Antisite-related defects in plastically deformed GaAs

P. Omling
Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

E. R. Weber
Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 and Department of Materials Science, University of California, Berkeley, California 94720

L. Samuelson
Department of Solid State Physics, University of Lund, P. O. Box 118, S-221 00 Lund, Sweden
(Received 12 August 1985)

Optical absorption measurements on plastically deformed GaAs show that the total extrinsic absorption increases with deformation, while the quenchable EL2 absorption stays constant. The nonquenchable extrinsic absorption is observed to be proportional to the EPR measured As_{Ga} containing defects produced during deformation. Since the As_{Ga}-related defects produced by plastic deformation anneal at $T \sim 650\,°C$, the implication for any correlation between EL2 and As_{Ga} antisites is that only those As_{Ga}-related EPR centers which are stable up to at least 950 °C can possibly be responsible for the EL2 level.

INTRODUCTION

Plastic deformation (PD) of GaAs introduces several defects, some of which have been observed to give rise to energy levels deep in the band gap.[1-5] These deep-level defects have previously been studied by several methods such as photoconductivity,[1] space charge techniques,[2,3] and electron paramagnetic resonance (EPR)[4,5] techniques. The most detailed results on a specific center seem to come from the EPR investigations of the antisite defect As_{Ga}.[5,6] The large interest in this defect is partly due to the fundamental interest in native defects, and partly to its possible connection to the controversial EL2 level.[7-9] In fact, the original measurements which led to the As_{Ga}-EL2 connection were performed in PD GaAs.[5] The reason for performing these measurements in PD GaAs rather than in as-grown "undoped" GaAs was the observation that the As_{Ga} signal increases by PD. In strongly deformed samples the spin concentration has been observed to exceed 5×10^{16} cm^{-3}, while the concentration in as-grown material is as low as 10^{16} cm^{-3} or below.[10]

In order to confirm the suggested As_{Ga}-EL2 correlation, an attempt was previously made to investigate whether there was a corresponding increase in the EL2 concentration with PD.[10] The only known method to measure the EL2 concentration in semi-insulating material (which was required in order to measure EPR on the same samples) was the optical absorption method as suggested by Martin.[11] He had established relationships between the absorption coefficient (at certain photon energies) and the EL2 concentration as determined by space charge techniques. Comparison of the EPR measurement and the straightforward absorption measurements gave a one-to-one relationship between the As_{Ga} spin-concentration and the apparent EL2 concentration. This relationship was found to range over more than two orders of magnitude by also incorporating data from as-grown and neutron-irradiated GaAs.[10]

By using an improved absorption technique[12] for EL2 measurements, where the absorption signal from the quenchable EL2 center and the absorption signal from the background could be separated, it was shown that the quenchable EL2 concentration was actually the same in a PD sample as in the material prior to deformation.[13]

Since this has important consequences for the As_{Ga}-EL2 correlation, we will in this Brief Report present optical absorption data and EPR results on GaAs material deformed by different amounts. Based on these experimental data, we will discuss the origin of the observed absorption bands and the relationship between As_{Ga} antisite defects and the EL2 level.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental work, EPR and optical absorption measurements, has been performed on semi-insulating GaAs before and after plastic deformation. The deformations were obtained by static compression (resolved shear stress $\tau = 30$ MPa) along [110] at 400 °C in an atmosphere of 8 vol% H_2 and 92 vol% N_2, resulting in up to 9% deformation of the crystals. These deformations increased the dislocation densities from low 10^4 cm^{-2} to high 10^8 cm^{-2}. For comparison, neutron-irradiated samples of the same starting material were also investigated. The experimental procedure for spin-concentration measurements has recently been described.[14]

Optical transmission measurements are typically used to obtain an absorption spectrum. In the case of EL2, this technique was used early on to investigate optical properties as well as concentrations of this deep level.[11] This type of measurement is, however, not suitable for EL2 characterization when other deep-level defects contribute to the absorption spectra, i.e., when $\alpha = \alpha_{EL2} + \alpha_l$ (where α_{EL2} is the EL2 absorption and α_l the absorption from other defects). In the case of EL2, one can easily separate the α_{EL2} contribution by measuring the transmission spectra before $[T(h\nu)]$ and after $[T_Q(h\nu)]$ bleaching of the EL2 levels.[12] This bleaching of the EL2 levels is performed by strong illumination in the 1.0 eV $\lesssim$ 1.3 eV band. The absorption coefficient α_{EL2} is now directly determined from

$$\alpha_{EL2}(h\nu) = (1/d)\ln[T_Q(h\nu)/T(h\nu)] \quad . \tag{1}$$

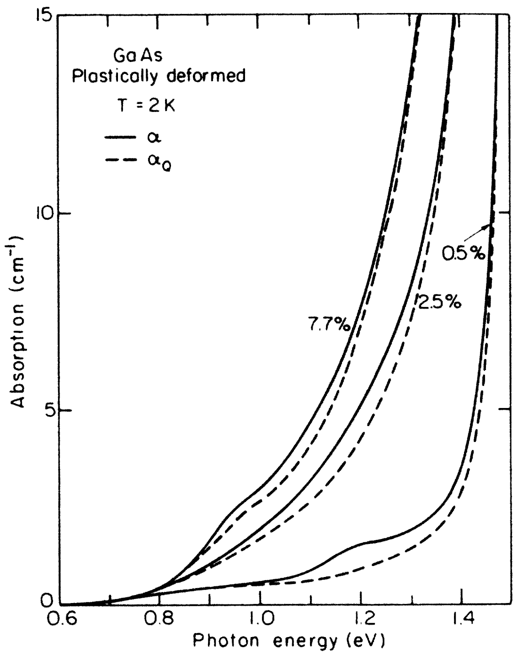

FIG. 1. Optical absorption measurements performed on as-grown and differently plastically deformed GaAs before (α) and after (α_Q) quenching of the EL2 levels.

In this way, assumptions about wavelength-dependent reflectivities, refractions, etc., are unnecessary, thereby making the measurement of α_{EL2} more reliable.

Typical results from such measurements in PD material are shown in Fig. 1 where the low-temperature absorption spectra obtained before and after quenching of the EL2 levels are presented for several deformed GaAs crystals. This shows that the total absorption in PD material consists of two different parts; a quenchable part which is EL2 related, and a nonquenchable part.

Comparing these two parts in samples subjected to different degrees of PD (Fig. 2), it is observed that the nonquenchable part increases strongly with deformation while the quenchable part is, in magnitude, the same as in the as-grown material prior to deformation. The shape of the quenchable spectrum is similar to the shape of the EL2 spectrum in the as-grown material (Fig. 3), even though an increasing distortion of the spectrum with deformation is observed. This probably indicates a distortion of the ideal EL2 centers by the increasing strain in the crystal. Similar deformation-introduced distortions of electronic spectra have been observed in PD silicon.[15] One can also see an absorption band around 0.9 eV, probably indicating the hole ionization process to EL2. It should be noted that the total absorption in the PD samples is very large near the band gap (10^4 cm^{-1}), which makes an accurate determination of α_{EL2} difficult, especially in the high-energy region.

From this we conclude that the quenchable EL2 concentration in the differently deformed materials is the same as in the as-grown material before deformation. We also conclude that PD GaAs shows strong extrinsic absorption that increases with deformation. This absorption, however, is not related to the quenchable EL2 levels.

These results also show that the observed one-to-one

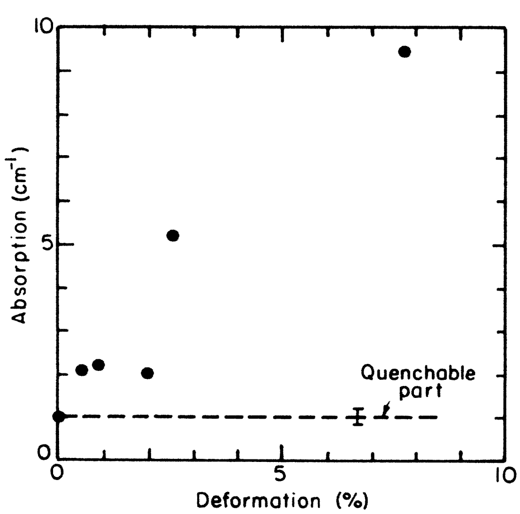

FIG. 2. The magnitude of the optical absorption after quenching (α_Q) at $h\nu = 1.24$ eV (●), and the corresponding magnitude of the quenchable part (— — —) for different deformations. The error bar indicates the spread of data for the whole line.

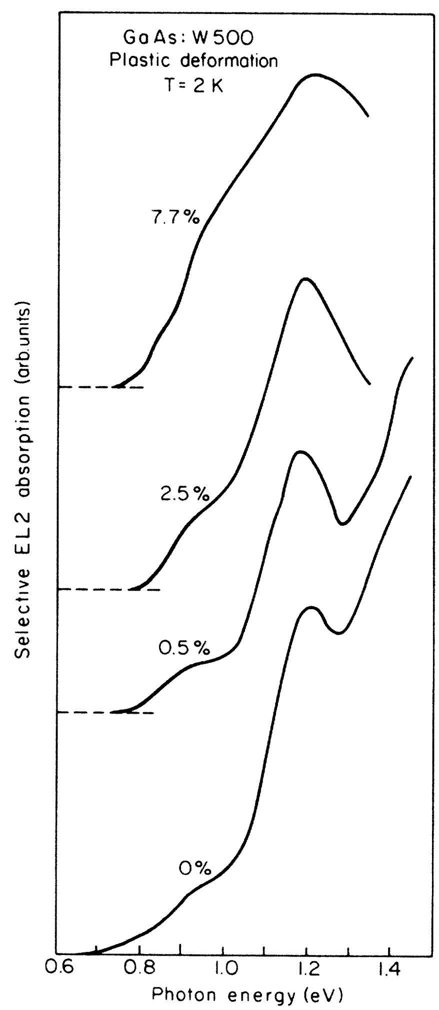

FIG. 3. The spectral dependence of the selective EL2 absorption for differently PD GaAs. The as-grown material used for the deformations (0%) is also included. The vertical scale is the same for all spectra.

correspondence between the As_{Ga} spin concentration and the total absorption in PD material is not a relevant argument when discussing a correlation between the As_{Ga} defect and the quenchable EL2 level. The question is, rather, if it excludes such a correlation. To answer this we have to consider several recent findings concerning the origin of the As_{Ga} EPR spectrum.[9] The different annealing behavior of the As_{Ga} EPR signal in as-grown, PD, and neutron-irradiated GaAs,[10] as well as investigations of the temperature dependence of the As_{Ga} spectrum,[16] shows that more than one As_{Ga}-containing defect can contribute to the EPR signal. Investigations of the introduction rate of As_{Ga}-containing defects during electron irradiation also suggest the existence of different As_{Ga}-related defects.[17] Unfortunately, the different centers cannot be distinguished in EPR measurements due to the complex (unresolved) superhyperfine interactions. However, optically detected ENDOR directly demonstrated the existence of various As_{Ga}-containing defects in both as-grown and PD GaAs.[18,19] On the other hand, the fact that both EL2 and the antisite defect are "common" defects, formed in similar concentrations under similar stoichiometric conditions in as-grown GaAs, may suggest some kind of connection.

The conclusion from our data is, therefore, that the EL2 level cannot be related to all As_{Ga} defects observed by EPR, but it might be related to a part of the EPR spectrum. It is interesting to note that a small part of the EPR spectrum in PD material does not anneal at 650 °C, where the major part of the EPR signal disappears, but at or above 950 °C where the EPR centers in as-grown material also vanish. These more stable EPR centers could, therefore, be the As_{Ga}-containing centers already present in as-grown material. Furthermore, since EL2 is also stable at least up to 950 °C, and has the same concentration in as-grown and PD samples, it seems tempting to suggest that these stable As_{Ga}-containing defects are responsible for the EL2 level.

By comparing the spin-lattice relaxation times, saturation behavior, and absorption versus dispersion measurements obtained by EPR and optically detected ENDOR, it was only recently feasible to experimentally exclude the possibility that the EL2 level is the ideal undistorted As_{Ga} defect.[19,20] Moreover, the ODENDOR investigations showed the existence of several different As_{Ga}-containing defects in as-grown GaAs as well as in PD GaAs.[18,19] Therefore, the most likely possibility is that the EL2 level is an As_{Ga}-containing defect, the exact nature of which remains to be determined.

It has previously been argued that the extrinsic absorption signal introduced by PD is directly related to the dislocations which are generated during the deformation process.[21] This is apparently supported by our optical data, where it is observed that the absorption increases with deformation. On the other hand, it has been shown that plastic deformation results in the formation of dislocations as well as point defects and point defect clusters.[22] Therefore, a change of a physical property (like absorption) by plastic deformation is not a strict proof that this effect is related exclusively to dislocations.

Instead, based on the fact that the nonquenchable absorption is directly proportional to the total As_{Ga}-related EPR concentration (see Fig. 4), we suggest that the absorption signal is due to As_{Ga}-containing defects produced during the deformation and is not directly due to the dislocations. This conclusion is further supported by the observation that this

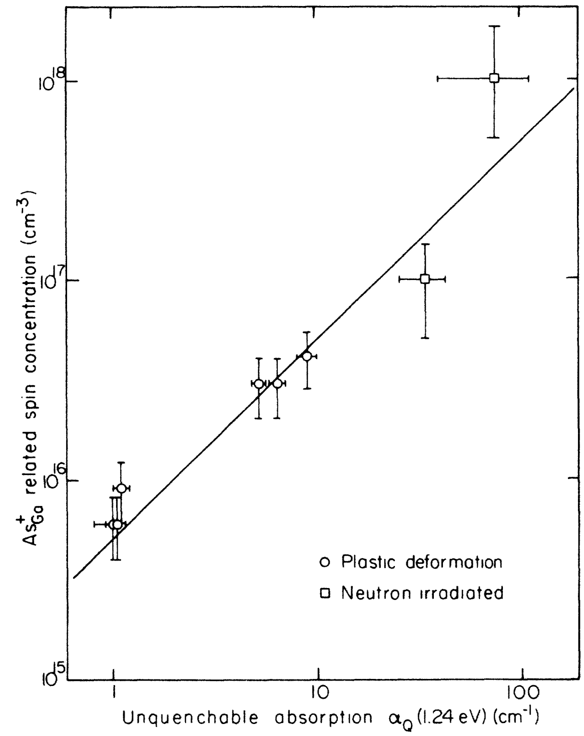

FIG. 4. The As_{Ga}-related spin concentration plotted vs the absorption after quenching of the EL2 levels for plastically deformed and neutron-irradiated GaAs.

proportionality is also observed in neutron-irradiated GaAs, in which the dislocation density has not increased correspondingly. In this latter case, the quenchable EL2 concentration is the same before and after irradiation. It is interesting to note that all of these As_{Ga}-related defects seem to give rise to levels in the band gap. These levels, which are observed here by optical absorption and EPR, may be the midgap levels seen by DLTS, but not the quenchable EL2 defect, as originally suggested for plastically deformed[2,23] GaAs. The reason for this collection of different energy levels is not understood, but it probably means that we are studying almost identical defects with only slight variations in microscopic structure. This is supported by the findings by optically detected ENDOR.[18,19]

CONCLUSION

Absorption and EPR measurements have been performed on GaAs exposed to different levels of plastic deformation. Absorption measurements show that the quenchable absorption due to EL2 is not (within experimental uncertainties) affected by the plastic deformation and is the same as in the undeformed material. The nonquenchable absorption is found to increase proportional to the As_{Ga}-related EPR signal. Contrary to previous suggestions that the increased extrinsic absorption is due to dislocations, we suggest that it is related to the PD-induced As_{Ga}-related defects. This is supported by a comparison with neutron-irradiated GaAs. We also conclude that a major portion of the observed As_{Ga} EPR signal in plastically deformed GaAs is not EL2 related. However, our results do not exclude the possibility that the thermally stable part of the As_{Ga}-containing EPR signal can be EL2 related.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge E. E. Haller, R. McMurray, Jr., and W. Walukiewicz for helpful discussions and critical reading of the manuscript. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, and Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1]H. Nakata and J. Ninomiya, J. Phys. Soc. Jpn. **47**, 1912 (1979).

[2]T. Ishida, K. Maeda, and S. Takeuchi, Appl. Phys. **21**, 257 (1980).

[3]T. Wosinski, A. Morawski, and T. Figielski, Appl. Phys. A **30**, 233 (1983).

[4]T. Wosinski, Phys. Status Solidi A **60**, K149 (1980).

[5]E. R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982).

[6]E. R. Weber and J. Schneider, Physica B **116**, 398 (1983).

[7]S. Makram-Ebeid, P. Langlade, and G. M. Martin, in *Semi-Insulating III-V Materials*, edited by D. C. Look and J. S. Blakemore (Shiva, Nantwich, 1984), p. 184.

[8]J. Lagowski and H. C. Gatos, J. Electron. Mater. **14a**, 73 (1985).

[9]E. R. Weber and P. Omling, in *Festkörperprobleme, Advances in Solid State Physics, Vol. XXV*, edited by P. Grosse (Vieweg, Braunschweig, 1985), p. 623.

[10]E. R. Weber, in *Semi-Insulating III-V Materials*, edited by D. C. Look and J. S. Blakemore (Shiva, Nantwich, 1984), p. 296.

[11]G. M. Martin, Appl. Phys. Lett. **39**, 747 (1981).

[12]L. Samuelson, P. Omling, E. R. Weber, and H. G. Grimmeiss, in *Semi-Insulating III-V Materials*, edited by D. C. Look and J. S. Blakemore (Shiva, Nantwich, 1984), p. 268.

[13]P. Omling, L. Samuelson, and H. G. Grimmeiss, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, 1984*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985), p. 751.

[14]T. Chang and A. H. Kahn, Nat. Bur. Stand. (U.S.) Spec. Publ. **260**, 59 (1978).

[15]R. Sauer, J. Weber, J. Stolz, E. R. Weber, K. H. Küsters, and H. Alexander, Appl. Phys. A **36**, 1 (1985).

[16]A. Goltzene, B. Meyer, and C. Schwab, J. Electron. Mater. **14a**, 937 (1985).

[17]R. C. Newman, J. Electron. Mater. **14a**, 87 (1985).

[18]D. M. Hofmann, B. K. Mayer, F. Lohse, and J. M. Spaeth, Phys. Rev. Lett. **53**, 1187 (1984).

[19]J. M. Spaeth, D. M. Hofmann, and B. K. Mayer, in *Microscopic Identification of Electronic Defects in Semiconductors*, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (Materials Research Society, Pittsburgh, 1985), p. 185.

[20]E. R. Weber, P. Omling, and J. M. Spaeth (unpublished).

[21]J. L. Farvacque and D. Vignaud, J. Electron. Mater. **14a**, 373 (1985).

[22]E. R. Weber and H. Alexander, in *Radiation Effects in Semiconductors, Dubrovnik, 1976*, Institute of Physics Conference Series No. 31, edited by N. B. Urli and J. W. Corbett (IOP, Bristol, 1977), p. 266.

[23]T. Wosinski, A. Morawski, and T. Figielski, Appl. Phys. A **30**, 233 (1983).