Ion-beam synthesis of GaN in silicon

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Abstract. The structure and composition of a subsurface silicon layer subjected to a dual implantation of Ga and N ions with subsequent annealing have been investigated using X-ray photoelectron spectroscopy, electron spin resonance, X-ray diffraction, Raman microscopy, transmission electron microscopy. The results indicate a possibility of ion-beam synthesis of GaN composite nanostructures in silicon-based materials.

1. Introduction

New development stage of electronic technologies is characterized by the transfer from conventional microelectronics to optoelectronics and integrated optics. This requires synthesis of light emitters and photodetectors on a single chip for different ranges of wavelengths, including the ultra-violet range. A key material of conventional microelectronics – silicon – cannot be used as an efficient light source because of its indirect band gap. This fact has stimulated the search for other light-emitting materials compatible with silicon technology. Such a compatibility would allow the usage of tremendous long-term achievements of silicon technology and could give high economic effect. For example, the cost of a silicon wafer is seven times lower than that of a GaAs wafer of the same area.

It is known that LEDs, lasers and photodetectors on the basis of III-nitrides, in particular gallium nitride, have excellent performance as well as high resistance to radiation, chemically aggressive environment and temperature. However, there is a problem of high cost of GaN and difficulties of its integration into a silicon or other low-cost substrates. Fabrication of high-quality epitaxial III-nitride layers on silicon is difficult due to the high lattice mismatch and differences in thermal expansion coefficients of the materials [1]. It results in a high dislocation density (more than 1·10^6 cm^-2) and the degradation of device performance.

One of the perspective solutions to this problem is the ion-beam synthesis of III-V (especially GaN) nanocrystals by dual (sequential) ion implantation into silicon or into dielectric films (SiO_2, Si_3N_4, Al_2O_3, HfO_2, etc.) deposited on silicon substrate. An advantage of ion implantation over the other synthesis methods (like epitaxy) is in a high controllability of the implanted layer composition and concentration of implanted atoms (not restricted by the thermodynamic solubility limit), an ability of local phase synthesis with focused implantation, and perfect compatibility of this method with the existing CMOS-technology. Using ion implantation with subsequent annealing permit to synthesize not only continuous layers, but semiconductor nanocrystals in different matrices, including amorphous matrices.
The possibility of ion-beam synthesis of GaN nanocrystals is based on the fact that nanocrystals of some semiconductor compounds of a number of III-group elements have been already synthesized in silicon, SiO$_2$ and Al$_2$O$_3$ and, in some cases, the expected light emission has been demonstrated [2,3,4,5,6]. However, the literature on GaN ion synthesis in silicon or in Si-compatible matrices is almost absent. Only one research group [7,8] has reported on the synthesis of light-emitting GaN crystallites in SiO$_2$ and Al$_2$O$_3$ matrices after co-implantation of gallium and nitrogen ions and subsequent annealing in ammonia atmosphere.

In addition to the applications in optoelectronics and integrated optics, GaN nanocrystals in different matrices could be used as ultra-violet detectors, solar panels with high efficiency (owing to the conversion of shortwave part of solar radiation into electric energy), and possibly as semiconductor ferromagnetic material for spintronic devices, non-classical photon emitters in quantum communication devices, in biosensors, etc. GaN-based nanostructures are also important for biomedical applications because GaN is almost non-toxic material.

Thus, the problem of GaN nanocrystals ion synthesis in different matrices, especially silicon-compatible materials, is very relevant. In this paper, the possibility of GaN synthesis in Si matrix by dual implantation of gallium and nitrogen ions with subsequent annealing is studied.

2. Experimental
The investigated GaN-nanostructures were obtained by dual implantation in silicon of Ga$^+$ ions with energy of 80 keV and N$_2^+$ ions with energy of 40 keV. Implantation of molecular N$_2^+$ ions instead an N$_1^+$ ions was used to shorten the duration of implantation (in this case, every N$_2^+$ ion splits into two ions with two time lower energy at the first collision with target atoms). Ion implantation was carried out in two ways: first, Ga$^+$ ions were implanted with the dose of 5·10$^{16}$ cm$^{-2}$ or 1·10$^{17}$ cm$^{-2}$, and then, N$_2^+$ ions with the corresponding doses of 2.5·10$^{16}$ cm$^{-2}$ or 5·10$^{16}$ cm$^{-2}$ were implanted and vice versa.

Energy and doses of ions were chosen to obtain the correspondence of Ga and N depth distributions according to the SRIM calculation [9].

The ion-irradiated samples were annealed at 900°C (30 min) in dry nitrogen atmosphere. The structure, chemical composition of implanted layers and state of the implanted atoms were analyzed by several techniques: electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) with depth profiling by Ar$^+$ ion etching, X-ray diffraction (XRD) in Bragg-Brentano geometry and confocal Raman spectroscopy/microscopy.

Some of the samples before and after annealing were investigated by the cross-section transmission electron microscopy (XTEM) using the JEOL JEM-2100F microscope operated at accelerating voltage of 200 keV. The electron beam was focused to the diameter of 0.7 nm in the bright-field scanning transmission electron microscopy (STEM) mode, which was used also for the analysis of local chemical composition by the INCA Energy TEM 250 X-MAX X-ray energy-dispersive spectrometer (EDS). The cross-sections were prepared by standard techniques on the Gatan equipment.

3. Results and discussion
The ESR data (figure 1) show that ion implantation into the Si surface layer transforms it into the amorphous state (typical dangling bonds with $g = 2.0055$ are detected with the concentration in the range of $5·10^{17}$–$6·10^{18}$ cm$^{-3}$ depending on the order and dose of ion implantation). After annealing at 900°C, the defect concentration is reduced, but remains still noticeable. It is related to the non-ideal crystalline structure – disordered areas such as grain boundaries and mosaic blocks in the implanted layer.
Figure 1. ESR spectra of silicon samples subjected to irradiation with gallium and nitrogen ions: before (a) and after (b) annealing at 900°C.

XRD data (figure 2) show that there is not any crystalline phase in the silicon subsurface layer after ion implantation. After annealing, the recrystallized Si is formed at the depth where amorphization has occurred. The formed crystallites do not have preferential orientation, this leads to the appearance of Si (111) XRD line for the lower dose. For the higher dose, Si line has lower intensity. The XRD lines from GaN are not revealed probably due to a small volume fraction of GaN.

Figure 2. Diffraction patterns of Si samples irradiated by N and Ga ions with different sequence and doses, before annealing (a) and after annealing (b) at 900°C.

On the Raman spectrum (figure 3) for Si implanted by Ga\(^+\) (5\(\times\)10\(^{16}\) cm\(^{-2}\)) and N\(_2^+\) (2.5\(\times\)10\(^{16}\) cm\(^{-2}\)), then annealed at 900°C, we can clearly observe several Si-related peaks. The main peak (521 cm\(^{-1}\)) is asymmetric due to the existence of Si nanocrystallites (nc-Si) in the implanted layer. Inclusions with the sizes about hundred nanometers are identified on image of a part of the surface obtained by scanning with primary laser beam. Raman scattering in the synthesized GaN phase is revealed as a weak peak, the small intensity of which can be also related to low volume fraction of GaN phase.
Figure 3. Raman spectrum of Si implanted by Ga\(^+\) (5·10\(^{16}\) cm\(^{-2}\)) and N\(_2^+\) (2.5·10\(^{16}\) cm\(^{-2}\)) after annealing at 900°C. Surface morphology is illustrated on the inset (frame size 50×50 μm).

The XTEM data show (figure 4), that there is a clear edge between the irradiated layer and underlying substrate before annealing. The depth of the edge agrees well with the ion projected range. Electron diffraction has not revealed any crystallites in the irradiated layer, but the existence of small nanoclusters could be observed as dark heterogeneity on the XTEM image.

![XTEM images of Si sample irradiated with Ga\(^+\) (5·10\(^{16}\) cm\(^{-2}\)) and N\(_2^+\) (2.5·10\(^{16}\) cm\(^{-2}\)) before (a) and after (b) annealing at 900°C. Electron diffraction picture for the implanted layer after annealing is shown on the inset.](image)

There is a lot of disoriented nanocrystals in the implanted layer after annealing, which are identified with silicon. A dark layer is located closer to the edge of the implanted layer; presumably, this is a recrystallized Si layer coherent to matrix. The corresponding diffraction picture is shown on the inset. Interpretation of this diffraction picture doesn’t reveal any crystalline phases except silicon. However, the EDS analysis shows that nanometer-sized areas with the most pronounced dark contrast contain a high concentration of Ga (up to 25 at.%) and correspond to the Ga-rich nanoclusters in silicon matrix.

The XPS data have given an integral information about the chemical and phase composition of Si samples irradiated with Ga\(^+\) (5·10\(^{16}\) cm\(^{-2}\)) and N\(_2^+\) (2.5·10\(^{16}\) cm\(^{-2}\)) ions in a different order, without and
after annealing at 900°C. The depth distributions of species and their chemical bonding have been analyzed based on the position, shape and intensity of the corresponding photoelectron lines.

The depth distributions of gallium and nitrogen in the implanted Si layer before and after annealing are demonstrated in figure 5. The SRIM-calculated ion profiles are also shown. The distribution of gallium bonded to nitrogen is shown in figure 6. From the analysis of these data and data for distribution of nitrogen bonded to gallium or silicon (not shown), we can come to the following conclusions.

Figure 5. The depth distribution profiles of Ga and N for different sequences of implantation, before and after annealing at 900°C.

The excess of nitrogen concentration over the gallium concentration indicates that a part of implanted gallium ions is lost during implantation; this conclusion should be considered as preliminary. The distribution of implanted atoms (gallium and nitride) before annealing is wider than estimated. This could be explained by the radiation enhanced diffusion during the implantation process, which isn’t a trivial fact and can be explained by disordering of the structure caused by ion implantation of high doses of heavy ions (Ga⁺).

Figure 6. The depth distribution profiles of Ga bonded to N.

As a result of annealing Ga atoms migrate to the surface. Some of them leave the sample, others form elementary gallium and some part of Ga atoms (up to 2 at.%) reacts with nitrogen. Migration of impurity atoms to the surface was detected before, when Ga⁺ and N⁺ were implanted in SiO₂ film [8].
This was a result of diffusion enhancement because of radiation defects. When Ga\(^+\) is implanted before N\(_2^+\), the migration of gallium atoms to the surface after annealing is more significant than for the reverse sequence. Those nitrogen atoms which have not reacted with gallium form bonds with silicon (SiN\(_x\), Si\(_3\)N\(_4\)).

4. Conclusions

Ion synthesis of gallium nitride is difficult because of the diffusion and evaporation of Ga atoms forming phases of elementary Ga and silicon nitride. At the used synthesis conditions, we are able to synthesize Ga-N bonds with the concentration about several atomic percents. Further optimization would allow improving the conditions of gallium nitride synthesis. For that aim, we need to change annealing regime and irradiation dose. Also we should use oxygen or nitrogen coating layer to prevent the evaporation of gallium atoms.

The work is supported by the Ministry of Education and Science of the Russian Federation (RFMEFI58414X0008).

References

[1] Kumar M, Roul B, Bhat T N, Rajpalke M K, Misra P, Kukreja L M, Sinha N, Kalghatgi A T and Krupanidhi S B 2010 Materials Research Bulletin 45 1581
[2] White C W, Budai J D, Zhu J G, Withrow S P and Aziz M J 1996 Appl. Phys. Lett. 68 2389
[3] White C W, Budai J D, Zhu J G, Withrow S P, Zuh R A, Hembree D M, Henderson D O, Ueda A, Tung Y S, Mu R and Magruder R H 1996 J. Appl. Phys. 79 1876
[4] Kanemitsu Y, Tanaka H, Fukunishi Y, Kushida T, Min K S and Atwater H A 2000 Phys. Rev. B 62 5100
[5] Komarov F, Vlasukova L, Milchanin O, Mudryi A, Dunetz B, Wesch W and Wendler E 2012 Phys. Stat. Sol. A 209 148
[6] Prucnal S, Facsok S, Baumgart C, Schmidt H, Liedke M O, Rebohle L, Shalimov A, Reuther H, Kanjilal A, Mucklich A, Helm M, Zuk J and Skorupa W 2011 Nano Letters 11 2814
[7] Borsella E, Garcia M A, Mattei G, Maurizio C, Mazzoldi P, Cattaruzza E, Gonella F, Battaglin G, Quaranta A and D’Acapito F 2001 J. Appl. Phys. 90 4467
[8] Borsella E, de Julian Fernandez C, Garcia M A, Mattei G, Maurizio C, Mazzoldi P, Padovani S, Sada C, Battaglin G, Cattaruzza E, Gonella F, Quaranta A, D’Acapito F, Tagliente M A and Tapfer L 2002 Nucl. Instr. Meth. B 191 447
[9] Ziegler J F, Ziegler M D and Biersack J P 2010 Nucl. Instr. Meth. Phys. Res. B. 268 1818