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Formation and light-emitting properties of ion-synthesized Ga_2O_3 nanoinclusions in the Al_2O_3/Si matrix

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Abstract. The regularities of ion synthesis of gallium oxide nanocrystalline inclusions by implantation of gallium and oxygen ions into dielectric Al_2O_3 films on silicon substrates and subsequent thermal annealing are considered. The composition of the implanted samples before and after annealing was investigated by X-ray photoelectron spectroscopy with layer-by-layer profiling. The formation of Ga-O chemical bonds was demonstrated, and after annealing gallium is predominantly in the fully oxidized state. According to X-ray diffraction data, the formation of β-Ga_2O_3 crystalline phase was confirmed. The study of photoluminescence of the synthesized samples revealed the presence of luminescence band, which is presumably caused by radiative recombination of donor-acceptor pairs.

Keywords: nanocrystals, gallium oxide, ion synthesis, photoluminescence, X-Ray photoelectron spectroscopy, X-Ray diffraction

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Формирование и светоизлучающие свойства ионно-синтезированных нановключений Ga_2O_3 в матрице Al_2O_3/Si

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Аннотация. Рассмотрены закономерности ионного синтеза нанокристаллических включений оксида галлия при имплантации ионов галлия и кислорода в

диэлектрические пленки Al_2O_3 на подложках кремния и последующего термического отжига. Методом рентгеновской фотоэлектронной спектроскопии с послойным профилированием исследован состав имплантированных образцов до и после отжига. Продемонстрировано образование химических связей Ga-O, причем после отжига галлий находится преимущественно в полностью окисленном состоянии. По данным рентгеновской дифракции подтверждено формирование кристаллической фазы β-Ga_2O_3. Исследование фотолюминесценции синтезированных образцов выявило наличие полосы люминесценции, которая предположительно обусловлена излучательной рекомбинацией донорно-акцепторных пар.

Ключевые слова: нанокристаллы, оксид галлия, ионный синтез, фотолюминесценция, рентгеновская фотоэлектронная спектроскопия, рентгеновская дифракция

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Introduction

The study of properties of gallium oxide-based materials has attracted great interest in the last few years due to its unique properties, including a large band gap width (~ 5 eV), high values of breakdown voltages, as well as sensitivity to UV radiation and various gases [1]. This opens up prospects for the application of Ga_2O_3 as a basic material for a new generation of power electronics devices, solar-blind photodetectors, gas sensors and other devices. Despite the availability of technology for the growth of large-diameter single-crystal wafers, due to their low availability and high cost, they have not yet found practical application. Difficulties also remain in the development of thin-film technology of Ga_2O_3 deposition on crystalline substrates. An alternative to such approaches is the development of technology for the fabrication of Ga_2O_3-based nanostructures. However, to date, the results have been obtained only for the synthesis of nanoinclusions using chemical technologies [2], which is not compatible with microelectronics. One of the promising variants for the development of technology of nanostructuring is the ion synthesis of Ga_2O_3 nanocrystals (nc-Ga_2O_3) in solid-state matrices. Ion implantation has already demonstrated its efficiency in Ga_2O_3 technology [3, 4]. At the same time, the ion synthesis method has also been successfully validated for the formation of semiconductor nanoinclusions of Si [5], SiC [6], ZnO [7] and In_2O_3 [8]. Previously, the possibility of ion synthesis of nc-Ga_2O_3 in SiO_2/Si matrix was demonstrated [9, 10]. In this work, we investigate the formation and light-emitting properties of ion-synthesized Ga_2O_3 nanoinclusions in Al_2O_3/Si matrix.

Materials and Methods

Al_2O_3 films (200 nm) deposited on Si (100) substrates by electron-beam evaporation were used as initial samples. The samples were irradiated with Ga^+ ($5 \cdot 10^{16}$ cm^{-2}, 80 keV) and O^+ ($6 \cdot 10^{16}$ cm^{-2}, 23 keV) ions with variation of the irradiation order. Implantation of only Ga^+ ions without additional oxygen irradiation was also carried out. The irradiation parameters were selected for maximum coincidence of the ion distribution profiles calculated with the SRIM program (www.srim.org). The samples were annealed in a tube furnace at temperatures of 300, 500, 700, and 900 °C (30 min each) in dried N_2 atmosphere.

The chemical composition of implanted samples before and after annealing was studied by X-ray photoelectron spectroscopy (XPS) with layer-by-layer ion etching. The photoelectron lines O 1*s*, C 1*s*, Ga $2p_{3/2}$ and Si 2*s* were registered. To obtain the depth distribution profiles, etching with 1-keV Ar^+ ions was used. The depth calibration was carried out by measuring the step height after etching by atomic force microscopy. The structure of the samples was studied by X-ray diffraction (XRD) on a Bruker D8 Discover diffractometer using Cu Kα radiation. The spectra were recorded using a LinxEye linear PSD detector. Photoluminescence (PL) spectra were recorded using the standard lock-in technique at room temperature. Laser-driven light source XWS-65 with optical light filter, highlighting the spectral region with a width of ~ 10 nm with a maximum at a wavelength of 245 nm, was used as a source.

Results and Discussion

Ion synthesis of nanocrystalline inclusions in dielectric matrices assumes the appearance of chemical bonds between phase-forming atoms with the subsequent formation of first small clusters and then clusters of large size. To analyze the chemical composition of the implanted samples before and after annealing, the XPS method was used, which, along with information on the depth distribution of elements, also provides information on their chemical state. Fig. 1 shows the depth distributions of implanted gallium with regard to its chemical state for different ion synthesis variants used. Let us consider the chemical bonding distribution for the implanted Al_2O_3/Si samples without annealing. In the sample implanted only with Ga^+ without oxygen ion irradiation, all gallium atoms are presented in the elemental state. The observed effect is different from the case of Ga^+ implantation in the SiO_2/Si matrix, where its oxidation was previously found when implanted under the same conditions without additional annealing [10].

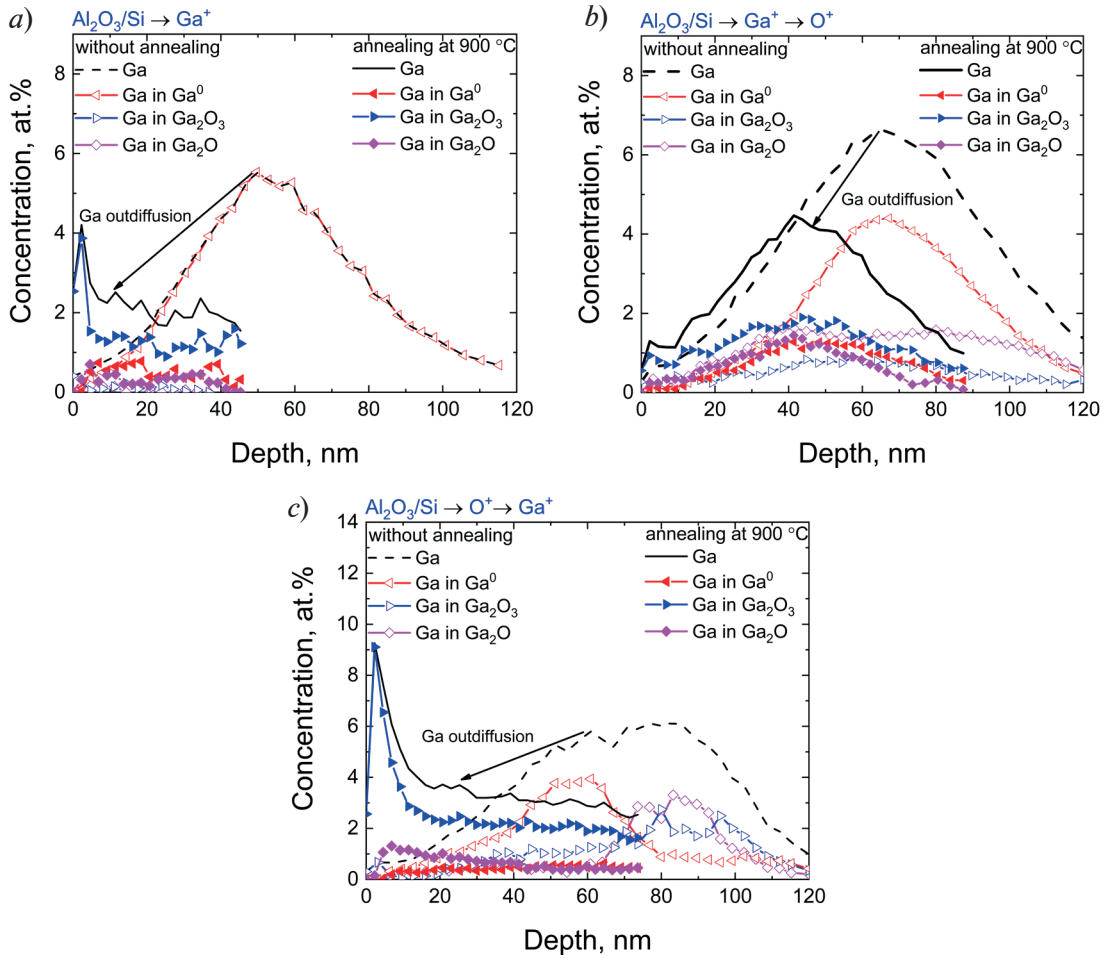

Fig. 1. XPS spectra for the Al_2O_3/Si samples, implanted with Ga^+ (*a*), $Ga^+ \rightarrow O^+$ (*b*) and $O^+ \rightarrow Ga^+$ (*c*), before and after annealing at 900 °C

Apparently, this may be due to the higher resistance of the Al_2O_3 matrix to ion irradiation compared to the SiO_2 matrix. Oxygen ion irradiation after Ga^+ irradiation leads to partial oxidation of gallium mainly in the oxygen-deficient state (Ga_2O). In the case of O^+ ion irradiation before Ga^+ implantation, a bimodal profile of impurity distribution is observed, with the first maximum containing gallium mainly in the elemental state and located closer to the surface, whereas the deeper maximum is due to gallium in the oxidized state with approximately the same concentration in the stoichiometric (Ga_2O_3) and non-stoichiometric (Ga_2O) states. It can be assumed that Ga^+ ion irradiation of a sample supersaturated with oxygen promotes redistribution of the latter toward greater depths as a result of interaction with stopping gallium atoms. This leads to the fact that a part of implanted gallium stopped closer to the surface, where it forms the elemental gallium phase, while its other part in the region of the end of ion range appears in the strongly oxygen supersaturated region, which leads to more favorable conditions for gallium oxidation.

Annealing at 900 °C leads to a significant outdiffusion of implanted gallium. This effect is most noticeable for implantation of Ga^+ ions only, where a decrease in its concentration to a value not exceeding 2 at % is observed. In the sample implanted in the $Ga^+ \rightarrow O^+$ order, annealing leads to a slight decrease in the total gallium concentration in the sample, with the concentration of Ga in the elemental state decreasing, whereas the concentration of gallium in the stoichiometric Ga_2O_3 state increased compared to the sample without annealing. For the sample in which O^+ ions were implanted before gallium, a significant change in the shape of the distribution profile with a pronounced diffusion of gallium atoms towards the surface is observed. At the same time, practically all the introduced gallium appears in the oxidized state of stoichiometric oxide Ga_2O_3. This fact demonstrates that annealing leads to an increase in the efficiency of formation of Ga-O chemical bonds, which is a necessary condition for the formation of Ga_2O_3 nanoinclusions.

The structure of the samples after annealing at 900 °C was studied by X-ray diffraction in θ-2θ geometry. The diffraction patterns are shown in Fig. 2. For the sample irradiated only with Ga^+ ions, no diffraction peaks appeared. In the case of additional irradiation with oxygen ions, both before and after Ga^+ implantation, a peak at $2\theta \approx 31.5°$ appears on the diffraction curves, which corresponds to the reflection from the (002) planes for crystalline β-Ga_2O_3 (JCPDS Card No. 41-1103). The intensity of this peak is rather low, which indicates a small volume fraction of the formed nanocrystals.

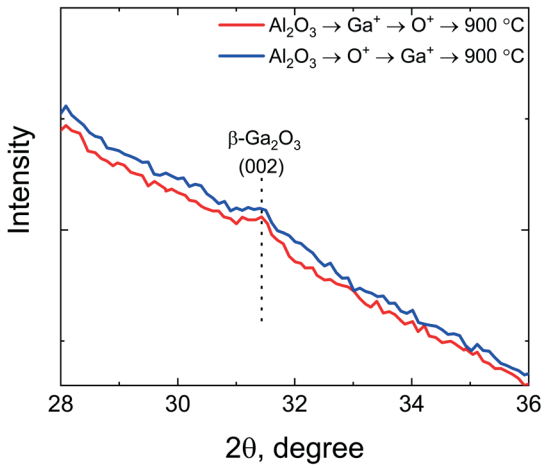

Fig. 2. XRD spectra for the Al_2O_3/Si samples, implanted with Ga^+ and O^+ ions with the different sequence of irradiation, after annealing at 900 °C

Let's proceed to consideration of light-emitting properties of irradiated samples before and after annealing (Fig. 3). The study of photoluminescence of irradiated samples without annealing and samples after annealing at 300 °C did not reveal the appearance of luminescent lines in the studied region. Annealing at 500 °C leads to the appearance of PL in the region of 400–500 nm for the sample irradiated first by Ga^+ ions, then by O^+ ions. Increasing the annealing temperature up to 700 °C leads to the appearance of PL also for the sample irradiated only by Ga^+ ions, and after the final annealing at 900 °C PL in the region of 380–550 nm is observed for all the

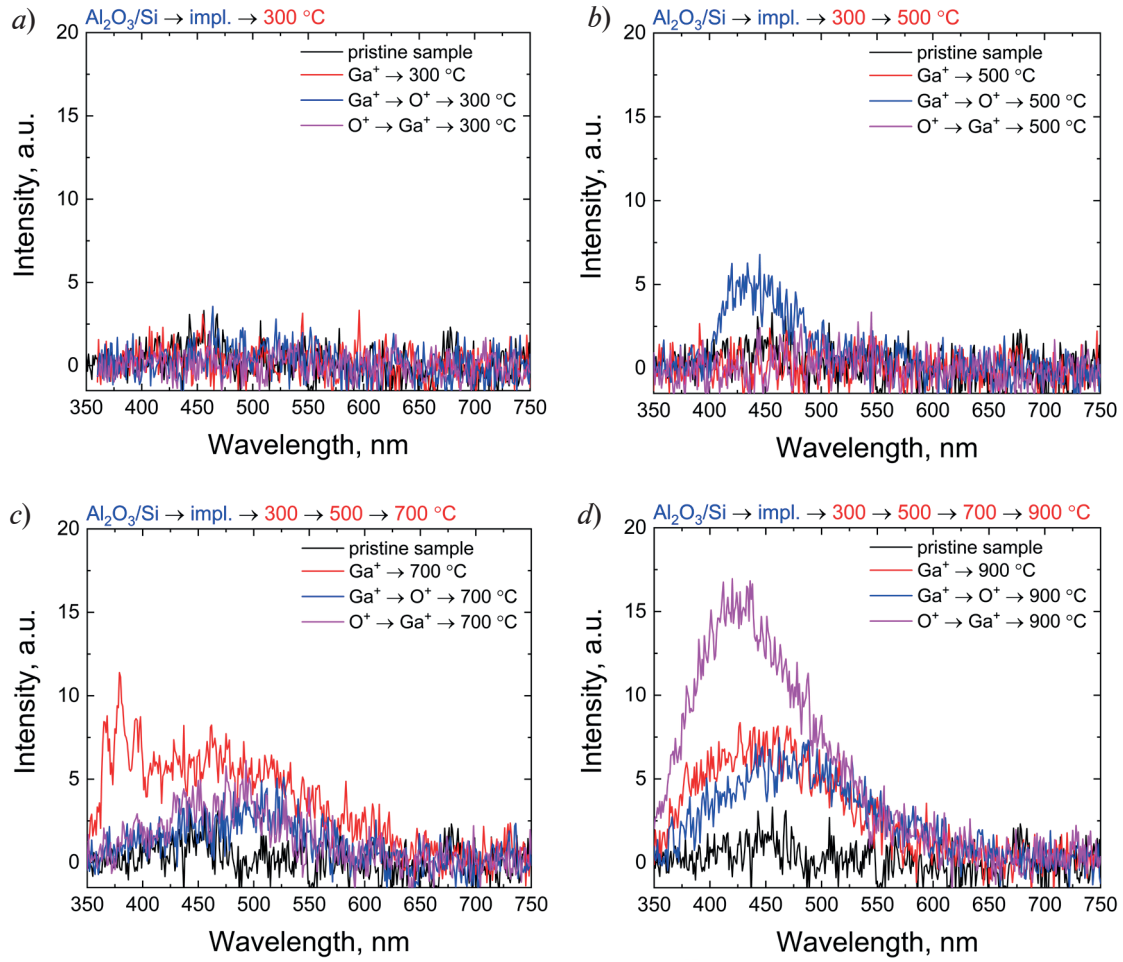

Fig. 3. PL spectra for the Al_2O_3/Si samples, implanted with Ga^+ and O^+ ions, after annealing at 300 (*a*), 500 (*b*), 700 (*c*) and 900 °C (*d*)

studied samples, while the intensity and shape of the line depends on the order of ion irradiation. The sample that was irradiated with oxygen before gallium implantation has the highest PL intensity. This correlates with the XPS data, according to which this sample shows the maximum concentration of gallium in the stoichiometric Ga_2O_3 oxide state.

The most probable mechanism of PL occurrence in the studied samples is radiative recombination of donor-acceptor pairs (DAP), where an oxygen vacancy (V_O) acts as a donor and a defect complex consisting of a pair of gallium and oxygen vacancies ($V_{Ga} + V_O$) acts as an acceptor. The spectral composition of this line is determined primarily by the defect composition of the synthesized nc-Ga_2O_3, since the energy of the radiative transition depends on the position of the V_O in the unit cell, which takes part in the formation of the defect complex – O_I, O_{II} or O_{III} [11]. The energies of these transitions, according to [11], are 3.04, 2.66, and 2.86 eV, respectively. The contribution to the resulting PL spectrum is determined by the ratio between the concentrations of these defects. Another important factor is a possible quantum-size effect with a shift of the luminescence maximum as a function of the nanoparticle size [12]. In favor of this factor is evidenced by the fact that the PL spectra differ for different synthesis conditions of nc-Ga_2O_3. Additional studies are required to establish precisely the mechanism of the observed PL.

Conclusion

The regularities of formation of light-emitting Ga_2O_3 nanoinclusions obtained by ion synthesis in Al_2O_3/Si matrix have been investigated. The study of the chemical composition demonstrated the formation of Ga-O bonds, which are the structural element for the formation of nanoinclusions,

both before and after high-temperature annealing. Annealing leads to gallium outdiffusion, however, the content of gallium in the stoichiometric Ga_2O_3 oxide state increases. X-ray diffraction study of the structure revealed the appearance of a diffraction peak due to reflection from the (002) planes for β-Ga_2O_3 nanocrystals. Annealing at 900 °C for all used variants of ion synthesis leads to the appearance of photoluminescence in the region of 400–500 nm, presumably associated with the recombination of donor-acceptor pairs in gallium oxide. Thus, in this work, the possibility of synthesizing light-emitting Ga_2O_3 nanocrystals in Al_2O_3 on silicon matrix was demonstrated. This opens up the prospect of using this approach for creating gallium oxide nanomaterials for the development of new generation electronic devices.

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