

FIG. 4. 1-MHz C - V curves of Al_2O_3 films on InP ($N \approx 10^{16} \text{ cm}^{-3}$) substrates. The sweep rate is 100 mV/s. (a) Case for plasma beam parallel to magnetic field lines with oxides thickness of $\sim 400 \text{ \AA}$; (b) case for plasma beam normal to the magnetic field lines with oxide thickness of $\sim 1080 \text{ \AA}$.

indicates the minimum capacitance that is expected from theoretical calculation. Figure 3(b) shows the case where the SiO_2 film was deposited with the plasma beam normal to the magnetic field. The large reduction of fixed charge and surface states as evidenced by the C - V curve indicates that by

eliminating charged particles during deposition one can greatly improve the qualities of the film. The SiO_2 films have a breakdown field strength $\approx 5 \times 10^6 \text{ V/cm}$ and an estimated fixed charge density of about $3.5 \times 10^{11} \text{ cm}^{-2}$.

Similarly, Figs. 4(a) and 4(b) show the C - V curves (taken at 1 MHz of Al_2O_3 (deposited at 100°C) on InP ($N \approx 10^{16} \text{ cm}^{-3}$) without post-annealing treatment for cases when the plasma beam is parallel to [Fig. 4(a)] and normal to [Fig. 4(b)] the magnetic field. Again we see that by eliminating charged particles, the C - V curve has less surface states. It is believed that if the present experiments were performed in an ultra-clean vacuum system with proper surface preparation before film deposition, greatly improved electrical properties will be obtained!

In conclusion, we have proposed a method of depositing dielectric thin films and demonstrated its feasibility by depositing SiO_2 and Al_2O_3 on substrates with temperatures down to 30°C . Utilizing the low-temperature nature of this technique we have also patterned μ -width SiO_2 features using photoresist masked substrates and the lift-off technique. We are currently depositing other oxides, as well as nitrides. A more detailed account of this work will be reported elsewhere.

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Residual double acceptors in bulk GaAs

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By using infrared absorption, photoluminescence, and Hall measurements we have observed an additional level associated with a residual acceptor in liquid encapsulated Czochralski GaAs. These results indicate that the defect is a double acceptor with levels 78 and 200 meV above the valence band.

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An understanding of native defects which occur in undoped GaAs is critical to materials development for GaAs devices. Recent studies have indicated that the resistivity of undoped liquid encapsulated Czochralski (LEC) GaAs is controlled by the stoichiometry of the melt through the presence of two defects and residual carbon acceptors. In material grown from melt compositions of greater than 0.47 As

mole fraction, the resistivity is controlled by the deep donor EL2 and by residual compensating carbon acceptors.¹ In material grown from melts of less than 0.47 As mole fraction the resistivity is primarily determined by the presence of a residual 78-meV acceptor.² It has been suggested that EL2 is the antisite As_{Ga} defect.³ We have tentatively identified the 78-meV acceptor as the antisite Ga_{As} from far infrared

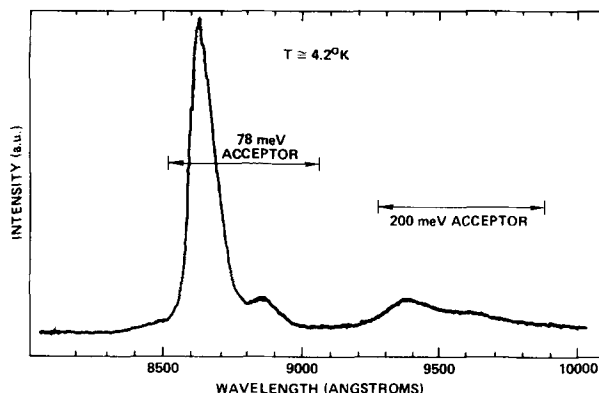


FIG. 1. Photoluminescence of silicon compensated liquid encapsulated Czochralski GaAs. Two bands are observed from pair recombination associated with 78- and 200-meV acceptor levels. The lower energy peaks in the two bands are LO phonon replicas.

transmission measurements.²

In this letter we present photoluminescence and infrared absorption data which indicate the presence of an additional level associated with the 78-meV defect approximately 200 meV above the valence-band edge. The electronic properties of this level are consistent with those expected for the second ionization of a double acceptor, the first ionization being the 78-meV level.

The growth of the GaAs crystals used for this study has been described elsewhere.² The crystals were grown in the $\langle 100 \rangle$ direction from pyrolytic boron nitride crucibles using a high pressure LEC crystal puller with dry (< 500 ppm H_2O) B_2O_3 encapsulant. The material was characterized by secondary-ion mass spectrometry (SIMS), room-temperature Hall measurements, and infrared absorption. The predominant background impurity as determined by SIMS was boron (1×10^{16} – 5×10^{17} cm^{-3}). Local mode spectra indicated the presence of carbon typically between 3×10^{15} and 1.5×10^{16} cm^{-3} in concentration. Other background impurities (Si, S, Fe, Mn) were all typically $< 3 \times 10^{15}$ cm^{-3} and usually were $< 10^{15}$ cm^{-3} .

An additional crystal included in this study was grown under identical conditions but was intentionally doped with a small amount of silicon. This crystal was p type although partially compensated with silicon donors. SIMS measurements indicate Si(3×10^{16} cm^{-3}) and B(2×10^{18} cm^{-3}) in this material.

Far infrared (FIR) transmission measurements and photoluminescence measurements indicated the presence of the 78-meV acceptor in each of the samples studied. For the samples uncompensated with silicon, no absorption or luminescence due to deeper levels was observed. In the crystal compensated with silicon, as shown in Figs. 1 and 2, we also observed features associated with an acceptor level approximately 200 meV from the valence band.

In the low-temperature photoluminescence measurements we find a peak occurring at 1.32 eV presumably corresponding to a pair transition associated with the 200-meV level. A LO phonon replica is observed at lower energies. In the FIR spectra we obtain a more detailed spectrum asso-

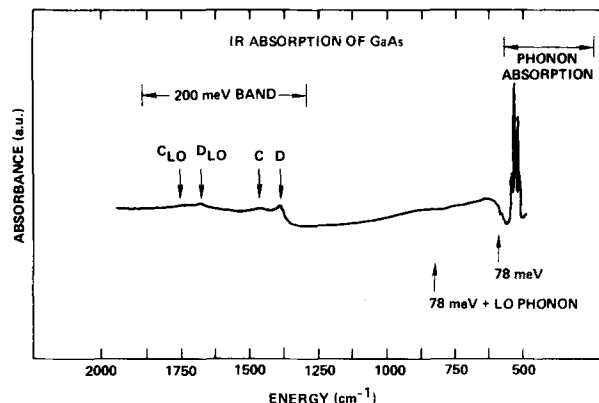


FIG. 2. Infrared absorption spectra of silicon compensated bulk GaAs. In addition to the 78-meV band, absorption associated with the 200-meV level produces peaks labeled C and D at 172.3 and 181.0 meV in energy together with their phonon replicas. These peaks are associated with ground state to excited state transitions of the defect.

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The presence of the deeper level is also indicated in variable temperature Hall measurement and in variable temperature C - V measurements. These measurements indicate that within experimental uncertainty the deeper level occurs in the same absolute concentration as the 78-meV level. Our Hall measurements agree with those made by researchers at other laboratories on similarly grown material and thus will not be presented here.^{4,5} These studies have indicated the presence of two levels at 73 and 200 meV from the valence band in similar concentrations. The behavior suggests that the defect is a double acceptor.

A more detailed analysis of the FIR data in Fig. 2 supports this interpretation. We see two lines in the FIR spectra occurring at energies of 172.3 and 181.0 meV ± 0.5 together with LO phonon replicas at higher energies. We compared the experimental energies with the expected energies for isocoric double acceptors by using arguments based on the point defect model described previously.² To obtain the appropriate energies by using this model for the antisite Ga_{As} in GaAs, one simply scales the values for the acceptor Zn in Ge by the ratio of effective Rydbergs, 2.6, for the two materials. The results of this procedure are tabulated in Table I showing excellent agreement with the experimental data. On the basis of such a comparison we can identify the line at

TABLE I. Estimated and experimental energies for the residual double acceptor in GaAs. E_{Acc} refers to the hole binding energy and C - D is the energy difference between the excited states observed in the FIR absorption.

	C - D (cm^{-1})	Energy E_{Acc} (meV)
Experimental Ga_{As}	16	78
Estimated Ga_{As} (Zn_{Ge} scaled by 2.6)	15.9	83
Experimental Ga_{As}	70	200
Estimated Ga_{As} (Zn_{Ge} scaled by 2.6)	70	221

* See Ref. 6.

172.3 meV with the $2P_{5/2}(\Gamma_8)$ state and the line at 181.0 meV with the $2P_{5/2}(\Gamma_7)$ state of a doubly ionized center. Taking 28 meV for the binding energy of the $2P_{5/2}(\Gamma_8)$ state we obtain a value of 200 meV for the ground state energy. We have chosen this value for the binding energy to be four times the single acceptor value used previously² to reflect the quadratic dependence of the effective Rydberg on the charge of the defect.

The absence of the 200-meV level in the FIR and luminescence spectra for uncompensated material can be explained by the double acceptor nature of the defect. In both cases the defect center is occupied by two holes for uncompensated material. Since the 200-meV energy reflects the energy with which one hole is bound to the fully ionized center, this level cannot be observed unless one of the two holes is first removed from the defect. This only occurs when the material is compensated as is the case for the Si-doped material.

One remaining question concerns the appearance of the 78- and 200-meV levels in the crystal compensated with silicon. In the uncompensated crystals, these levels are only observed in samples grown from melts containing less than 0.47 atom fraction of As and increases in concentration as the melt becomes more Ga rich. The crystal which was compensated with Si, however, was grown with 0.50 As atom fraction and was not expected to contain the 78-meV acceptor. The fact that we see this level indicates that the defect chemistry of the crystal has been significantly altered by the addition of Si to the melt. SIMS measurements have indicated both Si ($3 \times 10^{16} \text{ cm}^{-3}$) and B ($2 \times 10^{18} \text{ cm}^{-3}$) impurities in substantial concentration. It is possible that these impurities may play a role in the incorporation of the defect.

In addition we cannot *a priori* reject a different identification

of the defect as the defect B_{As} in view of the relatively high B content of this crystal. It should be pointed out that B_{As} and Ga_{As} defects should have very similar properties and that most of the arguments we have stated for a Ga_{As} identification of the defect work equally well for B_{As} defects. Nevertheless, to date we have found no correlation between the boron content and the 78-meV defect concentration in the crystals uncompensated with silicon.

In conclusion, we have observed an additional level associated with a residual acceptor in liquid encapsulated Czochralski GaAs by using infrared absorption, photoluminescence, and Hall measurements. The presence of this level indicates that the defect is a double acceptor consistent with an antisite Ga_{As} identification of the defect.

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Infrared to visible up-conversion using GaP light-emitting diodes

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Electroluminescence excited by infrared radiation has been observed in GaP light-emitting diodes (LED's) at low temperatures providing a new efficient method to convert infrared radiation within a broad spectral range into visible light. Using 10.6- μm radiation of a CO_2 laser an up-conversion quantum efficiency of 3.4×10^{-6} was found. If a low dark current photomultiplier is employed to detect the LED emission the dominant noise source is due to conversion of thermal background radiation yielding a noise equivalent power of $\text{NEP} = 1.6 \times 10^{-9} \text{ W/Hz}^{1/2}$.

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In recent years several techniques for conversion of infrared radiation into the visible spectral range have been realized. These permit infrared detection by sensitive photon counting detectors and infrared-to-visible image up-conversion. These techniques include optical mixing of infrared radiation with an intense visible laser beam in nonlinear crys-

tals,¹⁻³ up-conversion utilizing the infrared quantum counter scheme proposed by Bloembergen,⁴⁻⁶ and up-conversion fluorescence in semiconductors by an optical two-step excitation of electrons involving midgap impurity levels.^{7,8}

In this letter we report on a novel method of efficient