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Lattice contraction in carbon-doped GaAs epilayers

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Epitaxial GaAs layers, heavily doped with carbon, have been grown by gas-source molecular-beam epitaxy using an electron-beam-evaporating graphite source for doping. Lattice strain and electrical compensation in these samples have been studied theoretically and experimentally. Most of the carbon acceptors can be activated by post-growth annealing at 490 °C in the N_2 ambient, probably due to the reduction of C-H bonds formed during growth. Annealing at higher temperatures reduces the electrical activity and causes an abrupt change in lattice strain, likely due to the formation of C-C interstitial couples. [S0163-1829(98)04920-0]

Carbon is an attractive alternative to beryllium as a p-type dopant for GaAs and related compounds because of its lower diffusion coefficient and possibility of obtaining a higher free-carrier concentration.[1] Very high doping levels in GaAs have, indeed, been achieved.[2–5] On the other hand, self-compensation effects begin to play an important role at carbon concentrations greater than about 5×10^{19} cm^{-3}.[6] The compensation effects are associated with the generation of donors, mainly due to the formation of interstitial carbon, substitutional carbon in gallium sites, and the precipitation of carbon.[7,8] If hydrogen is present in the growth ambient, as in the case of gas-source molecular-beam epitaxy, an additional compensation effect appears, namely, hydrogen passivation that is caused by the formation of C-H bonds.[9]

Besides electrical compensation, C doping in excess of 10^{19} cm^{-3} causes lattice contraction. This is because C has a small covalent radius (0.77 Å) compared to As (1.20 Å) or Ga (1.26 Å).[10] Lattice contraction can be determined by a high-precision measurement, such as double-crystal x-ray diffractometry (DCXRD), and be related to carbon concentration in a rather straightforward way.[11] The situation is somewhat more complicated if the C-H bonds are present.

In this work we shall study lattice strain and electrical properties of heavily doped GaAs:C grown by gas-source molecular-beam epitaxy (MBE) (for gas-source MBE, see Ref. 12). We first describe the experiments and then discuss the results obtained.

The GaAs:C samples were grown homoepitaxially at 580 °C. The background pressure was 10^{-5} mbar during growth, due to hydrogen from cracked AsH_3. Carbon was evaporated from a graphite rod of an electron-beam-heated source. The C flux was controlled by the filament voltage and emission current. Upon growth, the samples were thermally annealed (RTA) *ex situ* in 100% N_2. The annealing procedure consisted of an initial N_2 purge, a temperature ramp at 50 °C/s to a final temperature, and a 5 min anneal at this temperature.

The carrier density and van der Pauw Hall mobility were measured at room temperature. The DCXRD rocking curves were measured in a nondispersive Bragg geometry to determine the lattice strain and carbon concentration.

Carbon incorporates substitutionally into the arsenic sublattice where it becomes an acceptor (C_{As}^-). At high doping levels, greater than 10^{19} cm^{-3}, it may also occupy gallium sites (C_{Ga}), acting as a donor. The density of C_{Ga}^+ is, however, four orders of magnitude smaller than the density of C_{As}^- because of a higher formation energy of C_{Ga}^+.[13] Carbon may also occupy an interstitial site and reduce lattice strain. Interstitial carbon is unstable. It readily captures a neighboring C_{As}^- acceptor to form a C-C interstitial couple that acts as a donor. The formation of C-C bonds can become a dominant compensation effect in GaAs:C at a very high doping concentration.

One may calculate the lattice mismatch $\Delta a/a_0$ caused by the carbon-related defects. If the calculation is based on Pauling's covalent bonding radii of atoms and Vegard's law,[14] we obtain the amount of lattice contraction due to the presence of C_{As},

$$\begin{aligned}\Delta a/a_0 &= 4(r_C - r_{As})N_{C,As}/a_0 N_0\sqrt{3}\\ &= -7.9478\times10^{-18}\ N_{C,As}\ \text{(ppm)},\end{aligned}$$

where r_C and r_{As} are the covalent radii of C and As, respectively, $N_0 = 2.21\times10^{22}$ cm^{-3} is the density of Ga or As atoms in pure GaAs, and $N_{C,As}$ is the concentration of C_{As}^-. Similarly, lattice strain caused by the C-C interstitial couple is[15]

$$\begin{aligned}\Delta a/a_0 &= (d_b - r_{Ga} - r_{As})(c_{11}+2c_{12})N_{\text{C-C}}/2N_0 c_{11}(r_{Ga}+r_{As})\\ &= -1.4956\times10^{-18}\ N_{\text{C-C}}\ \text{(ppm)},\end{aligned}$$

where $d_b = (\sqrt{3}/3)r_C + \sqrt{[(r_C+r_{Ga})^2 - 2r_C^2/3]}$ is the distance of the C-C couple from its nearest neighbors; c_{11} and c_{12} are the stiffness coefficients of GaAs, and $N_{\text{C-C}}$ is the concentration of C-C couples. Our calculations show that interstitial carbon has no contribution to the lattice strain.

The hydrogen passivation effect should be taken into account. Hydrogen is incorporated into interstitial sites forming C-H bonds with C_{As}^-. Lattice mismatch generated by the C-H bond is

$$\Delta a/a_0 = -6.9432\times10^{-18}\ N_{\text{H-C}}\ \text{(ppm)},$$

where the effective bond radius is taken to be $(r_C+r_H)/2 = 0.545$ Å, and $N_{\text{C-H}}$ is the concentration of C-H bonds.

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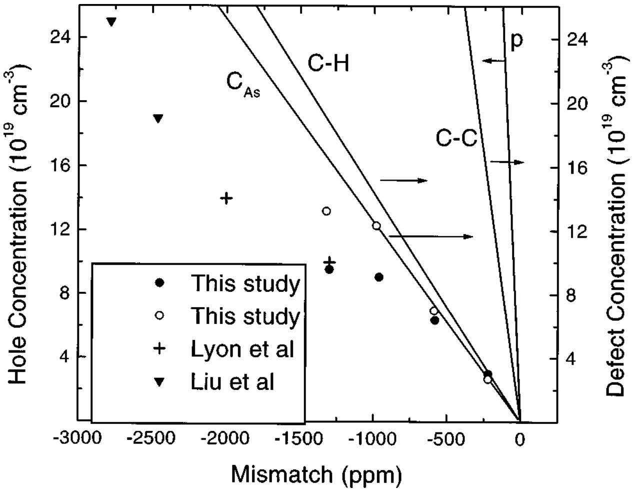

FIG. 1. Plot of the calculated lattice mismatch as a function of C-related defects. The relationship between hole concentration and lattice mismatch is determined from Hall effect and DCXRD measurements for as-grown (●) and RTA treated (○) GaAs:C. Data of Liu *et al.* (Ref. 19) and DeLyon *et al.* (Ref. 7) are included for comparison.

In consideration of a hole in the valence band decreasing the energy of covalent bond,[16] high concentration of holes could also lead to the lattice contraction of GaAs:C, which can be described by

$$\Delta a/a_0=(D_p/3B)p=-0.4978\times10^{-18}p \quad \text{(ppm)},$$

where p is the hole concentration in the top of the valence band, $D_p=-0.7$ eV is the deformation potential of this maximum,[17] and $B=7.5\times10^6$ N/cm^2 is the bulk modulus.[18] When all the factors are taken together, one may write

$$\Delta a/a_0=-(7.9478N_{\text{C,As}}+6.9432N_{\text{C-H}}+1.4956N_{\text{C-C}} \\ +0.4978\ p)\times10^{-18} \quad \text{(ppm)}.$$

The net hole concentration is $p=N_{\text{C,As}}-N_{\text{H-C}}-N_{\text{C-C}}$ and the total carbon concentration $N_{\text{C,tot}}=N_{\text{C,As}}+N_{\text{H-C}}+2N_{\text{C-C}}$.

$N_{\text{C-H}}$ can be estimated from the postgrowth annealing experiments. When $N_{\text{C-H}}$, $N_{\text{C,As}}$, and $N_{\text{C-C}}$ are known, one can provide the relationships between $\Delta a/a_0$ of GaAs:C, hole concentration, and carbon-related defect concentration, based on Hall and DCXRD measurements.

Figure 1 shows our calculations together with experimental results. It can be seen that at doping levels lower than 1.0×10^{20} cm^{-3} the carrier compensation is mainly due to hydrogen passivation of C acceptors. At a higher doping level C-C interstitial couples could be formed to further reduce the doping efficiency.

Effects of postgrowth annealing on the electrical properties and $\Delta a/a_0$ of GaAs:C are studied in Figs. 2 and 3. The samples studied in Fig. 2 exhibit the Hall hole densities around 7.0×10^{19} cm^{-3}, as measured after growth. Relative changes in hole concentration and Hall mobility are determined as functions of postgrowth annealing temperature (T_{anneal}). The figure shows that there is a significant (~10%) improvement in electrical activation when the sample is annealed at 450–530 °C for 5 min. Figure 3 shows that annealing only causes a slight change in strain level when $T_{\text{anneal}}\leq530$ °C, but yields a more remarkable, abrupt change of about 10% with the opposite sign of strain if $T_{\text{anneal}}>560$ °C. Similar results were also reported in Ref. 20.

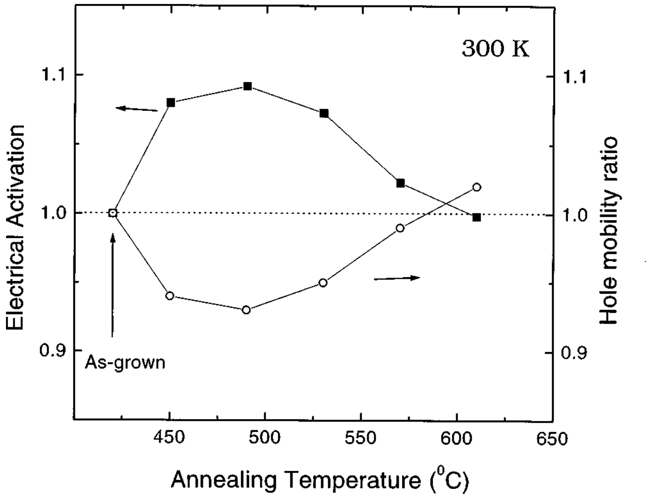

FIG. 2. Electrical activation and hole mobility for postannealed GaAs:C as functions of annealing temperature. The dotted line is a guide to the eye.

We relate the observed improvement in electrical activity to a postgrowth annealing effect that is thought to remove hydrogen passivated carbon acceptors, the C-H bonds. The optimal annealing temperature is $T_{\text{anneal}}\sim490$ °C. Higher temperatures are not desired because they cause carrier compensation, likely due to the formation of C-C interstitial couples that result in a decrease in the lattice contraction with an increase in mobility. According to the calculations, the relative change of 7.4% in strain observed for $T_{\text{anneal}}>560$ °C corresponds to an increase of 2.3×10^{18} cm^{-3} in the density of C-C couples.

In summary, heavily doped GaAs:C layers have been grown by gas-source molecular-beam epitaxy using an electron-beam-evaporating graphite source for doping. Lattice mismatch, due to C at arsenic sites, C-H bonds, C-C interstitial couples, and free charge, has been calculated

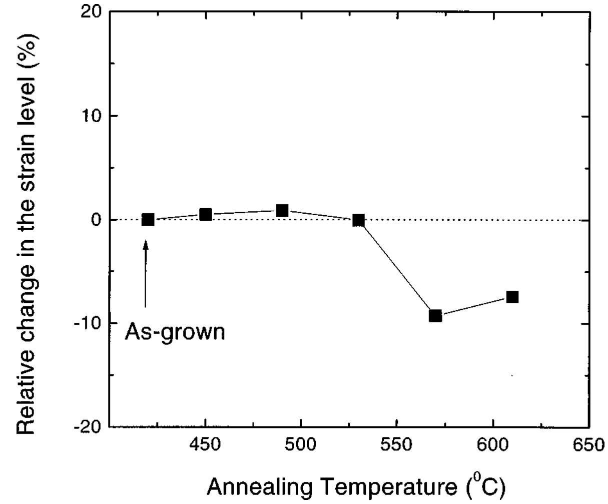

FIG. 3. Relative change in strain for post-annealed GaAs:C as a function of annealing temperature. The dotted line is a guide to the eye.

and compared with that experimentally obtained by x-ray diffraction. The largest mismatch is caused by C_{As}. The C-H bonds are believed to passivate carbon acceptors and cause carrier compensation in as-grown samples. They can be removed to a large extent by postgrowth annealing at 490 °C resulting in an increase of several percent in hole concentration. Annealing at higher temperatures decreases the hole concentration, likely due to an increase in C-C interstitial couples.

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