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Defect induced Raman transition in non-stoichiometric Ga-rich GaAs: A pseudolocalized vibrational mode of the Ga_{As} antisite?

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Raman scattering with below band gap excitation has been used to study as grown GaAs pulled from Ga-rich melts. A vibrational pseudolocalized defect mode is observed at 225 cm^{-1} in material, which also contains the 78/203 meV double acceptor. The temperature variation of the 225 cm^{-1} Raman peak is found to depend on the charge state of the double acceptor. These findings indicate that the 78/203 meV acceptor levels and the 225 cm^{-1} vibrational mode may arise from the same defect center. Possible models for this center are discussed including the Ga-antisite defect.

Impurities or intrinsic defects in semiconductors may produce low energy resonances or pseudolocalized modes (designated simply as LVM below) lying within the spectrum of intrinsic lattice vibrations, which can be observed as relatively sharp features in the infrared absorption or Raman scattering spectra. Although the symmetry of the defects can be determined, their identification relies on supplementary data. For example, boron impurities introduced into GaAs during crystal growth and detected by true LVM lines at 517 and 540 cm^{-1} for $^{11}B_{Ga}$ and $^{10}B_{Ga}$, respectively, produce an infrared active resonance at 123 cm^{-1} the strength of which correlates with the high energy lines [1]. The assignment of this resonance can be made with certainty. However, the assignment of resonances to intrinsic defects in GaAs is in general much more difficult and relies on (a) details of the crystal growth, (b) DLTS and EPR measurements, (c) annealing studies and (d) predictions of theoretical models.

In order to observe defect induced vibrational breathing modes (Γ_1 symmetry), Raman spectroscopy has to be employed. The only experimental results on defect induced breathing modes in GaAs are those reported by Berg et al. [2-4]. These authors studied semi-insulating liquid encapsulated Czochralski (LEC) grown GaAs, which was irradiated with either high energy electrons or neutrons. They observed a vibrational breathing mode of an intrinsic point defect at 227 cm^{-1}. Based on the annealing behaviour of this Raman peak it was suggested that the mode is associated with an As vacancy.

In the present study we report a pseudolocalized mode at 225 cm^{-1} in as-grown Ga-rich GaAs, which also shows the 78/203 meV double acceptor. The temperature variation of this mode depends on the charge state of the double acceptor, which has been associated with the Ga-antisite defect (Ga_{As}) [5].

The GaAs samples were cut from LEC grown Ga-rich material. The stoichiometry of the melt was $Ga_{.55}As_{.45}$ (sample No. 1) and $Ga_{.53}As_{.47}$ (sample No. 2). Sample No. 1 contains the 78/203 meV double acceptor in its neutral (78 meV) charge state in the as-grown material and in its singly ionized (203 meV) state after 2 MeV electron irradiation at a dose of 1.9 x 10^{16} e^-/cm^2. In sample No. 2, neither charge state of this double acceptor is observed. For reference purposes undoped semi-insulating LEC material was also studied (sample No. 3). The thickness of the samples was 2-3 mm for the as-grown and approximately 0.5 mm for the electron irradiated specimens.

The samples were mounted in a variable temperature liquid He cryostat. The Raman spectra excited with the 1064.4 nm line of a Nd-YAG laser were recorded in backscattering from a (100) surface. The scattered light was dispersed in a scanning double spectrometer and detected with an intrinsic Ge-diode. The spectral resolution was set to 7 cm^{-1}.

Fig. 1a displays the 77 K Raman spectrum of sample No. 1 in the as-grown state. The spectrum shows intrinsic first order scattering by the LO (longitudinal optical) and TO (transverse optical) phonons, second order scattering by 2TA (transverse acoustic) [6] phonons at $\simeq$120 - 230 cm^{-1} and an additional peak at 225 cm^{-1} (labelled LVM), which is superimposed on the second order phonon spectrum. Fig. 1b shows the same spectrum as Fig. 1a but with the second order phonon background subtracted as is seen e.g. from the absence of the 2TA phonon peak at 160 cm^{-1}. This difference spectrum clearly shows the 225 cm^{-1} line. The broad feature below 200 cm^{-1} arises from scattering by free holes [7], as this material contains a fairly large concentration of residual shallow acceptors (see below). The 225 cm^{-1} peak is neither found in standard semi-insulating LEC GaAs (sample No. 3, Fig. 1d) nor in sample No. 2 (Fig. 1c), which was less Ga-rich grown than sample No. 1.

The 225 cm^{-1} Raman line is observed in such scattering configurations for which Raman tensors of Γ_1 or Γ_5 symmetry are allowed. Both contributions of Γ_1 and Γ_5 symmetry have about equal scattering intensities. Thus the contribution of Γ_1 symmetry does not arise from the underlying second order Raman spectrum.

Fig. 2 shows Raman spectra of sample No. 1 in the as-grown state recorded at different temperatures. At 6 K electronic scattering (1s-2s transitions) of neutral carbon and zinc acceptors [8,9] is observed in addition to the 225 cm^{-1} peak. Raising the sample temperature to 77 K the electronic scattering from shallow acceptors disappears whereas the 225 cm^{-1} peak is observable up to $\cong$150 K.

Electron irradiation of the as-grown material shifts the Fermi level upwards towards the mid-gap position, causing a change of the charge state of the 78/203 meV double acceptor. This is illustrated in Fig. 3. Fig. 3a shows the electronic Raman spectrum ($1s^2$-1s2s excitations E and E′) of the neutral double acceptor (78 meV level), whereas Fig. 3b displays the electronic spectrum (1s-2s (E) and 1s-2p (C and D) excitation) of the singly ionized acceptor (203 meV level) observed after electron irradiation [10].

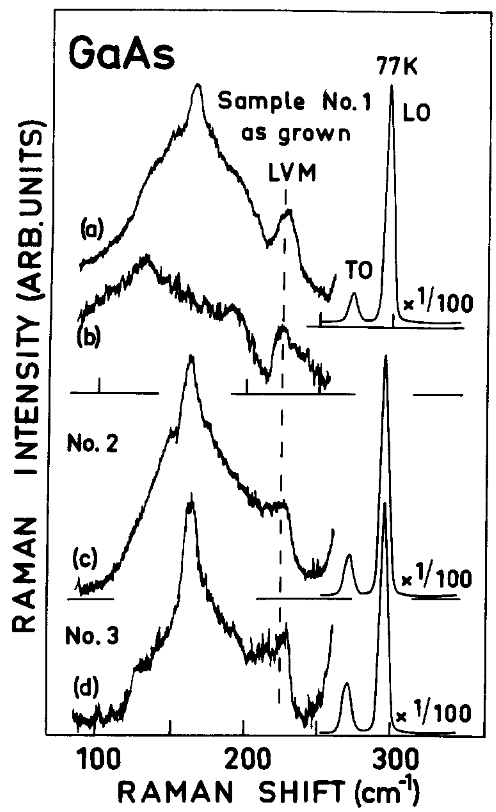

Fig. 1 Low temperature (77 K) Raman spectra of two different Ga-rich GaAs samples (a-c) and undoped semi-insulating LEC GaAs (d). The spectra were excited at 1064.4 nm and recorded at a spectral resolution of 7 cm^{-1}. LVM denotes the pseudolocalized 225 cm^{-1} defect mode. Spectrum (b) is the same as (a) but with the intrinsic two phonon background subtracted.

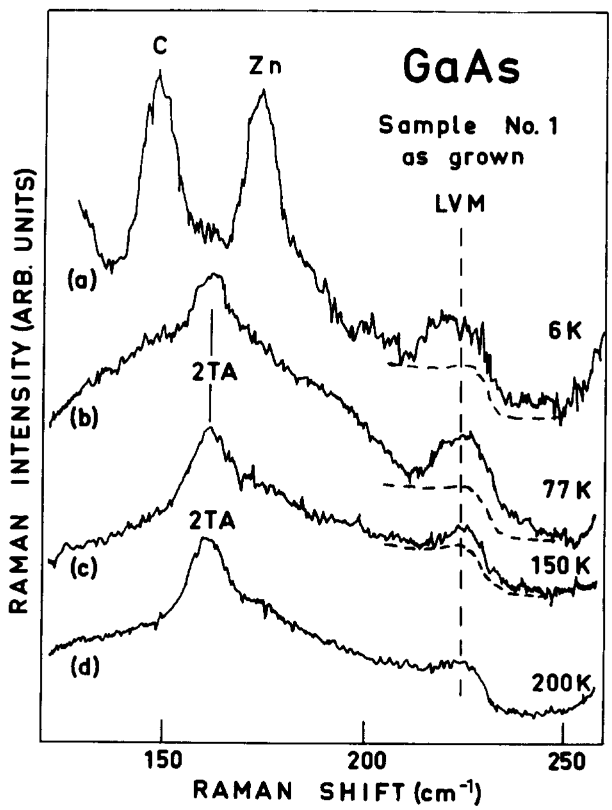

Fig. 2 Temperature dependence of the Raman scattering from the 225 cm^{-1} defect mode for sample No. 1 in the as-grown state. The dashed curves indicate the shape of the two phonon spectrum.

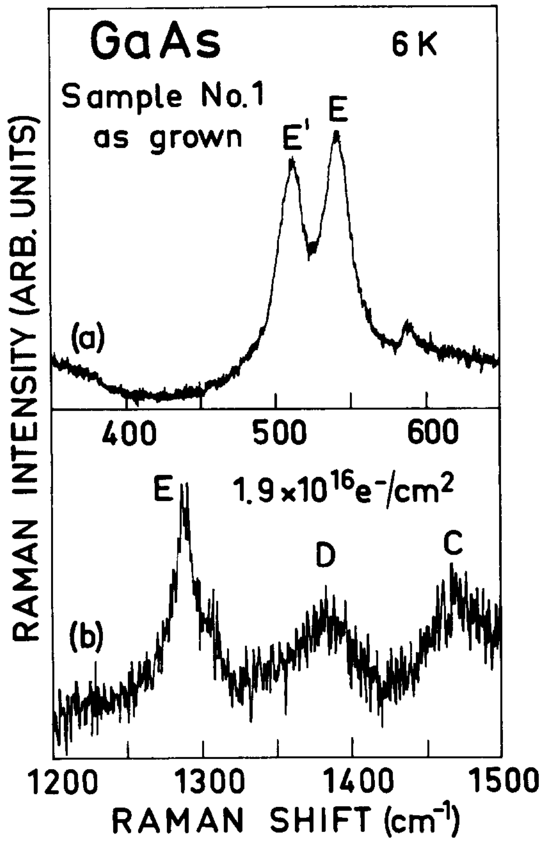

Fig. 3 Electronic Raman scattering of the 78 meV acceptor level (a) in sample No. 1 in the as-grown state (lines E and E′) and of the 203 meV level (b) after 2 MeV electron irradiation (lines E, D, and C).

Fig. 4 depicts a series of Raman spectra of sample No. 1 after electron irradiation recorded at different temperatures. The 6 K spectrum shows the intrinsic second order phonon spectrum (2TA) with a maximum at 160 cm^{-1} as well as the 225 cm^{-1} peak. No electronic scattering from carbon and zinc is observed as these acceptors are ionized due to the electron irradiation. Increasing the sample temperature to 40 K leads to a significant reduction in the intensity of the 225 cm^{-1} peak. At 77 K the 225 cm^{-1} peak has disappeared and only the second order phonon spectrum is observed. This is in sharp contrast to the Raman spectra of sample No. 1 in the as-grown state, where the 225 cm^{-1} peak is still seen at its full intensity at 77 K.

Based on the temperature dependence of the 225 cm^{-1} peak in the as grown material as well as on the fact, that it is still observed after electron irradiation, we conclude that this peak does not arise from electronic excitations of shallow defects. We cannot exclude the possibility, that it might originate from a transition between two rather deep lying electronic levels, the occupation of which is temperature independent up to 150 K and is not

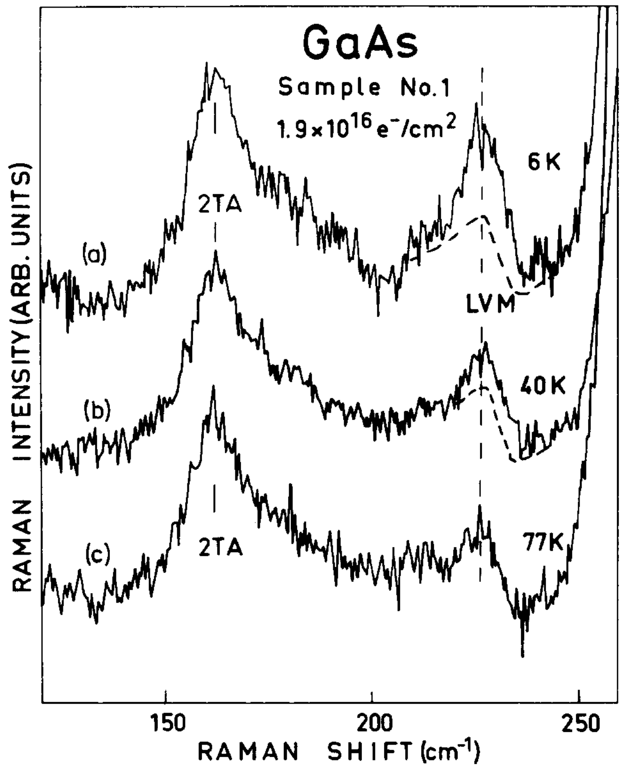

Fig. 4 Temperature dependence of the Raman scattering from the 225 cm^{-1} defect mode for sample No. 1 after 2 MeV electron irradiation. The dashed curves indicate the shape of the two phonon spectrum.

affected by the present electron irradiation. However we would then expect a rather small scattering cross section as the electronic states involved would be strongly localized, making it unlikely that such a transition would be observed [11]. Thus we conclude that the 225 cm^{-1} peak is due to a pseudolocalized defect mode (LVM).

The temperature dependence of the 225 cm^{-1} LVM Raman peak is somewhat puzzling. Unlike other LVM Raman lines as e.g. from Si in GaAs, which are also observed at 300 K [12], the 225 cm^{-1} peak is observed only up to $\simeq$150 K in the as-grown sample and up to $\simeq$40 K in the electron irradiated sample. A possible explanation is, that there is a significant reduction of the lifetime of this mode at elevated temperatures. The reduction would result in a considerable broadening of the peak making it undetectable because it is superimposed on the two phonon background. An alternative explanation would be that the Raman scattering matrix element is temperature dependent.

The fact that the 225 cm^{-1} LVM peak is only observed in material containing the 78/203 meV acceptor as well as the correlation of the temperature dependence of this Raman peak with the charge state of the 78/203 meV acceptor suggests, that both the 225 cm^{-1} LVM and the

78/203 meV acceptor levels may arise from the same defect. The correlation of the temperature dependence of the LVM with the charge state is then understood in terms of a dependence of the coupling between the pseudolocalized mode and the lattice phonons upon the electronic state of the defect.

The 78/203 meV acceptor levels have been attributed to the Ga_{As} defect, but the possibility that a complex is formed with an impurity such as the isoelectronic B_{Ga} cannot be ruled out [5]. In either case we may associate the 225 cm^{-1} LVM with a pseudolocalized vibrational mode of the Ga_{As} defect. However, in the present samples we do not observe the 119 cm^{-1} LVM found in infrared absorption, which has also been assigned to the Ga_{As} antisite defect [13]. This mode should also be Raman active (Γ_5 symmetry), but one may argue that the scattering cross section might be too small for this mode to be observed in Raman scattering for the present defect concentration.

Berg et al. [2-4] observed a LVM at 227 cm^{-1} in electron or neutron irradiated GaAs, which they assigned to a breathing mode around the As vacancy. This frequency (227 cm^{-1}) is slightly different than the one found here (225 cm^{-1}), but this shift has little significance compared to the relatively large linewidth of $\simeq$15 cm^{-1}. The assignment to the As vacancy also holds for the present observations because both Ga_{As} antisite defects and As vacancies are expected to occur in Ga-rich material. This alternative interpretation would, however, conflict with the correlation found with the 78/203 meV double acceptor, which most likely involves the Ga_{As} defect. Thus we are left with the possibility, that the defect mode at 227 cm^{-1} observed by Berg et al. [2] and the present 225 cm^{-1} mode may arise from two different defects-namely the As vacancy and the Ga_{As} antisite - which both produce resonances at almost the same frequency. This view is supported by the difference in the symmetries of the two transitions - mostly Γ_1 for the 227 cm^{-1} LVM [2] and $\Gamma_1 + \Gamma_5$ for the 225 cm^{-1} mode. One may argue that the Γ_1 component of the 225 cm^{-1} Raman peak might arise from the 227 cm^{-1} mode. However, both the Γ_5 and the Γ_1 component of the 225 cm^{-1} peak show the correlation with the double acceptor, making this assignment unlikely.

Based on theoretical calculations, Scheffler and Scherz [14] conclude, that the 227 cm^{-1} breathing mode reported by Berg et al. [2] is more likely to arise from an antisite defect than from a vacancy. Of the two antisite defects, these authors favour the As_{Ga} defect, although they cannot exclude the Ga_{As} antisite. They state that more theoretical work is necessary to resolve the questions.

In conclusion we have observed a pseudolocalized vibrational defect mode at 225 cm^{-1} in Ga-rich GaAs, which also contains the 78/203 meV double acceptor. The temperature variation of the 225 cm^{-1} Raman peak is found to depend on the charge state of the double acceptor, indicating that the acceptor levels and the 225 cm^{-1} mode may arise from the same defect. This correlation suggests that the 225 cm^{-1} mode is associated with the Ga_{As} antisite. However, further work is needed to clarify the proposed interpretation.

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