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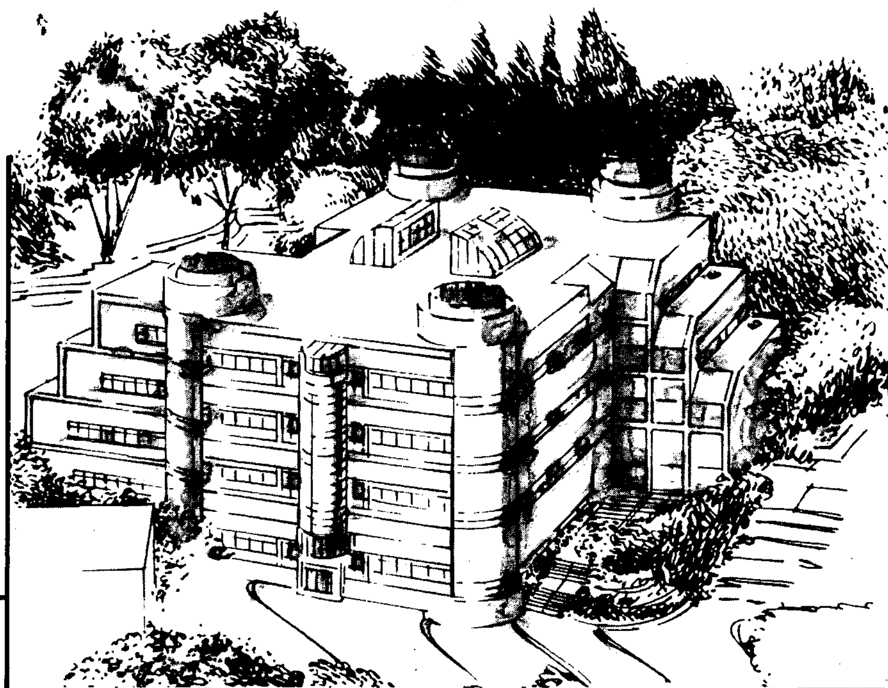

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CHARACTERIZATION OF INACTIVE CARBON IN GaAs

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Characterization of inactive carbon in GaAs

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Abstract. Independent of the doping technique, the electrical efficiency of C doped GaAs is less than 100%. We have shown that Raman spectroscopy provides direct evidence for the formation of C precipitates in GaAs. GaAs samples doped with C and annealed at various temperatures exhibit two broad peaks in the Raman spectra at 1585 cm^{-1} and 1355 cm^{-1} which are characteristic of two sp^2 bonded C atoms. Photoluminescence of annealed C doped GaAs indicates the presence of compensating defects as well. Both precipitation of C and compensation due to native defects play a role in the reduction of the electrical activity of C doped GaAs.

1. Introduction

Carbon is one of the technologically most important acceptor dopants in GaAs. Its diffusion coefficient is at least one order of magnitude lower than those of the other common p-type dopants in GaAs providing better device stability. A number of research groups have grown epitaxial layers with ultra high concentrations ($>10^{21}$ cm^{-3}) of free holes using C doping.[1,2] However, at high concentrations, the doping in these layers is not thermally stable.[3,4] Annealing above 650 °C results in a rapid decrease in the free hole concentration. Independent of the original C concentration or the growth technique, the hole concentration tends toward an ultimate limit of approximately 5×10^{19} cm^{-3}. In addition to the reduction in free carrier concentration, the mobility of the epitaxial layers and the strain in the epitaxial layers also decreases.

Doping with C by ion implantation into GaAs is also problematic. Above a bulk concentration of approximately 5×10^{18} cm^{-3}, the concentration of free holes in the valence band is less than 10% of the concentration of C atoms implanted into the substrate.[5] Co-implantation of Ga increases the activation significantly but hole concentrations greater than 5×10^{19} cm^{-3} cannot be attained with implantation.[6]

Various explanations for the inactive C in GaAs have been presented. They include self-compensation, interstitial C, precipitation, and compensation by point defects. No experimental evidence directly supporting any of these mechanisms has been published. The discussion below will concentrate on two specific mechanisms which account for the majority of the inactive C in both heavily C doped epitaxial layers which have been annealed and in implanted layers. These two mechanisms are precipitation of C and compensation of C acceptors by native defects. Other mechanisms which have been suggested include C_{Ga} donors, lone C interstitials, C complexes, and misfit dislocations. No conclusive experimental evidence exists to support these mechanisms. Although, they may occur in either epitaxial layers or implanted layers, the data presented here suggests that they do not play a major role in reducing the electrical activity of C.

Table 1. Doping parameters and presence of Raman peaks for samples from this study.

Doping Technique	Doping Parameters	Anneal Conditions	Raman Peaks
None		None	NO
None		950 °C, 10 s	NO
Implant	C: 1×10^{15} cm^{-2}, 80 keV	None	NO
Implant	C: 1×10^{15} cm^{-2}, 80 keV	950 °C, 10 s	YES
Implant	Zn: 2×10^{15} cm^{-2}, 180 keV	950 °C, 10 s	NO
MOMBE	C: 6×10^{20} cm^{-3}	None	NO
MOMBE	C: 6×10^{20} cm^{-3}	850 °C, 3 hrs	YES

2. Carbon precipitation

GaAs substrates were solvent cleaned, etched, and implanted with singly ionized C ions under various conditions as described in Table 1. Following implantation, the samples were rapid thermally annealed or furnace annealed under conditions listed in Table 1. Carbon doped GaAs epitaxial layers were grown by MOMBE at 400°C by procedures reported elsewhere.[7] The hole concentration as measured by Hall effect is approximately 6×10^{20} cm^{-3}. A 1 cm^2 piece was furnace annealed at 850 °C for 3 hours.

In Raman spectroscopy of perfect crystals, the only phonons which are observed are zone center phonons due to the requirement of k conservation. When disorder is introduced the conservation of k is relaxed and other phonons with a large density of states are seen. The Raman spectra of amorphous carbon (a-C) films consists of a "G-band" centered between 1540 cm^{-1} and 1590 cm^{-1}, and a "D-band" centered between 1340 cm^{-1} and 1390 cm^{-1}.[8] The G-band corresponds to the zone center phonon (allowed phonon of graphite) which shifts slightly with the introduction of disorder. The D-band is a disorder allowed phonon which corresponds to a peak in the phonon density of states of sp^2-bonded C. Presence of the G- and D- bands in a Raman spectrum indicate that "bulk" sp^2-bonded C is present.

Typical Raman spectra for various C-implanted GaAs and C-doped GaAs epitaxial layers are shown Fig. 1. The broad features centered near 1585 cm^{-1} and 1355 cm^{-1} are assigned to sp^2-bonded carbon. All of the samples where these peaks appeared are annealed. These two peaks in the Raman spectra can be unambiguously identified as arising from C precipitates in the doped layer.[9] Only bulk-like sp^2 bonded C can display such a Raman spectrum.

The detection limit for sp^2 bonded C in these experiments is estimated to be 0.25 monolayers of graphitic C which corresponds to an areal C density of 2.5×10^{14} cm^{-2}. This detection limit was determined from the Raman spectrum of single crystal graphite.

Raman spectroscopy is a surface sensitive technique with probe depth in GaAs of 55 nm. C contamination of the surface is the principal difficulty in analyzing the Ràman spectra in these experiments. To study the affect of C contamination on the interpretation of the Raman results, several additional samples were characterized as described in Table 1. A piece of the GaAs substrate was processed and rapid thermally annealed in the same manner as the C implanted samples. A second piece of the same substrate was implanted with Zn and annealed using the same annealing schedule. Neither of these samples exhibited any Raman peaks in the region from 1300 to 1600 cm^{-1}. Also, a sample which had been implanted with

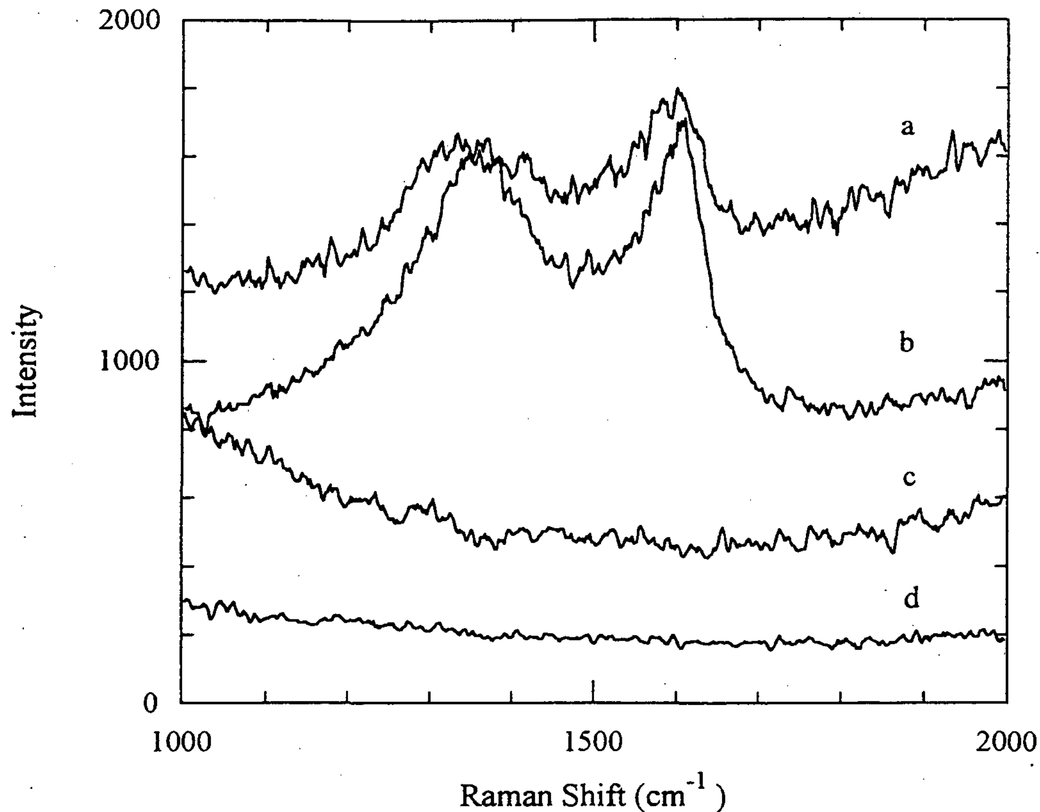

Fig. 1. Raman spectra of carbon precipitates in GaAs for the following samples: a) C implanted and annealed, b)MOMBE-grown and annealed, c)implanted and not annealed, and d) annealed substrate.

C but not annealed did not exhibit any peaks in this region. However, all the samples which had been doped with carbon and annealed exhibited two Raman peaks centered near 1585 cm^{-1} and 1360 cm^{-1}.

As mentioned above, the most difficult part of this experiment is eliminating C contamination during the annealing. To completely eliminate the possibility that the Raman signal was caused by C contamination, GaAs samples were implanted with ^{13}C using the same implant conditions described above. The Raman spectra for samples implanted with ^{12}C and ^{13}C are shown in Fig. 2. In the samples implanted with ^{13}C the two peaks are shifted to lower frequency by 4% ($\sqrt{12/13}$) as expected. Therefore, the Raman peaks can only be a result of the C clustering of implanted C and not from environmental contamination.

The size of the C precipitates can be estimated from the Raman spectra by comparison to amorphous C films which have been studied extensively.[8] The intensity ratio of the D- and G- bands, the I_d/I_g ratio is a function of sp^2 domain size in disordered graphite. An inverse relationship has been found between domain size, L_a, and I_d/I_g ratio in microcrystalline graphite by Tuinstra and Koenig:[10]

$$L_a(nm) = 4.4\ (I_d/I_g)^{-1}.$$

(The Raman spectrum of single crystal graphite is a single "G-band" peak at 1580 cm^{-1}, i.e., $I_d/I_g = 0$.) The spectra observed in this study are nearly identical to those observed by Dillon[11] from ion-beam films annealed at 900 °C. The I_d/I_g ratios in the C doped samples (computed using the peak heights) are in the range of 0.8 to 1.0. Using the Tuinstra and Koenig relationship, the C precipitates have an average sp^2 domain size of 5 nm.

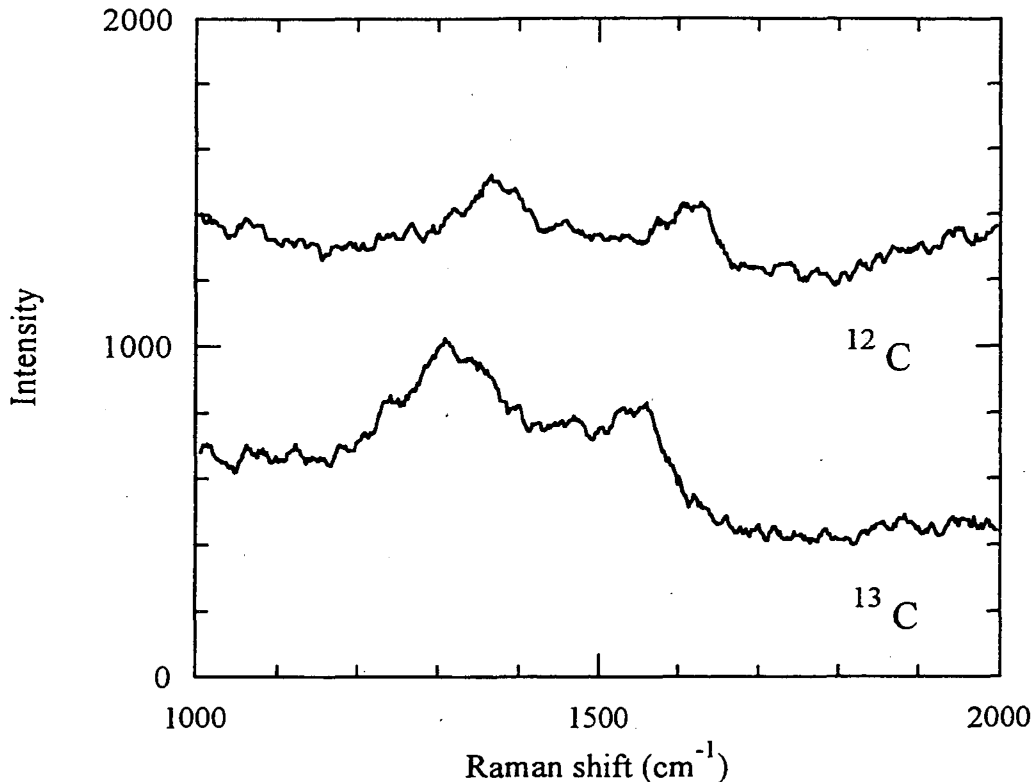

Fig. 2. Raman spectra of C precipitates in GaAs samples implanted with ^{12}C or ^{13}C and annealed.

A simple, rough estimate of the minimum diffusion coefficient required for a C precipitate to form can be calculated. Given the annealing conditions of 950°C for 10 s the diffusion coefficient required for precipitate formation can be estimated by:

$$x = (Dt)^{1/2}.$$

D is then approximately 2×10^{-13} cm^2/s. You et. al.[12] reported a diffusion coefficient of 7.8×10^{-15} cm^2/s for C diffusion at 960 °C. The diffusion coefficient calculated here is more than 10 times higher than that of You. Two possible explanations exist for this effect.

First, diffusion is enhanced either by loss of group V elements at the surface or by radiation damage in the crystal due to the implantation process. To examine the role of the surface in the precipitation of C, two GaAs samples with the same concentration of implanted C were rapid thermally annealed. One sample was capped using the proximity method. The second was not capped. The surface of the second sample was noticeably degraded due to the loss of As. In this sample the C-C peaks were more intense. This result suggests that the loss of the group V element near the surface enhances precipitation.

Another possibility for the larger diffusion coefficient compared to those reported in the literature relates to the method of determining this quantity. In general, diffusion coefficients are determined with the use of SIMS. SIMS experiments do not give any information on the bonding configuration of the C. Therefore, these experiments do not take into account C diffusion to a precipitate within the C doped layer. C in a precipitate has not diffused beyond the original doped layer so this movement is not detected by SIMS.

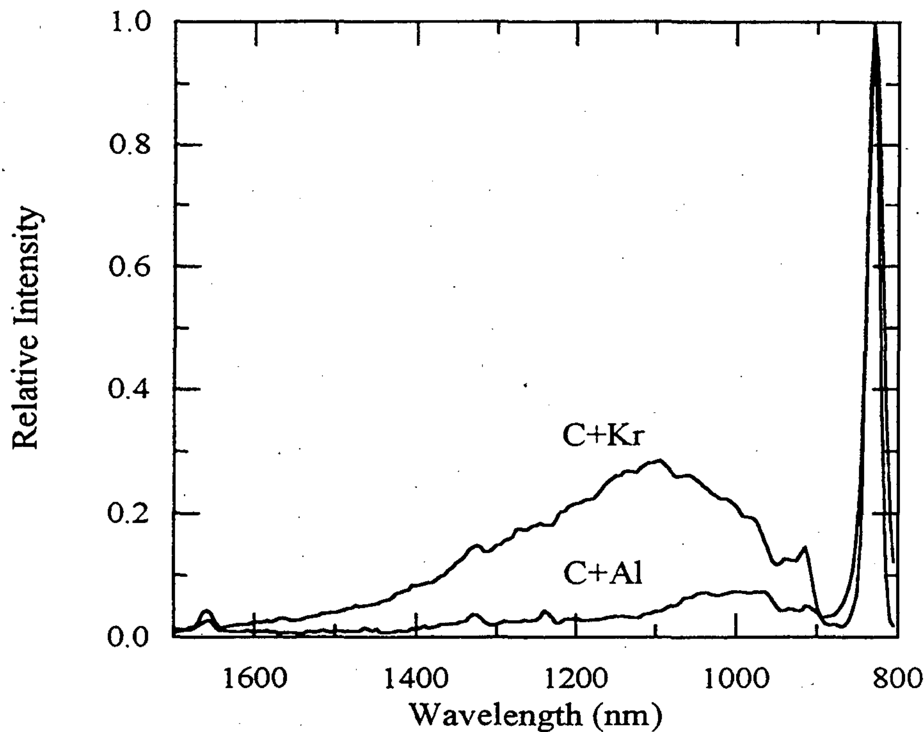

Fig. 3. Photoluminescence spectra for C+Al and C+Kr samples.

3. Compensation by native defects

Precipitation clearly accounts for at least a portion of the inactive C in implanted and epitaxial GaAs:C. The existence of precipitates can account for the reduction in free hole concentration and the decrease in strain in annealed epitaxial layers. However, the decrease in mobility cannot be explained by precipitation. In degenerately doped semiconductors, mobility is inversely proportional to the number of ionized impurities. Precipitation reduces the number of ionized impurities hence the mobility should increase. Evidently, precipitation is not the sole contributor to the decrease in free hole concentration.

In this section the role of native defects in reducing the free hole concentration and mobility in GaAs:C will be examined. In implanted layers, radiation damage provides an abundant source of defects. In annealed epitaxial layers, the precipitation of C can also create defects. C which moves from an As site to a precipitate will create an As vacancy. The accommodation of the precipitate in the lattice can also create defects. A model developed by Walukiewicz[13] indicates that native defects will form complexes and change their electrical character to compensate intentional dopants. In this case, native point defects will have donor character to compensate the C_{As} acceptors.

Experimental evidence for the existence of native defects can be found in the measurement of the mobility and in PL experiments. GaAs epitaxial layers heavily doped with C and annealed exhibit a reduction in hole mobility as well as a reduction in free hole concentration. In C co-implantation experiments described previously[5] the hole mobility was reduced in samples where the stoichiometry of the implanted layer was not maintained during implantation. Samples were co-implanted with Kr or Al and similar hole concentrations were attained in both. However using local vibrational mode spectroscopy the C+Kr sample was found to have nearly twice the concentration of C_{As} as the C+Al

the C+Kr sample was found to have nearly twice the concentration of C_{As} as the C+Al sample. The C+Kr sample also had a lower mobility at 77K then the C+Al sample (60 and 106 cm^2/Vs respectively) indicating the presence of compensating defects.

These defects may also be responsible for the increased PL intensity reported for annealed epitaxial layers and also seen in our implantation studies. The PL spectra for C+Kr and C+Al samples are shown in Fig. 3. The C+Kr spectrum is remarkably similar to those shown by Watanabe.[3] Watanabe's PL spectra are from heavily C-doped MOCVD layers ($p=1.3\times10^{20}$ cm^{-3}) annealed at 850°C Both the MOCVD epitaxial layer and the C+Kr implanted layer exhibit a large broad peak centered around 1100 nm in their PL spectra.

4. Conclusions

In conclusion, direct evidence of C precipitates in GaAs has been shown The Raman peaks are clearly not due to C contamination but come from the intentionally doped C. The precipitates are present in both implanted layers and epitaxially grown layers.

The striking similarity between the results of precipitation experiments and PL experiments on both implanted and epitaxial GaAs:C layers suggest that the limitations in C doping of GaAs are inherent to this system and not particular to the doping technique. At doping levels of 5×10^{19} cm^{-3}, doping of GaAs with C is not thermally stable. The solid solubility of C is exceeded, and the C will precipitate during annealing. The precipitation process decreases the $[C_{As}]$ and reduces the strain in the epitaxial layers. Precipitation also occurs in implanted layers. As well as precipitation, the free hole concentration is further reduced in both implanted and epitaxial layers through compensation by native defects.

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