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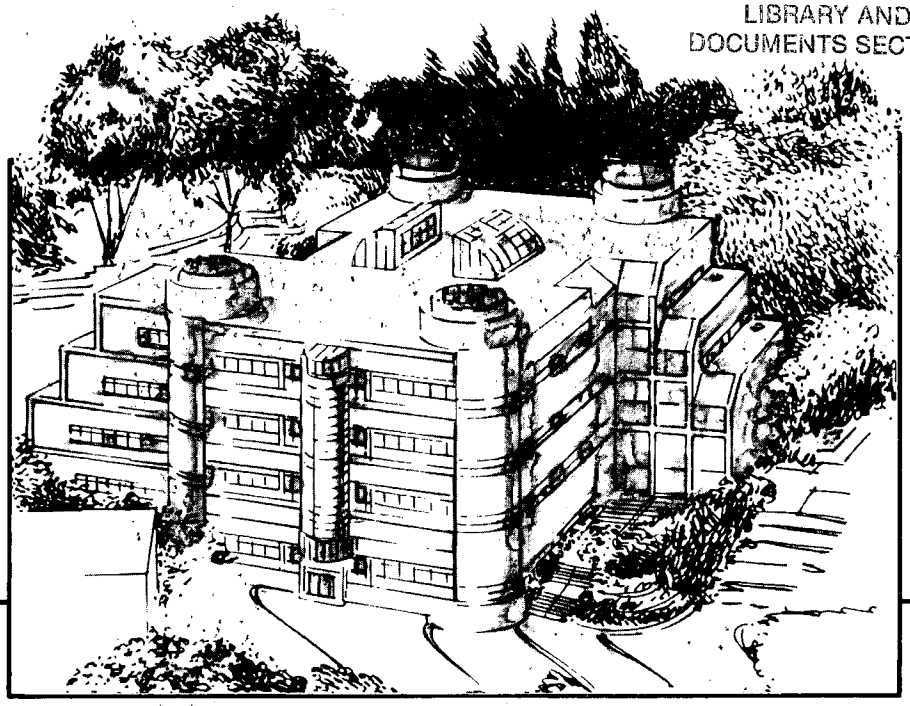

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SPATIAL DISTRIBUTION OF CARBON AND NATIVE DEFECTS IN LARGE-DIAMETER BULK GROWN GaAs

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SUMMARY

We have combined different spectroscopic techniques to measure concentrations of carbon on arsenic sites and of neutral EL2. Utilizing the recently found dependence of the high resolution local vibrational mode spectrum on the charge state of the carbon acceptors we have been able to separately determine concentrations of neutral and ionized carbon after EL2 has been optically quenched. The concentration of ionized carbon shows a very distinct W-shaped variation across the wafer whereas the total carbon concentration is close to constant. The variations are caused by the nonuniform distribution of donors which are shallower than EL2. They account for the commonly observed variations of the near infrared absorption. Radiotracer experiments with GaAs crystals intentionally doped with ^{14}C showed that carbon is very homogeneously distributed in GaAs grown by horizontal Bridgman method. No correlation between the distribution of carbon and dislocations has been found.

INTRODUCTION

Uniformity of electrical properties of large diameter, undoped semi-insulating (S.I.) GaAs crystals is one of the basic requirements for direct implantation device applications (ref. 1). Since the electrical and optical properties of such crystals are determined by a balance between residual impurities and native defects, a detailed knowledge about spatial distributions of major electrically active centers is essential for the evaluation of this material. Typical as-grown Liquid Encapsulated Czochralski (LEC) GaAs crystals exhibit very large spatial variations of electrical and optical properties. The variations were found to be correlated with structural defects, especially with dislocations. Thus it has been found that regions of about 100μm around dislocations show higher cathodo- and photo-luminescence intensities (refs. 2,3) and lower MESFET threshold voltages (ref. 4) than the regions far away from dislocations. Also, measurements of spatially resolved optical absorption (ref. 5) (in the wavelength range close to 1 μm) large diameter GaAs wafers have exhibited characteristic "W"-like distributions with high absorption coefficients at the wafer edge and in the center. There is some evidence that these variations correlate with the

distribution of an average dislocation density (ref. 6).

It has been assumed for the interpretation of near infrared absorption measurements that the absorption is due to intracenter optical transitions from a neutral EL2 level to an excited state of EL2 plus a continuum photoionization transition from the EL2 center to the conduction band. It is also known that in the 1μm wavelength range the optical cross section for the transitions from the valence band to ionized EL2 centers is much smaller than that from neutral EL2 to the conduction band (ref. 7). Therefore the intensity of the optical absorption in this spectral range can be related to the concentration of neutral EL2 centers (refs. 8,9). All of the near infrared absorption mapping techniques are based on this relationship (refs. 10,11). However, since the concentration of neutral EL2 centers depends on the total EL2 concentration as well as concentrations of other donors and acceptors, a simple absorption measurement itself cannot provide sufficient information to identify the impurity or native defects responsible for the actual spatial variation of the absorption.

The purpose of our study was to identify the electrically active centers responsible for spatial variations of the near infrared absorption, and also to clarify the role of the carbon acceptor distribution on variations of optical and electrical properties of regions close to dislocations. To illustrate our approach, which combines different spectroscopic techniques, we have used two representative LEC wafers and one wafer from a Bridgman grown crystal.

EXPERIMENTAL

Samples of undoped semi-insulating GaAs were grown using the high-pressure LEC technique. Both 2" and 3" wafers were studied. Radiotracer experiments were performed on horizontal Bridgman grown GaAs crystals doped with ^{14}C. Measurements of near infrared absorption were performed using a Bomem model DA3.01 FTIR Spectrophotometer with the GaAs sample at room temperature. Carbon local vibrational mode (LVM) spectra were obtained with a Digilab FTS-20/E Vacuum FTIR with a spectral resolution of $0.08cm^{-1}$. These measurements were performed at liquid helium temperature. The spatial resolution was ~2mm in both cases.

It is well known that high resolution (ref. 12) C_{As} LVM spectra show five separate lines caused by the statistical distribution of two stable gallium isotopes (^{71}Ga and ^{69}Ga) between the four neighbor-sites surrounding the carbon impurities. Recently Shanabrook et al. (ref. 14) have shown that the shape of the carbon LVM spectrum strongly depends on the charge state of the carbon impurity. The spectrum with well-resolved component lines

is observed only for ionized carbon acceptors. For neutral carbon the spectrum is substantially broadened and shifted to lower photon frequencies. When carbon acceptors are partially ionized, deconvolution into neutral and ionized carbon components of the spectrum can provide information on the ionized to neutral carbon concentration ratio. We applied these findings to our analysis of the LVM spectra.

A profile of the total carbon concentration N_c on the arsenic site across the 2" wafer is shown in fig. 1(a). The concentration was determined from the integrated LVM absorption intensity using the relation $N_c = \alpha_{int}/\sigma$, where α_{int} is represented by the area under the LVM absorption spectrum and σ is the effective LVM cross section per carbon impurity. We have used a recently reported value of $\sigma = 10^{-16}$ cm (refs. 15,16). As seen in fig. 1(a), the carbon concentration decreases slightly towards the center of the wafer, indicating a weak "U"-like distribution. The average carbon concentration was $\sim 10^{16} cm^{-3}$. We have found that the shape of the LVM spectrum changes when the sample is illuminated with sub-bandgap light at low temperatures. This indicates that after illumination the EL2 defect is transferred to the metastable state and the Fermi energy moves towards the valence band, affecting the charge state of the acceptors. Therefore the observed LVM spectrum is composed of the ionized and neutral carbon LVM spectra. The feature of the high resolution LVM spectrum which most prominently depends on the ratio of ionized to neutral carbon concentrations is the relative intensity I_1 and I_5 of the two strongest lines at 582.43 cm^{-1} and 582.93 cm^{-1}, respectively. Using the data of ref. 14 we obtain the following phenomenological relation for a neutral to total carbon concentration ratio expressed in terms of the intensity ratio $R = I_1/I_5$:

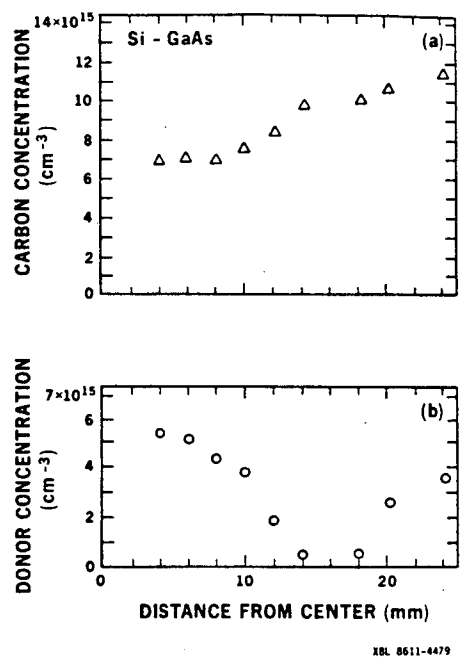

Fig. 1. Radial distribution of C_{As} acceptors (a) and compensating donors shallower than EL2 (b) in 2" diameter GaAs wafer.

$$N_n/N_c = \frac{R - 0.67}{0.85R - 0.35} \qquad (1)$$

Therefore, from the high resolution spectrum one can determine the concentration of neutral carbon acceptors. This allowed us to separately determine the spatially varying concentrations of neutral and ionized carbon acceptors after EL2 quenching. Since, in the present case, carbon is the dominant acceptor we can assume that the concentration of ionized carbon acceptors is equal to the concentration of donors other than EL2. In fig. 1(b) the spatial distribution of the concentration of ionized carbon acceptors which is equal to the concentration of the donors, is shown. It is seen that a very distinct "W"-like distribution is observed with a minimum donor concentration at ~9mm from the wafer edge. Measurements of the EL2 related optical absorption are shown in fig. 2. The value of 5.4×10^{-17} cm^2 for the neutral EL2 optical cross section at λ=1.06μm has been used (ref. 9). Again in this case the concentration of neutral EL2 shows a minimum at ~9mm from the edge. We find a good quantitative agreement between variations of neutral EL2 concentration and concentration of compensating donors.

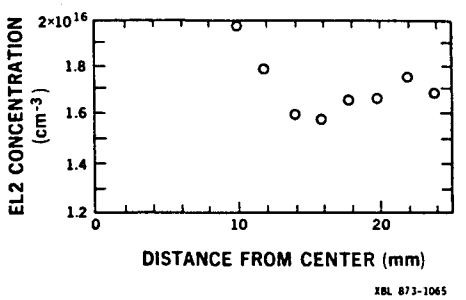

Fig. 2. Radial distribution of neutral EL2 in 2" wafer.

Measurements performed on a 3" LEC GaAs wafer show that the total carbon concentration (fig. 3) slightly decreases towards the wafer center. The average carbon concentration of $\sim 10^{15} cm^{-3}$ is about one order of magnitude lower than in the 2" wafer. Measurements of LVM spectra with and without EL2 quenching provided the same results, meaning that even after quenching of EL2 all carbon acceptors are ionized. Near infrared absorption measurements shown in fig. 4 indicate very small variations of the neutral EL2 center concentration ($<10^{15} cm^{-3}$) across the wafer.

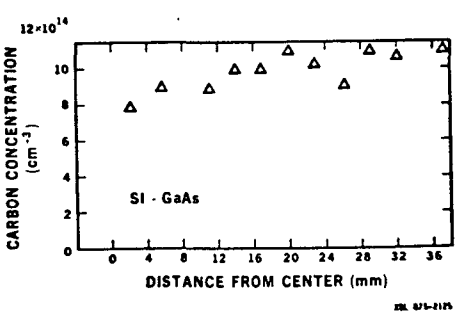

Fig. 3. Radial distribution of C_{As} acceptors in 3" diameter wafer.

We have also measured the distribution of carbon in a horizontal Bridgman grown crystal which was intentionally doped with ^{14}C. Barium carbonate enriched to 62.5 percent of ^{14}C was chosen as the source of the radiotracer. The distribution of carbon was determined using autoradiography, i.e. the exposure of X-ray film by the energetic electrons ejected during the decay of $^{14}_{6}C$ into $^{14}_{7}N$. Fig. 5b shows a portion of film exposed for 4 weeks to a GaAs wafer in direct contact with the film. The dislocation distribution in the same portion of the wafer obtained by photoetching is shown in fig. 5a. It is evident that no correlation between dislocations and the distribution of carbon is found. Since the spatial resolution of the autoradiograph is limited to >20μm we can conclude that the presence of dislocations has no noticable effect on the carbon

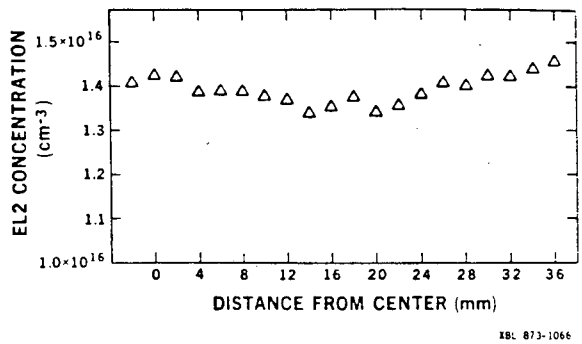

Fig. 4. Radial distribution of neutral EL2 in 3" wafer.

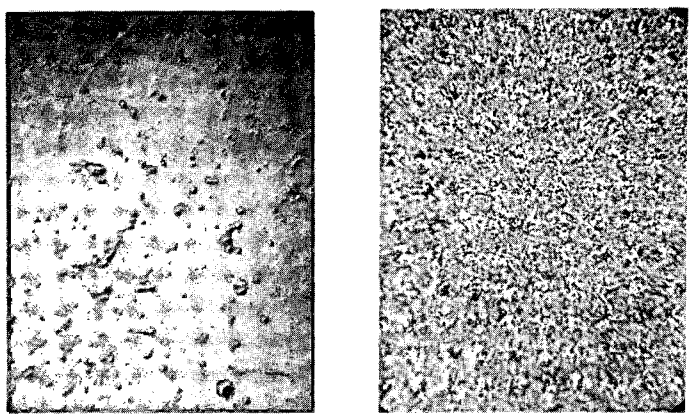

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Fig. 5. (a) Distribution of dislocations revealed by photo-etch. (b) Distribution of radioactive ^{14}C from autoradiogram in the same area of the crystal.

concentration for distances larger than 20μm from the dislocation.

DISCUSSION AND CONCLUSIONS

The semi-insulating properties of undoped GaAs result from a balance between the deep donor defects EL2, the donors N_D shallower than the EL2(0/+) level, and acceptors N_A below EL2(0/+). In semi-insulating GaAs, $N_A > N_D$ and EL2 is partially ionized, which results in stabilization of the Fermi energy close to the midgap. All acceptors below the Fermi level are ionized. At low temperatures, after EL2 has been transferred by optical pumping to the metastable state, the Fermi energy is determined by the balance between N_A and N_D. Two different cases can be envisioned: 1) The carbon concentration N_C is much higher than the concentration of any other acceptor; 2) The concentration of other acceptor impurities (e.g. Fe) or native acceptor defects located below the EL2(0/+) level is comparable with the carbon concentration.

The first case corresponds to the situation found in the 2" wafer with the carbon concentration of $N_C \sim 10^{16} cm^{-3}$. After quenching of EL2 the Fermi energy shifts downward and is determined by the difference of the carbon and the donor concentrations $N_C - N_D$. Thus the spatial variations of the ionized carbon concentration reflect spatial variations of the donor concentration. At room temperature EL2 participates in the charge balance. The Fermi energy is located close to the EL2(0/+) level. The concentration of neutral EL2 centers is given by $N^0_{EL2} = N_{EL2} - (N_C - N_D)$. Therefore the spatial variations of EL2-related absorption should correlate with the distribution of the donors shallower than EL2. This is precisely what is observed in the 2" wafer as shown in figs. 1 and 2. It is evident that the dominant part of the variation of EL2 related absorption is not caused by variation of the total EL2 concentration but by the spatial variation of the donors shallower than EL2.

In the second case, the concentration of carbon acceptors is lower than the concentration of donors. The semi-insulating behavior is in this case assured by other acceptor impurities such as iron or native acceptor defects. The energy levels of these acceptors are located above the carbon energy level. After quenching of EL2 the Fermi energy shifts downward and is stabilized well above the carbon level. Therefore all carbon acceptors are ionized and no change in the shape of the spectrum before and after EL2 quenching is observed. Because the total concentration of acceptors is much smaller in this case, the concentration of the donors must also be lower to preserve semi-insulating behavior. The above discussion explains well our results on the 3" wafer which contains a very low concentration of carbon. Even after quenching EL2 all carbon acceptors remain ionized. Also, the reduced

variation of the $EL2^0$ concentration ($<10^{15}cm^{-3}$, see fig. 5) is consistent with a much smaller donor concentration N_D in this material.

High intensity of carbon related luminescence at $h\nu$ = 1.49eV in the regions close to dislocations has been considered as an indication that carbon is accumulated in the strain field of the dislocations (ref. 2). Recent high resolution photoluminescence measurements indicated that the total variation could not be accounted for by a change of carbon concentration and it was thus suggested that spatial variations of the carrier lifetime are responsible for the observed luminescence contrast (ref. 3). Our measurements have shown that carbon is very uniformly distributed in Bridgman grown GaAs and there is no noticable effect of dislocations on carbon distribution. High spatial resolution PL measurements carried out on the same ^{14}C doped crystal have shown a high luminescence region of about 100 μm area around dislocations (ref. 17). The total contribution to the luminescence contrast is therefore attributable to variations of the carrier lifetime. This finding corroborates photo-etch experiments which show that the minority carrier controlled etching rate varies substantially in a region close to the dislocations (ref. 17).

In conclusion, our results show that two major defects which cause the semi-insulating behavior of GaAs are uniformly distributed in large diameter wafers. The observed inhomogeneities of optical and electrical properties result from variations of the concentration of the compensating donors shallower than EL2. Substantial uniformity improvement is observed upon reduction of the concentration of the shallow donors.

ACKNOWLEDGMENT

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REFERENCES

1. J.V.D. Lorenzo, A.S. Jordan, A.R. Von Neida and P. O'Connor, in Semi-Insulating III-V Materials, Kah-nee-ta 1984, edited by D.C. Look and J.S. Blakemore, (Shiva Publ. Ltd., Nantwich England) p. 308.
2. B. Wakefield, P.A. Leigh, M.H. Lyons and C.R. Elliot, Appl. Phys. Lett. 45, 66 (1984).
3. A.I. Hunter, Appl. Phys. Lett. 47, 715 (1985).
4. Y. Nanishi, S. Ishida, T. Honda, H. Yamazaki and S. Miyazawa, Jap. J. Appl. Phys. 21, L335 (1982).
5. G.M. Martin, G. Jacob, G. Poibland, A. Goltzene and A. Schwab, Inst. Phys. Ser. 59, 2811 (1980).
6. M.R. Brozel, I. Grant, R.M. Ware and D. Stirland, Appl. Phys. Lett. 42, 620 (1983).
7. A. Chantre, G. Vincent and D. Bois, Phys. Rev./ B23, 5335 (1981).
8. G.M. Martin, Appl. Phys. Lett. 39, 747 (1981).

9. M. Skowronski, J. Lagowski and H.C. Gatos, J. Appl. Phys. 59, 2451 (1986).
10. W. Wettling and J. Windscheif, Appl. Phys. A40, 191 (1986).
11. J.S. Blakemore and P. Dobrilla, J. Appl. Phys. 58, 204 (1985).
12. W.M. Theis, K.K. Bajaj, C.W. Litton and W.G. Spitzer, Appl. Phys. Lett. 41, 70 (1982).
13. R.S. Leigh and R.C. Newman, J. Phys. C: Solid State Physics 15, L1045 (1982).
14. B.V. Shanabrook, W.J. Moore, T.A. Kennedy and P.P. Ruden, Phys. Rev. B30, 3563 (1984).
15. A.T. Hunter, H. Kimura, J.P. Bukus, H.V. Winston and O.J. Marsh, Appl. Phys. Lett. 44, 74 (1984).
16. M.R. Brozel, E.J. Folkes, R.W. Series and D.T. Hurle, Appl. Phys. Lett. 49, 337 (1986).
17. E. Bourret, A.G. Elliot, B T. Lee and J.M. Jaklevic, this conference.

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