Semiconductors, 2024, Vol. 58, No. 10

Micro-Raman spectroscopy study of radiation defects formed by a focused Ga^+ ion beam in $GaAs/Al_{0.3}Ga_{0.7}As$ structures

© G.V. Voznyuk[1], I.N. Grigorenko[1], A.S. Lila[1,2], M.I. Mitrofanov[1], A.V. Babichev[2], A.N. Smirnov[1], D.N. Nikolaev[1], S.O. Slipchenko[1], V.Yu. Davydov[1], A.F. Tsatsulnikov[3], V.P. Evtikhiev[1]

[1] Ioffe Institute,
194021 St. Petersburg, Russia
[2] ITMO University,
197101 St. Petersburg, Russia
[3] Submicron Heterostructures for Microelectronics, Research and Engineering Center,
Russian Academy of Sciences,
194021 St. Petersburg, Russia

E-mail: glebufa0@gmail.com

Received May 3, 2024
Revised July 31, 2024
Accepted October 30, 2024

Raman spectroscopy was used to investigate lithographic patterns formed by a focused Ga^+ ion beam in a $GaAs/Al_{0.3}Ga_{0.7}As$ heterostructure. The results showed that radiation defects accumulate during etching, with their concentration dependent on ion energy and dose. By optimizing etching and annealing conditions, it is possible to restore the crystal perfection of the heterostructure.

Keywords: Micro-Raman spectroscopy, focused ion beam, radiation-induced defects, heterostructure.

DOI: 10.61011/SC.2024.10.59943.6609A

1. Introduction

Technology of direct nanolithography by a focused ion beam (FIB) is widely used to form prototypes and for diagnostics of devices based on semiconductor structures [1–3]. Papers [4,5] showed that during etching of semiconductor structures with the focused ion beam the decrease in quantum yield of luminescence occurs. The authors supposed that decrease in quantum yield was due to radiation-induced defects formed during etching. Study of defects occurred during irradiation of semiconductors by high-energy ions is considered in many papers [6]. But practically all them study defects formed during the ion implantation, where ion energies are higher (> 100 keV), and densities of ions in beam are significantly lower than during etching with FIB. Irradiation by high-energy (> 100 keV) with ions B^+, Ar^+, Si^+ of crystals GaAs leads in disordering of the crystalline structure resulting in occurrence of additional band in Raman scattering spectra [7–9]. In ion-beam lithography units for etching the beams of ions with significantly lower energies ($1-30$ keV) and with hundred times higher densities are used as compared to the ion implantation process. Literature practically does not contain results of study of crystalline perfection violation of semiconductor structures based on GaAlAs during etching with FIB ions Ga^+.

In our paper using micro-Raman spectroscopy we studied the effect of energy of ions Ga^+ in FIB and of ion dose on the formation of defects during etching of the heterostructure $GaAs/Al_{0.3}Ga_{0.7}As$.

2. Experiment

Experiment samples are prepared by method of metal-organic chemical vapor deposition (MOCVD). On substrate GaAs (100) a two-layer heterostructure $GaAs/Al_{0.30}Ga_{0.7}As$ was prepared with thicknesses of layers $1\,\mu$m each.

By FIB Ga^+ in surface layer GaAs a lithographic picture was formed containing square holes with lateral dimensions $20 \times 20\,\mu$m with different depth. Increase in depth of holes occurred due to increase in ion dose by multiple exposure. The lithography was performed with ion energies 15 and 30 keV. To prevent formation of Ga drops the lithography was performed in atmosphere of precursor-gas XeF_2. The basic technological parameters of the lithographic process and data on depth of etched holes measured by method of atomic-force microscopy (AFM) are given in Table. Depth of etched holes gradually increased with ion dose increasing, thus approaching the etched surface to the heteroboundary $GaAs/Al_{0.3}Ga_{0.7}As$.

Samples study by micro-Raman spectroscopy was performed using spectrometer LabRAM HREvo UV-VIS-NIR-Open (Horiba, France). To excite Raman spectra the line $\lambda = 532$ nm (2.33 eV) of Nd:YAG-laser was used. According to publication data, in this case depth of GaAs analysis is ~ 145 nm [10]. This value certainly exceeds the depth of radiation-induced defects formation, which is determined using modeling in package SRIM (≤ 100 nm) [11]. The exciting radiation was focused on sample surface into a spot $\sim 1-2\,\mu$m in diameter using the microlens Olympus 100× (NA $= 0.9$), which ensured

FIB technological parameters

Lithographic picture (group/number of hole)	Size of holes, μm	Ion energy, keV	Work current, nA	Full ion dose, cm^{-2}	Depth, nm
15 keV №1	20×20	15	2000	$6.25 \cdot 10^{16}$	100
15 keV №4	20×20	15	2000	$4.69 \cdot 10^{17}$	830
30 keV №1	20×20	30	2000	$6.25 \cdot 10^{16}$	100
30 keV №4	20×20	30	2000	$4.69 \cdot 10^{17}$	880

Raman spectra from etched holes with lateral dimensions $20 \times 20\,\mu$m.

3. Results and discussion

Raman spectra measured in holes formed with energies 15 and 30 keV are presented in Figure 1. Position in spectra of the peak with maximum at frequency of 291 cm^{-1} corresponds to longitudinal optical phonon LO GaAs (Figure 1, *a* and *b*) [7]. The second maximum at frequency of 267 cm^{-1} (solid line), well visible in spectrum, obtained from the unetched portion of sample, corresponds to the transverse optical (TO) phononic mode of gallium arsenide [7]. This mode of prohibited by symmetry for GaAs surfaces with orientation (100) in used geometry of „back scattering“, but can occur in spectra due to gathering of scattered radiation by the used microlens.

Raman spectra obtained from holes etched to depth 100 nm (Figure 1, *a*) differ from spectra of unetched structure by decrease in intensity of band 291 cm^{-1} by 1.3 times for samples of etched with ions with energies 15 keV and by 2.5 times for samples etched with ions with energy 30 keV. With the etching depth increasing to 830–880 nm (Figure 1, *b*) the peak intensity decreasing of optical phonon LO GaAs (291 cm^{-1}) by 2.7 times was observed for holes etched by ions with energy 15 keV. For holes etched by ions with energy 30 keV, in Raman spectra this line completely disappears. In all etched samples suppression of the peak 291 cm^{-1} was accompanied by occurrence of wide band with maximum at frequency ~ 245 cm^{-1} (Figure 1, *a*, and *b*), which is associated with occurrence of the amorphous phase.

Occurrence, as a result of etching with high-energy ions Ga^{+}, of the wide band with maximum at 245 cm^{-1} (Figure 1) is determined by inclusions of longitudinal optical (LO) phonon into X and L of Brillouin zone (BZ), transverse optical (TO) phonon into Γ, X and L of BZ, and longitudinal acoustic (LA) phonon into X and L of BZ, which occur in amorphous semiconductor with tetrahedral bonds [8]. This band relates to defect-induced scattering of 1-st order and confirms occurrence of disordered region in the irradiated crystal [8]. Increasing of ion energy of FIB and of the ion dose results in increase in intensity of band with maximum at 245 cm^{-1} (Figure 1, unfilled squares) and decrease in intensity of LO GaAs-peak (291 cm^{-1}), responsible for the crystalline phase. Comparison of spectra shows that at same ion dose and change in ion energy in beam by 2 times the etching depth changes by 10% only. The energy increasing from 15 to 30 keV result in concentration increasing of radiation-induced defects only.

To restore the crystal perfection of the heterostructure the annealing was performed under high vacuum ($\sim 10^{-6}$ Pa) at 300°C for 30 min. Raman spectra obtained after annealing are shown in Figure 2. In case of not deep etching with energies of 15 and 30 keV (Figure 2, *a*) intensity of line of longitudinal optical phonon LO GaAs (291 cm^{-1}) practically completely restores. Wide band with maximum at 245 cm^{-1} disappears, and clear peak appears with maximum at frequency of 267 cm^{-1} (TO GaAs) [7]. In case of deep etching by ions with energy 15 keV (Figure 2, *b*) incomplete restoration of line 291 cm^{-1} occurs, and during etching by ions with 30 keV the intensity of this line stays equal to zero. Besides, etching to depth > 800 nm leads to occurrence in spectrum of new lines (280 cm^{-1} and 377 cm^{-1}) (Figure 2, *b*, unfilled and filled squares).

In paper [9] the authors note that radiation-induced defects in GaAs, subjected to irradiation by high-energy ions, depending on annealing temperature (T_{ann}) can be conditionally divided into three groups: point defects, in particular monovacancies Ga ($T_{\text{ann}} = 220°\text{C}$) and monovacancies As ($T_{\text{ann}} = 240°\text{C}$), clusters ($T_{\text{ann}} > 400°\text{C}$) and completely amorphized material ($T_{\text{ann}} > 600°\text{C}$). In our experiment in sample etched by ions with energy of 15 keV to small depth (ion dose — $6.25 \cdot 10^{16}$ cm^{-2}), as a result of annealing at $T_{\text{ann}} = 300°\text{C}$ practically complete restoration of intensity of line of LO phonon GaAs (291 cm^{-1}) occurs (Figure 2, *a*). This result, based on paper [9], ensures the supposition that point defects prevail during such etching. In annealed etched (15 keV) sample with increased ion dose to ($4.69 \cdot 10^{17}$ cm^{-2}) (large depth) the intensity of line of LO phonon in Raman spectrum is $\sim 60\%$ of its intensity in spectrum of unetched sample (Figure 2, *b*), which indicates incomplete annealing of radiation-induced defects and possible occurrence of clusters of defects [9]. Etching by ions with energy 30 keV at low ion dose ($6.25 \cdot 10^{16}$ cm^{-2}) leads to concentration increasing of point defects and their partial clusterization. So, temperature 300°C is insufficient for complete annealing of the radiation-induced defects (Figure 2, *a*, unfilled squares). Upon increase in ion dose to $4.69 \cdot 10^{17}$ cm^{-2} the annealing does not result in occurrence of line of LO phonon GaAs in Raman spectrum (Figure 2, *b*, unfilled squares). We expect

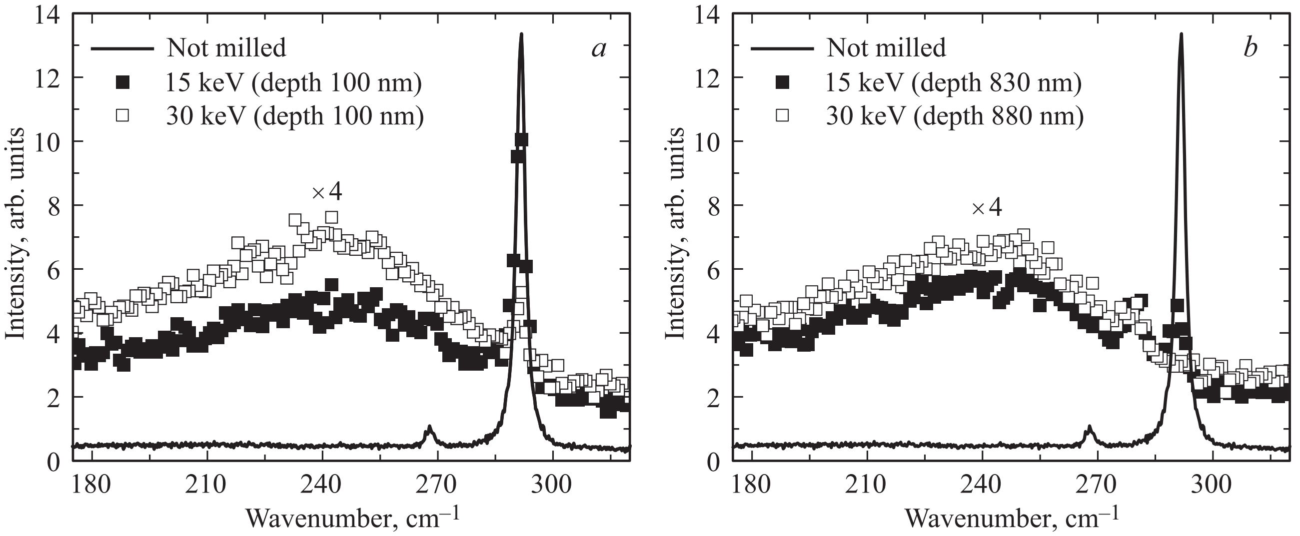

Figure 1. Raman spectra of heterostructure GaAs/$Al_{0.3}Ga_{0.7}As$ after etching with FIB with ion energies 15 keV (filled squares) and 30 keV (unfilled squares) to low 100 nm (*a*) and large 830–880 nm (*b*) depth. Solid line — spectrum obtained from unetched portion of heterostructure.

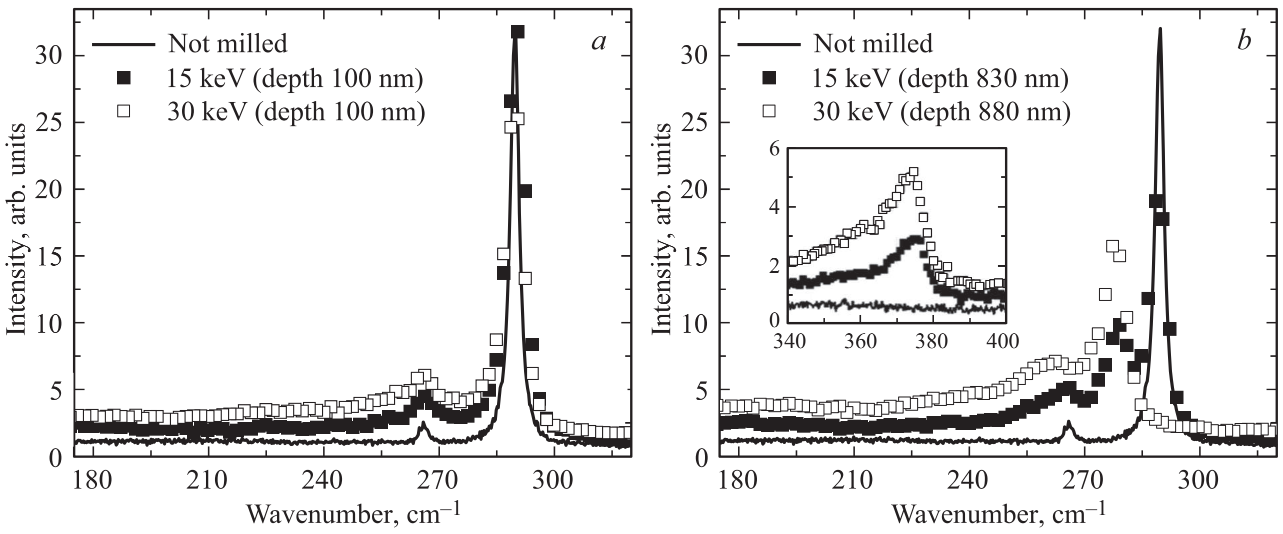

Figure 2. Raman spectra of heterostructure GaAs/$Al_{0.3}Ga_{0.7}As$ after annealing in ultrahigh vacuum at 300°C for 30 min: *a* — regions of etching to small depth; *b* — regions of etching to large depth. Ion energy 15 keV (filled squares) and 30 keV (unfilled squares). Spectrum obtained from unetched portion of heterostructure is shown by solid line.

that in this case the basic type of radiation-induced defects is clusters, which annealing occurs at higher temperatures [9].

In Raman spectra, see Figure 2, *b*, LO phonon modes of layer $Al_{0.3}Ga_{0.7}As$ are clearly visible, they have two-mode nature of behaviour (relating to sublattices GaAs ($280\,cm^{-1}$) and AlAs ($377\,cm^{-1}$)) [12]. Occurrence of these peaks after annealing indicates that at such etching depth (> 830 nm) the thickness of remained after etching and annealing layer GaAs (< 170 nm) is sufficient for Raman signal monitoring from layer $Al_{0.3}Ga_{0.7}As$, and also that radiation-induced defects formed by focused ion beam are detected in layer $Al_{0.3}Ga_{0.7}As$.

4. Conclusion

Paper shows that during etching of the heterostructure GaAs/$Al_{0.3}Ga_{0.7}As$ by focused ion beam Ga^+ the radiation-induced defects are formed in it. Studies of such structure by method of Raman spectroscopy showed that concentration and prevailing type of the FIB-induced radiation-induced defects depend on ion energy and ion dose. At low ion energies (15 keV) and low ion doses ($6.25 \cdot 10^{16}\,cm^{-2}$) Ga and As monovacancies prevail, they are annealed at 300°C. The ion dose increasing leads to accumulation of point defects and their clusterization. At high energy

(30 keV) and ion dose ($4.69 \cdot 10^{17}\,\text{cm}^{-2}$) the clusters of radiation-induced defects prevail, and restoration of crystal perfection of structure requires higher temperatures of annealing. Energy increasing of the ion beam Ga^+ from 15 to 30 keV practically does not change etching rate of material, at same time ion energy increasing is spent for additional defects formation.

Funding

A.V. Babichev thanks the Russian Science Foundation grant No. 20-79-10285-P, https://rscf.ru/project/20-79-10285/ for financial support in terms of developing the heterostructure design.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Manoccio, M. Esposito, A. Passaseo, M. Cuscunà, V. Tasco. Micromachines, **12**, 6 (2020). DOI: 10.3390/mi12010006

[2] P. Li, S. Chen, H. Dai, Z. Yang, Z. Chen, Y. Wang, Y. Chen, W. Peng, W. Shan, H. Duan. Nanoscale, **13**, 1529 (2021). DOI: 10.1039/d0nr07539f

[3] G. Seniutinas, A. Balčytis, I. Reklaitis, F. Chen, J. Davis, C. David, S. Juodkazis. Nanophotonics, **6**, 923 (2017). DOI: 10.1515/nanoph-2017-0008

[4] G.V. Voznyuk, I.N. Grigorenko, A.S. Lila, M.I. Mitrofanov, D.N. Nikolaev, V.P. Evtikhiev. Semiconductors, **56**, 894 (2022). DOI: 10.21883/sc.2022.12.55147.4423

[5] M. Takiguchi, G. Zhang, S. Sasaki, K. Tateno, C. John, M. Ono, H. Sumikura, A. Shinya, M. Notomi. Nanotechnology, **34**, 135301 (2023). DOI: 10.1088/1361-6528/acb0d5

[6] W. Wesch, E. Wendler. *Ion Beam Modification of Solids* (Springer International Publishing, 2016).

[7] S.V. Gotoshia L.V. Gotoshia. Phys. Status Solidi C, **10**, 646 (2013). DOI: 10.1002/pssc.201200847

[8] I.D. Desnica-Franković. J. Appl. Phys., **85**, 7587 (1999). DOI: 10.1063/1.370559

[9] A.N. Akimov, L.A. Vlasukova, G.A. Gusakov, F.F. Komarov, A.A. Kutas, A.P. Novikov. Radiat. Efa. Defects Solids, **129**, 147 (1994). DOI: 10.1080/10420159408229013

[10] J. Jimenez, J.W. Tomm. *Spectroscopic Analysis of Optoelectronic Semiconductors* (Springer International Publishing, 2016) p. 77.

[11] G.V. Voznyuk, I.N. Grigorenko, A.S. Lila, M.I. Mitrofanov, D.N. Nikolaev, V.P. Evtikhiev. Semiconductors, **56**, 12 (2022). DOI: 10.21883/sc.2022.12.55147.4423

[12] Z. Cevher, P.A. Folkes, H.S. Hier, B.L. VanMil, B.C. Connelly, W.A. Beck, Y.H. Ren. J. Appl. Phys., **123**, 161512 (2017). DOI: 10.1063/1.4986297

Translated by I.Mazurov