Influence of indium doping on the formation of silicon–(gallium vacancy) complexes in gallium arsenide grown by molecular-beam epitaxy at low temperatures

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Low-temperature photoluminescence (PL) studies of gallium-arsenide layers grown by molecular-beam epitaxy at low (200 °C) temperatures (LT GaAs) and doped with silicon or a combination of silicon and indium have been performed. The PL spectra of as-grown samples reveal a shallow acceptor-based line only. After annealing, an additional line at ~1.2 eV appears, which is attributable to $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes. The activation energy of complex formation is found to be close to the activation energy of migration of gallium vacancies and is equal to 1.9 ± 0.3 eV for LT GaAs : Si. It is found that doping with a combination of silicon and indium leads to an increase in the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes to 2.5 ± 0.3 eV. We believe that this increase in the activation energy is controlled by the gallium vacancy–indium interaction through local lattice deformations. [S1063-7826(99)00810-8]

INTRODUCTION

Gallium vacancies exert a substantial influence on the properties of bulk crystals and epitaxial layers of GaAs. When gallium arsenide is doped with shallow-donor impurities (e.g., Si), the interaction of the donors with the vacancies leads to the formation of stable complexes. Such complexes degrade the efficiency of doping and can have an effect on the lifetime of the charge carriers. To elucidate and investigate $\mathrm{Si}-V_{\mathrm{Ga}}$ type complexes, one usually measures the photoluminescence (PL) spectra, in which a characteristic band with energy near 1.2 eV is observed.[1–3] Gallium vacancies play an especially important role in GaAs layers grown by molecular-beam epitaxy (MBE) at low (<300 °C) temperatures. The main peculiarity of this material (LT GaAs), which defines its unique properties, is the large arsenic excess (as high as 1.5 at.%) acquired by the layer during growth. Although a large fraction of the excess arsenic enters into the crystal in the form of antistructural defects ($\mathrm{As_{Ga}}$), whose concentration reaches $10^{20}\,\mathrm{cm}^{-3}$ (Ref. 4), the gallium-vacancy concentration is also very large, $\sim10^{18}\,\mathrm{cm}^{-3}$ (Ref. 5). It is believed[6] that gallium vacancies (V_{Ga}) are the dominant compensating acceptors in LT GaAs, ensuring pinning of the Fermi level near the level of the deep donor $\mathrm{As_{Ga}}$. In addition, it is usually assumed[7] that migration of gallium vacancies plays a key role in the transport and precipitation of excess arsenic and the formation of the system of nanosize As clusters in the LT GaAs matrix during annealing. It is also assumed[8,9] that diffusion of gallium vacancies leads to enhanced interdiffusion (In–Ga, Al–Ga) and smearing of the interface in isolated quantum wells and in superlattices (AlAs/GaAs and InAs/GaAs) grown by molecular-beam epitaxy at low temperatures.

We have performed a photoluminescence study of the formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes in LT GaAs : Si layers annealed at various temperatures. We have also investigated the influence of indium doping on the formation of these complexes.

SAMPLES AND EXPERIMENTAL PROCEDURE

LT GaAs layers were grown on the molecular-beam epitaxy setup ''Katun''' on substrates of polished gallium arsenide 40 mm in diameter with (100) orientation. Growth occurred at the temperature 200 °C at a rate of 1 μm/h and an arsenic pressure of 7×10^{-4} Pa. The thickness of the LT GaAs layer was 0.5 μm. A layer of AlAs 50 nm in thickness was also grown on the surface of the samples to prevent arsenic evaporation during annealing.

Two groups of layers were grown. The first group was doped with only the shallow donor impurity, silicon (concentration $7\times10^{17}\,\mathrm{cm}^{-3}$), and the second, with silicon ($7\times10^{17}\,\mathrm{cm}^{-3}$) and the isovalent impurity, indium ($2\times10^{19}\,\mathrm{cm}^{-3}$).

After the growth procedure the samples were divided into several groups, one of which was held unannealed while the remaining groups were subjected to annealing at different temperatures. The samples were annealed in an atmosphere of pure hydrogen for 15 min. The annealing temperature was varied in the limits $600-850$ °C.

The photoluminescence (PL) studies were performed at a temperature of 4.2 K in the spectral range $0.8-1.2$ μm. An

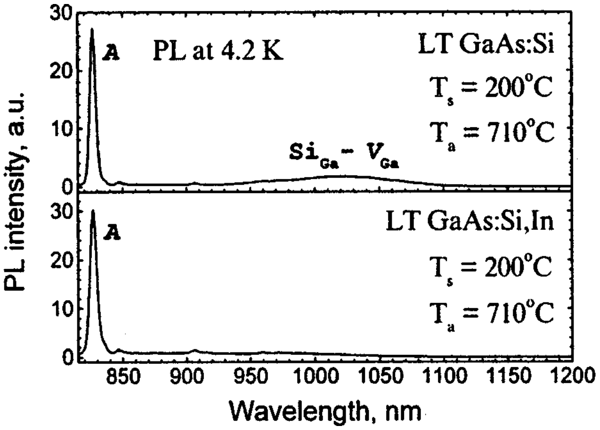

FIG. 1. Low-temperature photoluminescence spectra of *LT* GaAs : Si and *LT* GaAs : Si : In samples grown at 200 °C and annealed at 710 °C.

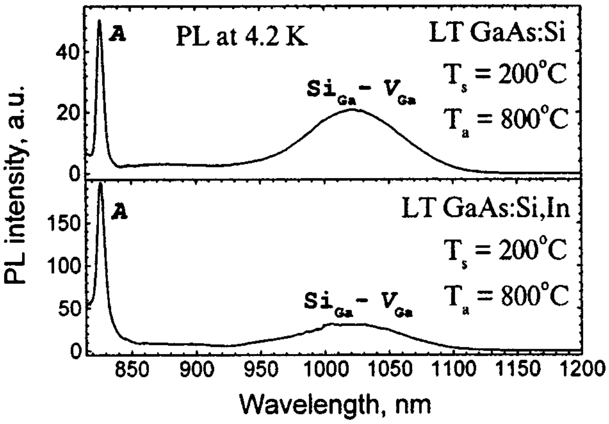

FIG. 2. Low-temperature photoluminescence spectra of *LT* GaAs : Si and *LT* GaAs : Si : In samples grown at 200 °C and annealed at 802 °C.

Ar^+ laser (the 514.5 μm line) was used to excite emission, and the signal was recorded with a FÉU-62 cooled photomultiplier.

EXPERIMENTAL RESULTS

Both the unannealed *LT* GaAs samples doped and not doped with indium were characterized by an extremely weak total photoluminescence intensity, which is due to the extremely short lifetime of the charge carriers in this material. A single line was observed in the spectra of unannealed *LT* GaAs which is associated with recombination at shallow acceptors (1.498 eV). We did not observe lines associated with recombination on free excitons, which is characteristic of *LT* GaAs (Ref. 10).

Figure 1 shows the photoluminescence spectra of *LT* GaAs samples doped and not doped with indium, annealed at 710 °C. It can be seen that in addition to the *A* line associated with shallow acceptors, a weak wide band appears in the region of 1.2 eV, which is associated with deep centers, namely, (gallium vacancy)–donor complexes (in this case $Si_{Ga}-V_{Ga}$).[1–3] It can be seen that in the indium-doped samples, the intensity of this band is much less than in the samples not doped with indium, which is evidence of a lower concentration of $Si_{Ga}-V_{Ga}$ complexes.

As the annealing temperature is raised (Fig. 2 shows photoluminescence spectra of samples of *LT* GaAs doped and not doped with indium, annealed at 800 °C), the total photoluminescence intensity increases due to intensification of the edge photoluminescence lines and due to a significant growth of the intensity of the line associated with deep centers. The increase in the intensity of the edge luminescence lines is apparently explained by an increase in the lifetime of the nonequilibrium charge carriers proportional to the extent that native lattice defects are annealed out. The intensity of the line associated with the $Si_{Ga}-V_{Ga}$ complexes, on the other hand, grows by two or three orders of magnitude, which can be explained only by an increase in the number of these complexes.

The variation in the intensities of individual photoluminescence lines in the spectra of the various samples cannot be used to judge the variation of the relative concentration of the defects responsible for the appearance of these lines since the photoluminescence intensity depends not only on the concentration of recombination centers, but also on the lifetime of the charge carriers in the investigated material. It is well known that during annealing significant changes take place in the structure of the *LT* GaAs samples associated with the formation of arsenic clusters and a decrease in the number of point defects. Clearly, in the process of such changes of the structure of the material the lifetime of the nonequilibrium charge carriers can vary over wide limits. Therefore, to determine the change in the concentration of the $Si_{Ga}-V_{Ga}$ complexes, instead of the absolute value of the intensity of the photoluminescence line associated with this defect we examined its ratio to the recombination line on shallow acceptors.

Figure 3 shows a semilog plot of the ratio of the intensity of the photoluminescence line associated with the $Si_{Ga}-V_{Ga}$ complexes to the intensity of the edge luminescence line as functions of the annealing temperature for samples of *LT* GaAs doped and not doped with indium. It can be seen that at low annealing temperatures the difference in the concentrations of the $Si_{Ga}-V_{Ga}$ complexes is quite

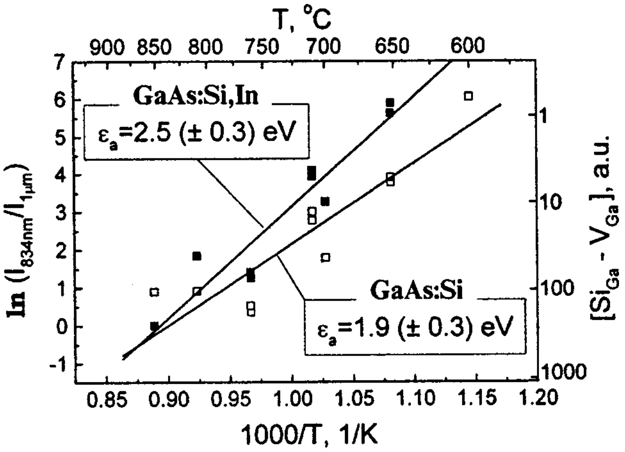

FIG. 3. Semilog plot of the temperature dependence of the ratio of the line intensity of recombination on a shallow acceptor to the intensity of the line associated with the $Si_{Ga}-V_{Ga}$ complexes.

significant while at high annealing temperatures their concentrations are roughly the same. From the slope of the line obtained by statistical processing of the results, it is possible to determine the activation energy of complex formation. For the samples not doped with indium, it is equal to 1.9 ±0.3 eV. For the indium-doped samples the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes is equal to 2.5 ±0.3 eV. The difference amounts to 0.6 eV, which exceeds the measurement error.

DISCUSSION OF THE RESULTS

The formation of complexes consisting of the pair gallium-vacancy and silicon in the gallium sublattice is typical of single crystals and epitaxial layers of gallium arsenide prepared by various methods. It is usually assumed[11] that the formation of (gallium vacancy)–(shallow donor) complexes in epitaxial layers occurs during crystal growth. Our studies show, however, that in the case of low-temperature molecular-beam epitaxy the concentration of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes formed during growth of the layers is small. Vigorous formation of complexes takes place during annealing of *LT* GaAs layers and intensifies as the annealing temperature is increased. This means that complex formation takes place as a consequence of migration of defects and impurities, i.e., by the mechanism characteristic of bulk single crystals.

In general, for a sufficiently high concentration of $\mathrm{Si_{Ga}}$ donors obtained as a result of doping, complex formation is the result of two consecutive processes: formation of a free vacancy and its migration to a lattice site at which a silicon atom is found. Motion of silicon atoms can be ignored since it is well known that the diffusion coefficient of vacancies in GaAs significantly exceeds the diffusion coefficient of substitution impurities. The activation energy of diffusion of gallium vacancies in GaAs is 1.7±0.5 eV according to the data of Ref. 12, and 1.7±0.3 eV according to the data of Ref. 13.

The energy of formation of gallium vacancies in GaAs is very large, 4.0±0.5 eV (Ref. 12). A peculiarity of gallium arsenide grown by molecular-beam epitaxy at low temperatures is that this material contains a high concentration of gallium vacancies $\sim 10^{18}\,\mathrm{cm}^{-3}$ (Ref. 5); i.e., the concentration of gallium vacancies in *LT* GaAs layers is comparable with the silicon concentration, and for formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes additional vacancies are not required.

Thus, in a layer of GaAs:Si grown by molecular-beam epitaxy at low temperatures, the concentration of gallium vacancies (V_{Ga}) and of $\mathrm{Si_{Ga}}$ donors is high [under conditions of a large arsenic excess, silicon atoms are embedded into the gallium sublattice (Ref. 14)]. The formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes, however, does not take place since the diffusion of defects and impurities at low temperatures is ''frozen.'' During annealing the gallium vacancies present in *LT* GaAs become mobile and as they diffuse they are captured by silicon atoms with subsequent formation of complexes. The activation energy of complex formation should be equal to the activation energy of migration of vacancies. According to our data, this energy for *LT* GaAs:Si layers not doped with indium is 1.9±0.3 eV. This quantity is indeed in good agreement with the data for the activation energy of gallium-vacancy diffusion.[12,13]

The data plotted in Fig. 3 indicate that the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes differs significantly in the samples doped with indium from those that are not doped. It can be seen that the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes in the indium-doped samples exceeds the activation energy of the complexes in the material not doped with indium by ~0.6 eV. Let us consider probable reasons for this phenomenon.

Since the concentration of gallium vacancies in our experiments was not measured, we can assume that an increase in the energy of complex formation is associated with an insufficient concentration of gallium vacancies in the indium-doped material, which leads to the necessity of generation of additional gallium vacancies (V_{Ga}) for complex formation to proceed. This assumption, however, is at variance with the data obtained in our previous studies.[15] Thus, optical absorption measurements in the near-infrared show that indium-doped *LT* GaAs contains a large concentration of excess arsenic and a large concentration of antistructural defects ($\mathrm{As_{Ga}}$) in comparison with the material not doped with indium. It is well known[16] that the concentration ratio $\mathrm{As_{Ga^+}}/\mathrm{As_{Ga^0}}$ remains roughly constant over a wide interval of growth temperatures and flux ratios As/Ga. An increase in the number of positively charged defects in turn, should obviously be accompanied by an increase in the concentration of gallium vacancies, which, as is suggested in Ref. 6, are the main compensating acceptors. It should also be noted that despite the high concentration of shallow Si donors ($7\times10^{17}\,\mathrm{cm}^{-3}$), the unannealed layers were high-resistance layers, i.e., the concentration of compensating acceptors should be higher than the concentration of shallow donors. In addition, earlier studies[15] of *LT* GaAs by transmission electron microscopy showed that during annealing the indium-doped material contains a higher concentration of large arsenic clusters in comparison with *LT* GaAs not doped with indium. It is now assumed that the formation of arsenic clusters occurs as a result of diffusion of excess arsenic in the gallium vacancies. Thus, we can rightfully and confidently conclude that doping of *LT* GaAs with indium should not be accompanied by a decrease in the gallium-vacancy concentration.

A probable reason for the increase in the energy of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complex formation in indium-doped samples is an interaction of the gallium vacancies with the indium atoms during diffusion of vacancies in the crystal. Indeed, in the investigated samples the indium concentration exceeds the silicon concentration by more than an order of magnitude, and although indium is an isovalent impurity and electrically inactive in gallium arsenide, the difference in the size of the indium and gallium atoms leads to the appearance of local elastic deformations in the vicinity of the lattice sites occupied by indium atoms. In other words, a vacancy creates local deformations of opposite sign in the material. It is clear that such defects, which create local deformations opposite in sign, have a tendency to come together and form complexes, lowering the free energy of the material. Such complexes can have a binding energy on the order of several tens of electron volts; however, they are less stable than defect complexes formed as a result of electrical interaction. As the annealing temperature is raised, these intermediate complexes decay, and the liberated gallium vacancy continues to diffuse about the crystal until it forms a more stable complex with a silicon donor.

CONCLUSIONS

Studies of the photoluminescence spectra at 4.2 K of GaAs layers, which have grown by molecular-beam epitaxy at low temperatures and which are doped with silicon showed that in the unannealed samples the concentration of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes is extremely small and is not detected experimentally; i.e., despite the high concentration of gallium vacancies and silicon donors, these defects virtually do not interact with one another during low-temperature molecular-beam epitaxy. Formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes takes place during annealing.

From the low-temperature photoluminescence data we determined the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes in LT GaAs layers doped with silicon. This energy is 1.9 ± 0.3 eV, which corresponds to the activation energy of diffusion of gallium vacancies.

We found that combined doping of LT GaAs by silicon and indium increases the activation energy of formation of $\mathrm{Si_{Ga}}-V_{\mathrm{Ga}}$ complexes to 2.5 ± 0.3 eV. A possible reason for this increase is an interaction between the gallium vacancies with the isovalent indium impurities due to local lattice deformations.

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