5-1-1992

Incorporation of Silicon and Aluminum in Low-Temperature Molecular-Beam Epitaxial GaAs

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(Received 26 November 1991; accepted for publication 1 March 1992)

The localized vibrational modes (LVMs) of silicon donor (Si_{Ga}) and aluminum isovalent (Al_{Ga}) impurities in molecular beam epitaxial GaAs layers grown at various temperatures are studied using the infrared absorption technique. It is found that the total integrated absorption of these impurities LVMs is decreased as the growth temperature decreases. This finding suggests a nonsubstitutional incorporation of Si and Al in GaAs layers grown at 200 °C. On the other hand, a subtitutional incorporation is obtained in GaAs layers grown at temperatures higher than 350 °C. A recovery of the Si_{Ga} LVMs in GaAs layers grown at 200 °C has not been achieved by thermal annealing.

It has been shown recently[1] that the arsenic-rich molecular beam epitaxial (MBE) GaAs layers grown at low temperature contain a large density ($\sim 10^{19}$ cm^{-3}) of deep defects that are closely related to the arsenic antisite (As_{Ga}) defect.[2,3] This material, when used for buffer layers in field-effect transistor devices, can substantially reduce backgating and sidegating.[4] For device applications and MBE growth kinetics studies[5] of low-temperature MBE GaAs, it is desired to dope this material with *n*- or *p*-type dopants. One method of studying the incorporation of low-mass dopants in this class of material is to measure their localized vibrational mode frequencies (LVMs). The optical absorption technique has the advantage of evaluating LVMs of isolated shallow impurities in GaAs regardless of their charge states.[6,7] In this letter, we report on optical absorption measurements of Si_{Ga} and Al_{Ga} LVMs in MBE GaAs layers grown at substrate temperatures ranging between 200 and 580 °C. It is observed that the total integrated absorption of these LVMs is reduced as the growth temperature decreases, suggesting a nonsubstitutional incorporation in layers grown at low temperatures. The effect of the thermal annealing on the Si_{Ga} LVM in layers grown at 200 °C will be presented.

The MBE layers were grown in Varian systems under normal, As-stabilized conditions at a growth rate of 0.8 μm/h. The beam equivalent As_4-to-Ga pressure ratio was about 20. The substrate was semi-insulating GaAs grown by the liquid-encapsulated Czochralski technique. The substrate temperature (T) was varied between 200 and 580 °C. Layer thicknesses were 5 and 20 μm for layers doped with Al and Si, respectively. Layers grown at 200 °C with a thickness larger than 2 μm are usually polycrystalline.[8] Grain boundaries may cause some broadening in the Si_{Ga} and Al_{Ga} LVMs, but a shift in the frequency of these LVMs has not been detected in polycrystalline bulk GaAs doped with Si and Al and grown by liquid-encapsulated Czochralski technique. Infrared absorption measurements were made at 77 K with a BOMEM spectrometer. Silicon-doped GaAs layers grown at $T \geqslant 350$ °C were electron irradiated at room temperature by using a 2.1 MeV, 2.1 μA electron beam from a van de Graaff accelerator in order to reduce the free-carrier absorption, which can obscure LVM spectra.

The optical absorption of the isolated Si_{Ga} LVM recorded at 77 K is shown in Fig. 1 for five samples grown at different temperatures but doped with the same silicon density ([Si]$\sim 1\times 10^{18}$ cm^{-3}). It is clear from this figure that the intensity of the Si_{Ga} LVM is decreased substantially in samples grown at $T \leqslant 250$ °C. Due to free-carrier absorption in samples grown at $T \geqslant 350$ °C, the Si_{Ga} LVM is observed only after irradiating these samples with a 2.1 MeV electron beam (dose $\sim 5\times 10^{17}$ cm^{-2}). Electron irradiation may also cause some damage to the isolated Si_{Ga} defect, but the number of Si_{Ga} atoms that are affected by electron irradiation should be a small fraction of the total Si density. The peak position energy of the Si_{Ga} LVM is about 383.5 cm^{-1} for all samples (within experimental error) except the sample grown at 200 °C which shows an apparent shift toward a higher energy. This shift may be due to the stress (strain) present in the MBE layer.[9]

In Fig. 2, we plot the Al_{Ga} LVMs for four GaAs:Al samples grown at different temperatures with a nominal aluminum concentration of $\sim 5\times 10^{19}$ cm^{-3}. The Al_{Ga} LVM in the sample grown at 414 °C is broad as compared to other samples, which may suggest that this sample is inhomogeneous. The Al_{Ga} LVMs behavior as a function of the growth temperature exhibits a trend similar to that of Si_{Ga} LVM. This is illustrated in Fig. 3, in which we plot the total integrated absorption of the LVM as a function of the growth temperature for both Si_{Ga} and Al_{Ga}. The reduction in LVM intensity as the growth temperature is decreased indicates a reduction in efficiency of the substitutional incorporation of silicon and aluminum in GaAs. A trend similar to that of Fig. 3 was observed[10] in the total carrier concentrations in GaAs:Si and AlGaAs:Si grown at a temperature ranging between 350 and 620 °C. The important conclusion here is that the substitutional incorporation rate of Si_{Ga} and Al_{Ga} in GaAs samples grown at $T < 250$ °C is

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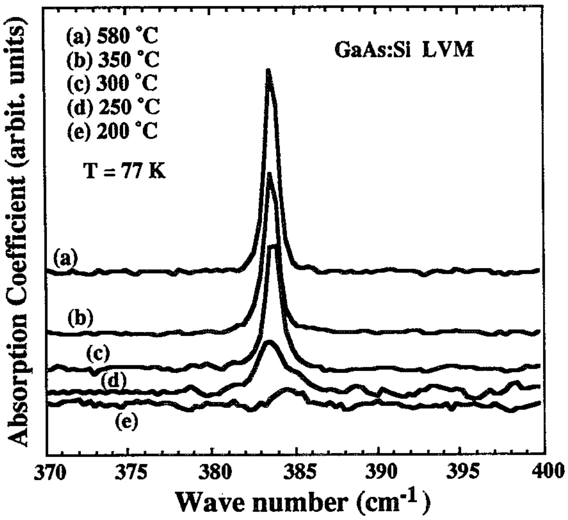

FIG. 1. The localized vibrational mode of Si_{Ga} in MBE GaAs grown at different growth temperatures. Spectra (a) and (b) were obtained after irradiating the samples with a 2.1 MeV electron beam. The spectra were recorded at 77 K.

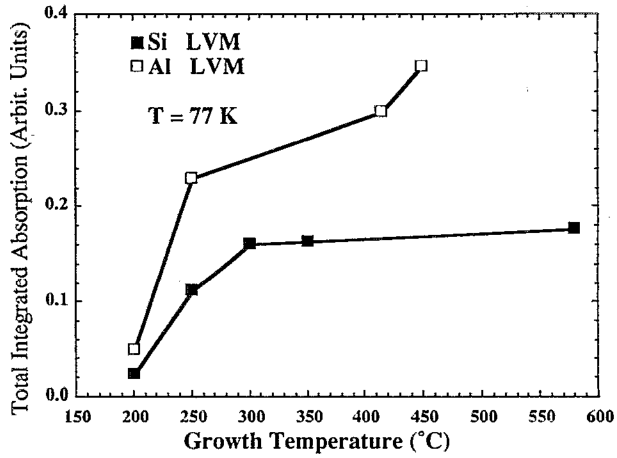

FIG. 3. The total integrated 77 K absorption of the localized vibrational modes of Si_{Ga} (close squares) and Al_{Ga} (open squares) in MBE GaAs as a function of growth temperature.

very small as compared to that of samples grown at $T > 300$ °C.

Aluminum in GaAs is an isovalent impurity when sitting on the Ga site, and thus it is electrically inactive. The nonsubstitutional incorporation of Al in MBE GaAs layers grown at 200 °C suggests strongly that epitaxial AlGaAs layers cannot be grown at $T \leqslant 200$ °C. This conclusion is tested in $Al_xGa_{1-x}As$ samples ($0.05 \leqslant x \leqslant 0.3$) grown at 200 °C, as follows. It is well known that either hydrostatic pressure or addition of Al to GaAs can alter the GaAs band structure. Thus, if Al is substitutionally incorporated in samples grown at 200 °C, then one would expect to observe a shift in what is called the intracenter transitions[11] of the EL2-like defect detected in low-temperature GaAs layers.[1,12] Unfortunately, a shift has not been observed in this intracenter transition of the EL2-like defect as the Al mole fraction is increased. In addition, if Al is substitutionally incorporated in these layers, then a photoinduced recovery of the EL2-like defect from its metastable configuration should occur at $T \leqslant 10$ K using photons with energy ~ 1.36 eV in analogy to the recovery of the metastable EL2 defect under hydrostatic pressure and 1.36 eV illumination.[13] Again, this effect has not been observed in $Al_xGa_{1-x}As$ samples grown at 200 °C, suggesting a nonsubstitutional incorporation of Al in agreement with the present LVM measurements (see Figs. 2 and 3). It should be pointed out that the Al_{Ga} LVM is observable in samples grown at 200 °C even though its intensity is very small as compared to that of samples grown at higher temperatures. This observation implies that a small fraction of aluminum is incorporated at the substitutional sites. However, we are unable to detect any emission from the $Al_xGa_{1-x}As$ band gap as x increases using the photoluminescence technique.

The thermal annealing effect on the Si_{Ga} LVM in GaAs grown at 200 °C is shown in Fig. 4. Spectrum (a) in this

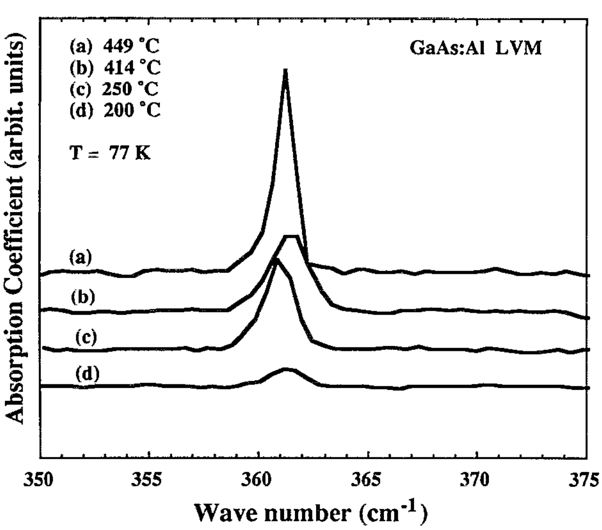

FIG. 2. The localized vibrational mode of Al_{Ga} in MBE GaAs grown at different growth temperatures. The spectra were recorded at 77 K.

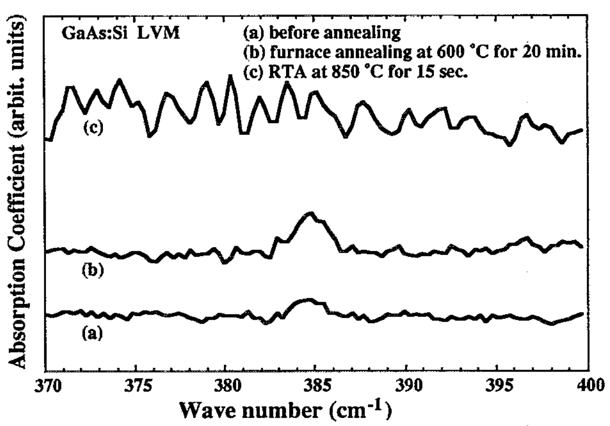

FIG. 4. The effect of thermal annealing on the Si_{Ga} localized vibrational mode in a GaAs sample shown at 200 °C. Spectrum (a) is obtained before thermal annealing, spectrum (b) is recorded after furnace annealing the sample at 600 °C for 20 min, and spectrum (c) is recorded after rapid thermal annealing (RTA) the sample at 850 °C for 15 s. All spectra were recorded at 77 K.

figure is the same as spectrum (e) in Fig. 1. Furnace annealing this sample at 600 °C for 20 min gives rise to the spectrum shown in Fig. 4(b). The total integrated absorption of the LVM in spectrum (b) is almost doubled after the furnace anneal, suggesting that a fraction of the silicon atoms are incorporated at the regular Ga site. However, rapid thermal annealing at 850 °C for 15 s seems to substantially reduce substitutional incorporation, as shown in Fig. 4(c).

So far, we assume that the reduction of the Si_{Ga} and Al_{Ga} LVMs integrated absorptions as the growth temperature decreases is due to nonsubstitutional incorporations. However, the present results do not rule out the possibility that these impurities are not present in the layers at all. For example, the lack of Si incorporation may be due to the desorption volatile Si-As complexes. On the other hand, preliminary measurements using the secondary-ion mass spectroscopy technique indicate that Si is present, with approximately the same concentration, in samples grown at 580 and 200 °C. It is also possible that Si and Al may form complexes with different LVM frequencies. Further investigation is in progress to determine the form of Si and Al in 200 °C-grown GaAs material.

The Si_{Ga} LVM results described here have a relevance with regard to compensation in low-temperature MBE GaAs. Basically, two compensation models have been proposed to explain the high resistivity in annealed low-temperature MBE GaAs: (1) a "point-defect" model in which a deep donor N_{DD} (As_{Ga} related defect) compensates a shallow acceptor N_{SA} (a few kT below the Fermi level) leaving the Fermi level near midgap; and (2) an "As-precipitate" model in which large ($\sim$60 Å), dense ($\sim 10^{17}$ cm^{-3}) precipitates of metallic As produce overlapping Schottky depletion regions as a result attracting the free carriers to the metal.[14] The depletion regions strongly overlap; the whole volume of the sample is essentially held at the Schottky potential, which is also near midgap. Let us first suppose that each of the shallow donor(N_{SD}) Si_{Ga} in the present samples contributes one conduction electron to the sample. Then low resistivity would be expected unless (1) the As precipitates were active, or (2) $N_{SA} > N_{SD}$, and N_{SA} were not too far below midgap. Indeed, N_{SA} can be quite large[2,3] ($> 10^{18}$ cm^{-3}) from electron paramagnetic (EPR) results in unannealed, 200 °C-grown MBE GaAs, but it is much lower in annealed materials, as determined by the lack of As^{+}_{Ga} related EPR signal. Thus, N_{SA} is annealed material cannot compensate 10^{18} cm^{-3} silicon atoms if each is electrically active (i.e., Si_{Ga}), and the As-precipitate model (or some totally different mechanism) must be invoked. However, the present Si_{Ga} LVM results show that Si is predominantly electrically inactive in either unannealed or annealed, 200 °C-grown MBE GaAs. Therefore, there is no need to invoke the As-precipitate model to explain the lack of conductivity in this material.

In conclusion, the optical absorption of the localized vibrational modes of Si_{Ga} and Al_{Ga} in MBE GaAs are studied for the first time as a function of growth temperature. The total integrated absorption of these localized vibrational modes is found to decrease as the growth temperature decreases, suggesting an increasing tendency towards nonsubstitutional incorporation in samples grown at low substrate temperatures. Post-growth thermal annealing of silicon-doped samples grown at 200 °C does not seem to significantly increase the substitutional incorporation of Si_{Ga}. The present results of the Si_{Ga} LVM in 200 °C-grown MBE GaAs suggest that the As-precipitate model[14] is not needed to explain the high resistivity in this type of material.

The authors are grateful to J. Ehret, E. Taylor, and C. Jones for the MBE growth and T. Cooper for the Hall measurements. This work was partially supported by the Air Force Office of Scientific Research.

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