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S. Dhar, Kanad Mallik, and B. R. Nag

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Characteristics of indium-doped GaAs layers grown by liquid phase epitaxy with indium content in the range $(0.3–7)\times 10^{19}\ cm^{-3}$

S. Dhar and Kanad Mallik
Department of Electronic Science, University of Calcutta, 92, A.P.C. Road, Calcutta-700 009, India

B. R. Nag
Institute of Radio Physics and Electronics, University of Calcutta, 92, A.P.C. Road, Calcutta-700 009, India

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GaAs layers grown by liquid phase epitaxy and doped with indium in the concentration range of $(0.3–7)\times 10^{19}\ cm^{-3}$ are studied by etch pit density (EPD), Hall, capacitance-voltage and current-voltage measurement techniques. Layers doped with indium in the range $(0.5–5)\times 10^{19}\ cm^{-3}$ show about 10%–15% increase in mobility and a corresponding decrease in the background impurity concentrations. In the same range, EPD is found to fall below $10^2\ cm^{-2}$. Above $5\times 10^{19}\ cm^{-3}$ In doping, mobility decreases drastically, and the dislocation density measured by EPD count goes above $10^3\ cm^{-2}$. This result, together with a comparison of free carrier concentrations measured by Hall and capacitance-voltage techniques indicate that dislocation-related scatterings are effective in lowering the mobility for high indium content layers. Reverse current-voltage characteristics of gold Schottky diodes fabricated on the layers do not show any dependence of breakdown voltages on In doping. Simple theoretical calculations give evidence to the fact that the reverse breakdown process in the diodes are, in fact, controlled by the normal avalanching mechanisms dependent on the electrically active background impurities.

I. INTRODUCTION

The growth of nearly dislocation-free crystals of GaAs by controlled indium doping is a matter of paramount interest today. The prime need is to get large diameter defect-free wafers which are potential substrates for high-yield manufacturing of metal-semiconductor field effect transistors (MESFETs) and integrated circuits. The work done in this area up to 1988 has been reviewed in detail by Winston and co-workers.[1] In a more recent publication, Leo *et al.* reported[2] that a combination of In doping and the application of a magnetic field to suppress turbulent flows during the liquid encapsulated Czochralski (LEC) growth of GaAs resulted in crystals with excellent values of carrier lifetime and radiation efficiency.

The process by which dislocations and other defects are reduced by In doping of GaAs is not absolutely clear. According to the solution-hardening model, proposed by Ehrenreich and Hirth,[3] an In atom, surrounded by four As atoms, forms a localized cluster in a solution of GaAs and resists the motion of dislocations within the latter. Such "hardening" of the GaAs solution may prevent the formation of new dislocations. This model is contradicted by Matsui and Yokoyama[4] who found no difference in dislocation velocities in undoped and In-doped GaAs. Yonenaga and Sumino,[5] on the other hand, reported that the velocity of the α-type dislocations greatly reduced upon In doping and they suggested that this phenomenon may alone prevent dislocation multiplication in In-doped GaAs. One may also take note of the generalized model proposed by Sher and co-workers.[6] It is based on dislocation hardening due to different bond lengths of the two kinds of anions in alloyed binary compounds. The authors commented that this mechanism can indirectly explain dislocation reduction in In-alloyed GaAs.

The In-doping method has also been successfully used in the growth of low defect-density epitaxial layers by liquid phase epitaxy (LPE),[7,8] vapor phase epitaxy (VPE),[9,10] metalorganic chemical vapor deposition (MOCVD),[11] and by molecular beam epitaxy (MBE)[12–15] techniques. In addition to the effect of preventing dislocation multiplication by hardening of the material, In doping may also reduce dislocations in epitaxial layers by way of layer-substrate misfits. For low values of In doping, this misfit has the effect of reducing threading dislocations, entering the layer from the substrate, by the glide forces acting between two misfit planes.[16] Another possible benefit of In doping may be that since In occupies the Ga vacant sites, both Ga vacancies as well as substitutional impurities sitting at these sites are likely to be decreased.[7]

However, all the above welcome advantages of In doping are likely to be destroyed at higher doping levels due to the generation of misfit dislocations at the interface. It is, therefore, natural to expect that there should be an optimum range of In doping at which the layers will assume best structural, electrical, and optical characteristics. Experimental evidence for this is obtained from the etch pit density (EPD) studies of Kim and Min[10] and from the Hall mobility and photoluminescence (PL) data of Uddin and Anderson.[15] It is, however, noted that the reported minimum value of dislocation density in Ref. 10 is rather high and the rise of Hall mobility of MBE-grown layers[15] might be due to a mixed effect of enhanced growth temperature and In doping.

We have attempted to investigate the matter by a care-

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ful and systematic study of LPE-grown GaAs layers doped with indium in the range $(0.3\text{–}7)\times10^{19}$ cm^{-3}. We have found that within a range of $(0.5\text{–}5)\times10^{19}$ cm^{-3} In doping, the measured EPD of the layers went below 10^2 cm^{-2}. In the same region, Hall mobility enhanced by 10%–15% with corresponding reduction in shallow donor densities measured by both Hall and capacitance-voltage (*C-V*) techniques. The reverse breakdown voltages of gold Schottky diodes fabricated on the layers did not show any definite improvement due to In doping, in contrast to the observations made by Narozny and Beneking.[8] Instead, they seem to be related to the background doping of layers following conventional theories of Avalanche breakdown. All the above characteristics showed definite degradation above In-doping concentration of 5×10^{19} cm^{-3}. The details of our growth technique, characterization, and the results are presented in this paper.

II. MATERIALS GROWTH

The In-doped GaAs layers used in our experiments were grown in a conventional horizontal LPE reactor using the sliding boat technique. The melt consisted of 99.9999% pure polycrystalline GaAs dissolved in 99.9999% Ga. Amount of In needed to get the required doping in grown layers was calculated taking into account the reported[1] distribution coefficient of In in GaAs, which is 0.12. This amount was carefully weighted in a microbalance and thereafter directly added to the melt. An undersaturated solution of GaAs in Ga was used as the etch-back melt. Ga for this melt and that for the growth melt were separately baked in the furnace at 820 °C for 20 h in an ambient of Pd-diffused H_2 in order to reduce the dissolved oxygen and other volatile impurities. Next, required amounts of materials were added to form the growth and the etch-back melts and baking was repeated at 800 °C for another 20 h. Growth was typically done at 780 °C for 30–40 min using a supersaturation of 5 °C and a cooling ramp of 0.3 °C/min which produced layers 8–10 μm thick. Layers were grown on LEC semi-insulating (SI) and Te–doped *n*-type (3×10^{17} cm^{-3}) GaAs substrates. Both types of substrates were procured from Cambridge Instruments, U. K., and had an average EPD of 10^4 cm^{-2}. Size of a typical layer was 1×1 cm^2.

III. CHARACTERIZATION

Thickness of each layer was measured from the microscopic observation of the cleaved layer-substrate interface revealed by A-B etchant. Dislocation density on the surface of the layer was estimated by counting the density of etch pits produced by molten KOH[17]. Layers grown on semi-insulating substrates were used for Hall mobility and carrier concentration measurements using the Van der Pauw technique. The magnetic field employed was 3.7 kG.

Evaporated gold Schottky-barrier diodes of about 0.4 mm diameter were fabricated on layers grown on conducting substrates with back ohmic contacts formed by In-Sn alloying. Some of the diodes were directly fabricated on the samples used for Hall measurements, with proximity

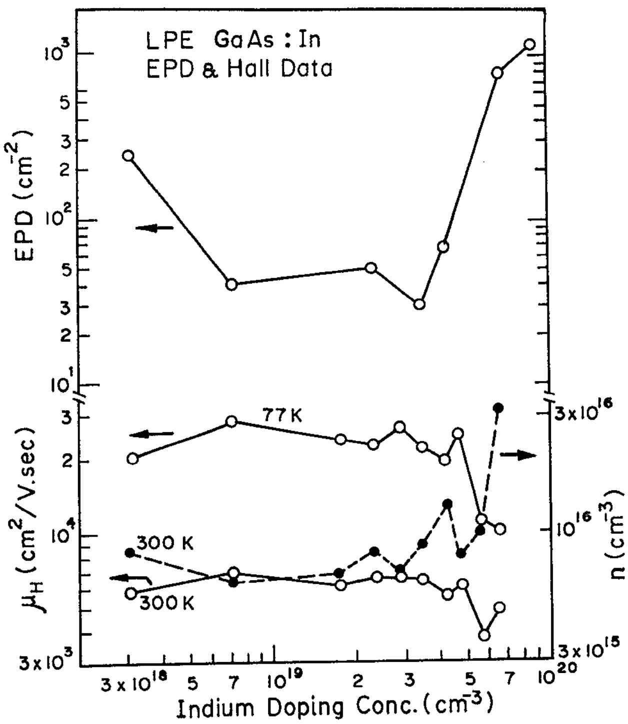

FIG. 1. Etch pit density (EPD), Hall mobility (μ_H) and Hall carrier concentrations (n) of GaAs layers grown with different amounts of indium doping.

ohmic contacts in order to get the proper correspondence between the Hall and *C-V* data. *C-V* measurements were done using an MSI Electronics digital *C-V* meter witfh sweep bias voltage capability. Reverse current-voltage (*I-V*) characteristics of the diodes were obtained using an HP 4140B pA meter-voltage source, controlled by an HP 9000/236 series computer. During a typical *I-V* scan, each current reading was taken in a time of 10 ms in order to reduce the dc heating effect at the junction near breakdown.

About forty layers were grown to complete the study and to check the reproducibility of the results. The average size of a layer was 1 cm$\times$1 cm and EPD, *C-V* and *I-V* measurements were done at different parts of the same layer to examine homogeneity of the results. We have found that the measured characteristics were similar throughout the layer except at the edges. However, the size of the layer was too small to conduct any such uniformity test for the Hall data. In general, at least three separately grown layers were used for getting the average Hall data corresponding to each value of indium doping concentration and efforts were made to cut the sample, each time, from a new location on the layer.

IV. RESULTS AND DISCUSSIONS

A. EPD measurements

In the upper part of Fig. 1, we plot the EPD measured on a number of samples with various degrees of In concentration. EPD went below 10^2 cm^{-2} for In-doping concentration of 5×10^{18} cm^{-3}. Above 5×10^{19} cm^{-3} of In dop-

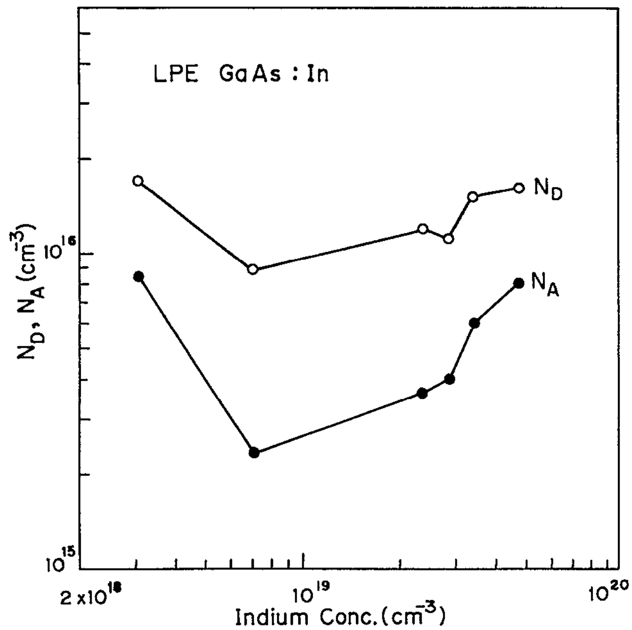

FIG. 2. Donor concentrations (N_D) and acceptor concentrations (N_A) calculated from the analysis of the Hall measurement data of GaAs doped with indium.

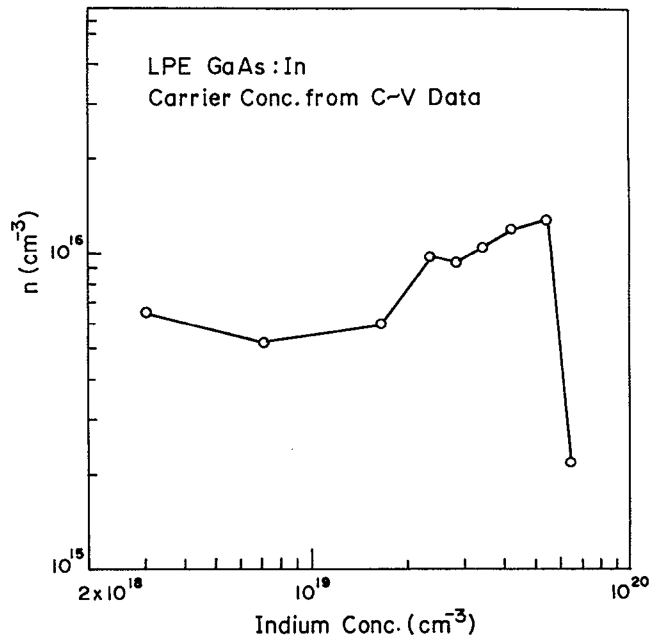

FIG. 3. 300 K free carrier concentrations (n) obtained from the C-V measurements of gold Schottky barrier diodes fabricated on In-doped GaAs layers.

ing, there is a sharp increase in EPD which we attribute to the generation of misfit dislocations. Microscopic observations of the layer at these In-doping values showed roughening of the surface, confirming increased lattice mismatch at the layer-surface interface.[9] This study was made for layers grown on both SI and n-type substrates, and the results were nearly the same in both cases. Since all our substrates had the same EPD of about 10^4 cm^{-2}, we could cannot have the chance to see any possible influence of the substrate defects on the measured EPD of the grown layers. However, since our layers are sufficiently thick (8–10 μm), it is reasonable to believe that any such influence is likely to be noticeable near the interface only. We propose to study this in detail in the near future.

B. Hall measurements

Lower part of Fig. 1 shows the results of Hall mobility (μ_H) and free carrier concentration (n) of GaAs layers grown with different amounts of In doping. Better values of these parameters are found to lie in the same range of In concentration which gave the lowest values of EPD in our previously described experiment. The trend is the same for both 300 and 77 K measurements. The 300 K results are similar to those of Uddin and Anderson[15] who found an improvement in the transport properties of their samples in almost the same range of In-doping as reported here. However, unlike these authors, we did not see any peaking of 77 K mobility at a particular value of In doping.

In Fig. 2, we present the donor concentration (N_D) and acceptor concentration (N_A) in our samples as functions of In concentration. N_D and N_A were approximately calculated from the measured mobility and free carrier concentration values using the curves prepared by Lancefield and co-workers.[18] It is interesting to see from Fig. 2 that the observed 10–15% rise in mobility upon In doping is a consequence of the decrease in both background donor and acceptor concentrations. How this reduction actually occurs or why it should be related to In doping is not very clear at this stage and the answers to these questions again may not be easy to get since the dopant indium may incorporate additional impurities in the layer.[14] As has been mentioned in Sec. I, it is often speculated that indium atoms occupying Ga vacant sites help to reduce the available cation sites for the group IV impurity atoms. From secondary ion mass spectroscopy (SIMS) we have identified the major donor impurity in our layers to be oxygen, and silicon as the major acceptor.

C. *C-V* measurements

Free carrier concentration values at 300 K obtained from the *C-V* analysis of gold Schottky-barrier diodes are presented in Fig. 3, as functions of In-doping concentration. The general behavior is in close agreement with that obtained from Hall measurements. However, for samples with In doping above 5×10^{19} cm^{-3} we see that, in contrast to Hall measurement data, the carrier concentrations implied by *C-V* measurements do not show any sharp increase. We thus conclude that the fall in μ_H, observed in this region, is related to the high density of defects generated from the mismatched interface. Again, any quantitative assessment of this effect is not easy to perform since dislocation tubes with all possible orientations relative to the interface may take part in this kind of scattering. In fact, the sudden fall in free carrier concentration near the

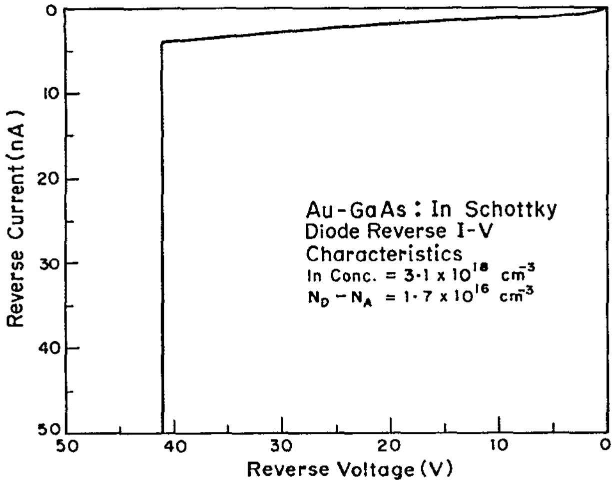

FIG. 4. Reverse current-voltage (I-V) characteristics of a typical Au-GaAs:In Schottky barrier diode.

end of the curve is indicative of impurity gettering by high density of dislocations.

D. I-V measurements

Figure 4 shows the reverse I-V characteristics of 0.4-mm-diam evaporated gold Schottky-barrier diodes fabricated on some of the In-doped layers grown on SI GaAs substrates. In contrast to the earlier observations,[7] we do not see any increase in diode breakdown voltage upon In-doping. The very low reverse leakage currents may, however, be the consequences of In doping which prevents localized breakdown in the material by rendering it more homogeneous. Figure 5 shows a plot of the inverse of breakdown voltage V_B against the measured values of

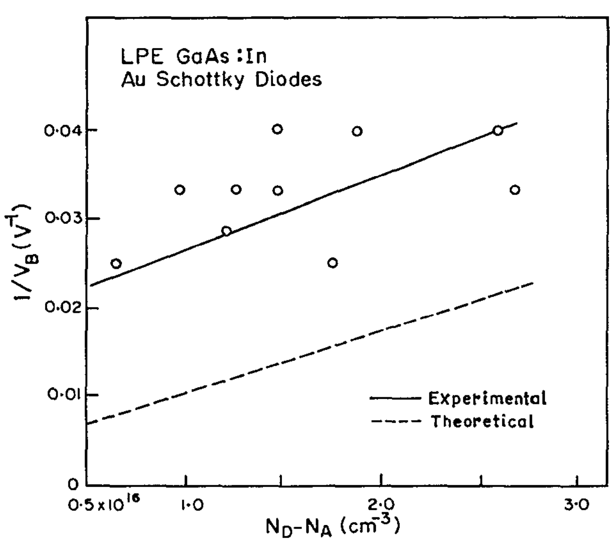

FIG. 5. Inverse of breakdown voltage V_B of Au-GaAs:In diodes plotted as a function of the measured values of N_D-N_A. The solid line is the best fit to the experimental data whereas the dashed line represents values calculated from theoretical models.

N_D-N_A where the solid line represents the best fit. The dashed line is a theoretical plot obtained from normalization of the general form of the ionization integral (assuming that the avalanche process is initiated by electrons),

$$\int_0^w \alpha_n \exp\left[-\int_0^x (\alpha_n - \beta_p)dx'\right] dx$$

and

$$V_B = \frac{q\, w^2 (N_D - N_A)}{2\epsilon_s},$$

where, the symbols have their usual significance.

In the calculations we have used recently reported[19] values of ionization coefficients for GaAs,

$$\alpha_n = 1.9\times 10^{15} \exp[-(5.75\times 10^5/E)^{1.82}]\ \mathrm{cm}^{-1},$$

$$\beta_p = 2.2\times 10^{15} \exp[-(6.75\times 10^5/E)^{1.75}]\ \mathrm{cm}^{-1},$$

where E is the magnitude of electric field appearing across the junction.

An important observation from Fig. 5 is that the slope of the experimental plot is in exact agreement with that of the theoretical plot. This indicates that the breakdown process in In-doped GaAs Schottky-barrier diodes is due to a normal avalanching of charge carriers, and the increase in In-doping concentration does not have any commendable influence on this process. However, the experimental data points are shifted towards lower breakdown voltages in comparison to the theoretically calculated values. We believe that this is due to the lowering of breakdown voltages by edge leakage effects in our diodes which were fabricated without any guard ring or mesa structure.

V. CONCLUSIONS

Etch pit density, Hall-effect studies, C-V, and I-V measurements have been used to investigate the properties of LPE-grown GaAs layers doped with indium in the range $(0.3\text{–}7)\times 10^{19}$ cm^{-3}. EPD of less than 10^2 cm^{-2} are obtained with In-doping concentrations lying in the range $(0.5\text{–}5)\times 10^{19}$ cm^{-3}. Above 5×10^{19} cm^{-3} In doping, EPD rises sharply, apparently due to the formation of misfit dislocations. This is also supported by the physical observation of the layer surfaces. Best values of mobility are also obtained in the same range. Comparison of free-carrier concentrations measured by Hall and C-V techniques shows that the rise in mobility in this particular In-doping range is due to a fall in unintentional donor densities, and the sharp fall of mobility above 5×10^{19} cm^{-3} indium concentration may be attributed to the increase in defect densities as is evident from EPD measurement results. Study of breakdown voltages of gold Schottky-barrier diodes, prepared on the material, demonstrates that the parameter is not directly related to In-doping effect, but is rather a consequence of variation of the shallow donor densities.

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