EFFECT OF IMPLANTATION AND ANNEALING REGIMES ON ION-BEAM SYNTHESIS OF InAs NANOCRYSTALS

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We reported the formation of nanosized InAs crystallites in silicon wafers by means of As (245 keV, \(4.1 \times 10^{16} \text{ cm}^{-2}\)) and In (350 keV, \(3.7 \times 10^{16} \text{ cm}^{-2}\)) implantation. The implantation was carried out at 25 and 500 °C. In order to verify the effect of getter on precipitates growth an additional procedure was carried out for the samples implanted with As and In species at the room temperature. This procedure included the implantation of \(\text{H}_2\) ions with the energy of \(1.2 \times 10^{16} \text{ cm}^{-2}\). Afterwards, the samples were annealed at 900 °C for 60 min in inert ambient. In order to characterize the implanted layers, Rutherford backscattering spectrometry in combination with the channelling (RBS/C) and transmission electron microscopy (TEM) techniques were used. TEM has revealed InAs nanocrystals in implanted samples after the annealing. It has been shown that average size and size distribution of InAs clusters depend on implantation temperature and annealing duration. Significant diffusional redistribution of implanted species has been revealed after “hot” implantation and post-implantation annealing. We have suggested that it is caused by non-equilibrium diffusion. The radiation-enhanced diffusivities at “hot” implantation have been determined for the abovementioned experimental conditions.

Keywords: crystalline silicon, high-fluence implantation of As and In ions, InAs nanocrystals

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1. Introduction

InAs is a narrow-gap A3B5 semiconductor with direct gap. Synthesis of InAs quantum dots inside the crystalline Si is of interest for applications in optoelectronic devices operating in IR range. MBE-technique has been used for the formation of an ensemble of InAs clusters on the Si (001) [1]. Such clusters covered with a Si cap layer show intense luminescence at 1.3 μm at 7 K. The other technique for fabricating of III-V quantum dots is high-fluence ion implantation followed by thermal treatment. InAs nanoclusters have been formed using this method in Si and SiO2 [2, 3]. The advantage of ion implantation is its compatibility with industrial device production lines. In our previous paper [4] we have reported the formation of InAs nanoclusters in Si matrix by high-fluence ion implantation at the elevated temperature followed with the annealing. Modifying the regimes of implantation and post-implantation annealing may provide a way to control the size and crystalline quality of the compound precipitates thus formed.

The aim of this work is to study the effects of the implantation and annealing regimes on ion-beam synthesis of InAs nanocrystals. We also present the depth concentration profiles of In and As atoms implanted in silicon at room and elevated temperature and analyse a diffusional redistribution of embedded impurity due to the post-implantation annealing.

2. Experiment

Single-crystalline n-doped (100) Si wafers were implanted subsequently with As and In ions. In accordance with [3] such a sequence of implantation results in the formation of smaller InAs crystals with a more
uniform size distribution in comparison with the case of In ions implanting first. In order to evaluate the effect of the implantation temperature a part of samples was implanted at the room temperature and another one at 500 °C. The ion energies and fluencies for arsenic were 245 keV and 4.1 \times 10^{16} \, \mu \text{m}^{-2} and for indium 350 keV and 3.7 \times 10^{16} \, \mu \text{m}^{-2}. In order to obtain maximum impurity concentrations of \approx 4.5 \times 10^{21} \, \text{cm}^{-3} at a depth of approximately 150–180 nm for both ion species, the distributions of species to be implanted were calculated by the SRIM’2003 code. In order to verify the effect of getter on precipitates growth an additional procedure was carried out for the samples implanted with As and In ions at the room temperature. This procedure included the implantation of H^+ ions with the energy of 100 keV at a fluence of 1.2 \times 10^{16} \, \text{cm}^{-2}. It was performed to create a deep damaged layer acting as an inner getter during the post-implantation annealing. Afterwards, the part of samples were annealed in an inert ambient at 900 °C for 60 min. The depth distributions of As and In into the silicon matrix were analysed using RBS. In all cases the RBS measurements were performed with 1.4 MeV He^+. The structural-phase modifications after annealing have been studied by means of transmission electron microscopy in cross-section (X) geometry using a Hitachi H-800 instrument operating at 200 keV.

3. Results and discussion

3.1. RBS data

Figure 1 represents RBS spectra of as-implanted at room temperature and annealed samples. At the random spectra one can see the implantation at the room temperature results in an amorphous layer formation in subsurface region. In the region of He^+ ions backscattering at impurities (channel numbers from 340 to 460) a superimposing of peaks from As and In is observed. The RBS spectra of room temperature implanted samples with getter and without it are entirely coincided. Due to this reason the RBS spectra of the samples with the getter are not shown. A comparison of random spectra of as-implanted and annealed samples reveals the impurity redistribution owing to intensive diffusion towards the surface and into the bulk during the annealing. Analysis of random and aligned spectra indicates the incorporation of more than a half of impurity atoms into the regular lattice sites for the room temperature implanted samples after the annealing.

Figure 2 shows RBS spectra of as-implanted at elevated temperature and annealed samples. At the random spectrum a “downfall” in the region of channel numbers from 180 to 200 is less expressed in comparison with a case of the room temperature implanted samples. The intensities of embedded impurities peaks are smaller, too. An increasing of the yield of backscattered He^+ ions in the region of channel numbers from 170 to 190 is related, in our opinion, to the existence
of a defect zone located deeper than the impurity maximum. From the analysis of random and aligned spectra one can see the incorporation of impurity atoms into the regular lattice sites during the implantation. These peculiarities of “hot” implantation were observed in our previous experiments on InAs nanocrystals formation, too [4]. In the case of “hot” implantation the incorporation of more than a half of impurity atoms into the regular lattice sites is registered after the annealing. It should be noted that the aligned spectrum yield of backscattered He$^+$ ions of the implanted at $500 \pm C$ and annealed samples resembles the random spectrum yield more than that for the room temperature implanted and annealed samples. In other words, the crystal lattice recovery after the annealing of the room temperature implanted samples is more expressed than that for implanted at $500 \pm C$ samples.

The depth distributions of In and As in the implanted samples were evaluated using RBS/C. Strictly speaking, the analysis of As and In depth profiles was impracticable due to an overlapping of As and In peaks. In order to solve this problem, the RBS spectra of 1.4 MeV He$^+$ ions were registered at two angles of ions’ incidence: normally and at $50^\circ$ in respect of the surface. It allowed us to separate peaks from As and In and calculate the depth profiles for the both implanted species. In order to calculate these profiles, the RBS spectra were simulated until the whole coincidence with the experimental spectra registered for two angles of ion incidence.

Figure 3 represents the calculated (SRIM) and obtained from RBS spectra depth profiles of As and In atoms implanted in silicon at 25 and $500 \pm C$. It should be noted that at given ion energies the Gaussian distribution describes rather well both the experimental and the theoretical depth profiles. Thus, the noticeable diffusion redistribution of impurities embedded at room temperature is not revealed even under high-fluence implantation conditions. One can see that “hot” implantation is accompanied by the significant diffusion redistribution of embedded atoms. The diffusion of both species towards the surface as the most effective sink for structure defects is predominant. The diffusion into the bulk of Si crystal is observed, too. The analysis of Fig. 3 reveals the loss of essential part of implanted atoms during “hot” implantation treatment. The calculated loss of As and In atoms amounts to 11.2 and 4.8%, respectively. The calculations have not predicted any noticeable impurity redistribution due to equilibrium thermal diffusion at the implantation temperature of $500 \pm C$. The impurity redistribution under the influence of equilibrium thermal diffusion starts at $T_{\text{impl}} = 900 \pm C$ only. The radiation-enhanced diffusivities of In and As atoms in Si at $500 \pm C$ were calculated using a numerical model described in Ref. [5]. The model takes into account the effects of ion-beam sputtering and radiation-enhanced diffusion. The radiation-enhanced diffusivities were determined by means of fitting of depth concentration profiles to the experimental ones. In the case of implantation at $500 \pm C$ we obtained diffusivity values of $D_{\text{As}} = 2.06 \times 10^{-17} \text{cm}^2/\text{s}$.
Fig. 3. (a) Calculated (SRIM 2003) and obtained from RBS spectra depth profiles of As and In atoms in silicon implanted (b) at the room temperature and (c) 500 °C.

and $D^*_{In} = 6.94 \times 10^{-18}$ cm$^2$/s. These values are much larger than the calculated equilibrium thermal diffusivities of In and As atoms at 500 °C. Apparently, embedded species redistribution experimentally observed at $T_{impl} = 500$ °C is resulted from non-equilibrium radiation-enhanced diffusion caused by the migration of “impurity atom – radiation defect” complexes. Figure 3 shows the depth concentration profiles of As and In atoms implanted in silicon at 25 and 500 °C and annealed at 900 °C samples. One can see from Fig. 3 that a rate of the implanted impurity loss increases significantly due to the annealing.

The high-fluence co-implantation of heavy ions such as In and As into silicon matrix leads to creation of system with high concentrations of implanted species as well as high densities of radiation defect complexes. Obviously, a decomposition of complex structure defects (microwtins and dislocation loops) takes place during the annealing. It is accompanied with the generation of great amount of point defects such as interstitial silicon atoms. It might stimulate the diffusional redistribution of implanted impurity by means of the diffusion of complexes “interstitial silicon atom–As” and “interstitial silicon atom–In” via interstitial mechanism.

3.2. TEM data

XTEM measurements show the formation of a heavily damaged crystalline layer with a thickness of about 300 nm after the (As+In) implantation (not shown). The disordered layer contains microwtins and precipitates. The annealing results in a rearrangement of the defect structure of the damaged layer combined with a noticeable recovery of the crystalline structure.

Figure 4 represents bright-field XTEM images of the precipitates for the annealed samples. The TEM image of the sample implanted at 500 °C shows the presence of faceted nanocrystals with the sizes from 2 to 70 nm. An interesting result has been obtained for the annealed sample implanted at the room temperature with As+In ions and afterwards additionally implanted with H$^+$ ions to create a getter layer (Fig. 4(a, c)). One can see the higher level of disorder in comparison with the sample implanted at 500 °C. Indeed, the subsurface damaged layer includes inclined dislocations and microcracks while the deep damaged layer at a depth of about 500 nm is characterized by a higher density of dislocation loops (see Fig. 4). At the same time the smallest clusters are registered in this sample. Their size ranges from 2 to 10 nm. A detailed investigation reveals that these precipitates are identical ones with the smallest clusters observed in the sample implanted at 500 °C (Fig. 4(d, e)). The crystalline nature of the precipitates is proved by the presence of moiré contrast in the TEM images. We have analysed the distance between the moiré bands using the procedure described in [4]. The experimental value of distance between the moiré bands is 1.8 nm (see insert in Fig. 4(c)). It is in a good agreement with the calculated one of 1.818 nm for the superposition of InAs and Si {220} planes. Thus, a layer with InAs crystallites is formed.
Fig. 4. Bright field cross-section images of the InAs precipitates in silicon matrix. Silicon has been implanted at (a, c) room temperature and (b, d) 500 °C with As (4.1 × 10^{16} \text{ cm}^{-2}) and In (3.7 × 10^{16} \text{ cm}^{-2}) and then annealed at 900 °C for 60 min. (e) Image with higher magnification of the precipitates in the sample implanted at 500 °C. In order to verify the effect of getter on precipitates growth an additional procedure was carried out for the samples implanted with As and In species at the room temperature. This procedure included the implantation of H^+_2 ions (100 keV, 1.2 × 10^{16} \text{ cm}^{-2}) before the high-temperature treatment.

In the annealed samples, in our previous paper the InAs nanocrystal formation in Si matrix implanted at 500 °C with 5 × 10^{16} \text{ }\text{As}^+/\text{cm}^2 and 4.5 × 10^{16} \text{ }\text{In}^+/\text{cm}^2 and annealed at 900 °C for 45 minutes have been studied [4]. Under the experimental conditions used in [4] the size of the precipitates ranges from 2 to 50 nm. However, most of the clusters had dimensions between 3 and 6 nm. Thus an increase of annealing duration results in a broader nanocrystal size distribution and larger average nanocrystal sizes. A possible reason for that could be the Ostwald ripening process in which larger clusters grow at the expense of smaller clusters. So the cluster size seems to be controllable in certain limits via the annealing time.

4. Conclusion

InAs nano-precipitates have been formed in crystalline silicon by high-fluence implantation at the room temperature and at 500 °C followed with the furnace annealing. In the case of the implantation at 500 °C the cluster size ranges from about 2 up to 70 nm. A comparison with the results of [4] has shown that the size of nanocrystals implanted at elevated temperature is influenced by the annealing time.

Interesting results have been obtained for the sample implanted at the room temperature with As+In ions and afterwards additionally implanted with H^+_2 ions. The higher level of disorder in comparison with the sample implanted at 500 °C has been found for this sample after the annealing. At the same time the smallest InAs clusters are registered in this sample. Their size ranges from 2 to 10 nm. Thus, for samples implanted at the room temperature we have obtained the most narrow size distribution and the smaller average cluster size. The possible reason of these phenomena may be an effect of getter layer formed as a result of H^+_2 implantation. A detailed study of InAs precipitation
in samples implanted at the room temperature is in progress.

RBS data analysis shows the better crystalline lattice recovery after the annealing for the room temperature implanted samples in comparison with the samples implanted at 500 °C.

A significant loss of both implanted species has been revealed as a result of “hot” implantation conditions and post-implanted annealing. We have suggested that it is caused by non-equilibrium enhanced diffusion. The radiation-enhanced diffusivities have been determined for implantation at 500 °C. The diffusivity values of \( D_{58} = 2.06 \times 10^{-17} \text{ cm}^2/\text{s} \) and \( D_{35} = 6.94 \times 10^{-18} \text{ cm}^2/\text{s} \) have been obtained using the model that takes into account the effects of ion-beam sputtering and radiation-enhanced diffusion.

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References


IMPLANTACIJOS IR ATKAITINIMO REŽIMŲ ĮTAKA JONŲ PLUOŠTELIŲ SINTETINANT InAs NANOKRISTALUS

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Santrauka

Aprašytas nanomatmenų InAs kristalų silicio matricoje susidarymas implantuojant As (245 keV, 4,1 \(^\times\) \(10^{16} \text{ cm}^{-2}\)) ir In (350 keV, 3,7 \(^\times\) \(10^{16} \text{ cm}^{-2}\)) atomus. Implantuota esant 25 ir 500 °C temperatūrai. Norint patvirtinti geterio (sutraukimo) reiškinį nuosėdos augant, As ir In implantuoti pavyzdžiui papildomai apdoroti kambario temperatūroje: jie apšvietinti 100 keV energijos 1,2 \(^\times\) \(10^{16} \text{ cm}^{-2}\) \(H^+\) jonų siauru. Po to pavyzdžiai buvo 60 min atkaitinami inertinėje aplinkoje 900 °C temperatūroje. Implantuotems sluoksniams apibūdinti naudoti Rezerfordo atgalinės sklai-