at room temperature. The crystalline nature of inclusions is proved by the presence of Moiré fringe patterns in the nanocluster TEM images. The precipitates are identified as InAs nanocrystals from a comparison of calculated and measured Moiré fringe distances.

A getter introduction by means of an additional implantation of H_2^+(100 keV, $1{,}2\times10^{16}$ cm^{-2}) does not influence on the precipitate density and size, but results in the formation of layer of densely packed small dislocation loops at the depth nearly of 300 – 400 nm.

"Hot" implantation conditions lead to remarkable increasing of size (up to 100 nm) and density of precipitates formed after annealing. It is marked an increasing of Moiré fringe period for large precipitates. We ascribe it to a presence of excessive amounts of As or In inside precipitates.

The effect of precipitate interfaces "glowing" was observed at the dark-field TEM images of large precipitates. We attribute it to the formation of a dislocation network around each precipitate due to relaxation of mechanical stresses on the boundaries between the nanocrystals and the silicon matrix. The process of stress relaxation at the boundaries of precipitates also leads to the formation of individual dislocations. In case of a high density of precipitates certain dislocations can interact with each other to form larger congestion such as cellular networks.

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