

Carbon site switching in carbon doped GaAs, its dependence on carbon concentration

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Carbon thermal site switching dependence on carbon and carbon dimers concentration in GaAs layers is studied. The atomic carbon and dimer concentrations ranged from $0.4 - 2 \times 10^{20} \text{ cm}^{-3}$ and $0.1 - 1.5 \times 10^{19} \text{ cm}^{-3}$, respectively. The hole concentration as a function of the annealing time, increases from the “as grown” value to a intermediate maximum whereupon the hole concentration decreases before resuming its increase to a higher value. Such behavior is explained by a double-site switch of one carbon from the $\text{C}_{\text{As}}\text{-Ga-C}_{\text{As}}$ dimer to an interstitial site and then to a substitutional one. The corresponding processes are first order. It is found that the corresponding involved kinetic coefficients are independent of the carbon and dimer concentrations.

Keywords: GaAs; Carbon stability; Switching; Hydrogen; Complexes.

1. Introduction

Carbon is the acceptor of choice to obtain p-type GaAs. It sits on the arsenic sub-lattice introducing the shallowest acceptor level known to now. Carbon in GaAs has not been reported occupying substitutional sites in the gallium sub-lattice and few reports in the literature place it found on an interstitial position [1-4]. However, it has been found that depending on the growth conditions, carbon doping efficiency might be quite low. Several mechanisms have been identified as to produce carbon neutralization. It is well known that growing carbon doped GaAs using precursors that release atomic hydrogen produces its incorporation into the growing layer, passivating some carbon. It has, also, been proposed the existence of interstitial carbon that should reduce the doping efficiency as well. Carbon doping stability in GaAs, rises some questions as under thermal annealing the hole concentration might decrease [1-4,7]. Additionally, the growth of carbon doped GaAs under non-optimal growth conditions creates carbon dimers; $\text{C}_{\text{As}}\text{-Ga-C}_{\text{As}}$ (C_2) [5] where one of the carbon shallow acceptor levels becomes deep, precluding its ionization at room temperature resulting on a “missing” hole [6]. It has been shown that at intermediate temperature long term annealing, a carbon in C_2 becomes interstitial. In this position carbon is a double donor decreasing hole concentration even more. Then this same carbon atom site switches to a farther As site introducing its normal shallow acceptor level allowing the recovering of the intermediate lost holes and the initially missing one. Both site carbon changes; first from the dimer to an interstitial position and the second one from this interstitial position to an As substitutional one but to an As site farther from

the initial dimer position, follow first order process [9]. In this work we study the dependence of those kinetic constants associated to each one of those processes as a function of the carbon atomic and carbon dimer concentrations.

2. Experimental details

The samples were grown by low pressure metalorganic chemical vapor deposition on semi-insulating 2° off GaAs substrates, extrinsically doped with CCl_4 (samples C11 and C12) and CBr_4 (samples BR1 and BR2) in a AIX2400 reactor. The layer thickness ranged from 1.6 – 1.8 μm . Carbon and hydrogen atomic concentrations were determined by secondary ion mass spectroscopy (SIMS) measurements using a Cameca ims-4f system with a Cs^+ primary beam. Ion implanted standards were employed to obtain absolute concentration values. The presence of C–H and $\text{C}_2\text{-H}$ complexes was determined by low temperature infrared absorption measurements using a BOMEM DA8 interferometer. For electrical measurements, ohmic contacts were produced using indium metal, Hall data were collected using the van der Paw method. Layer thermal annealing was performed at atmospheric pressure under argon atmosphere using a sliding furnace. The carrier concentration was accurately followed by series of multi-stage annealing experiments, measuring the carrier concentration and mobility as a function of duration of the heat treatment at each stage.

3. Results and discussion

Figures 1, 2 and 3 show the variation of the hole concentration as a function of the annealing time for an

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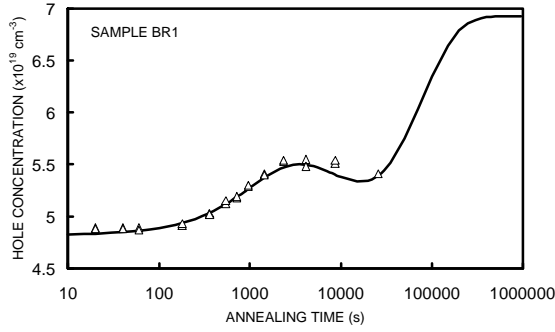


Figure 1. Room temperature hole concentration as a function of anneal time at a temperature of 500°C for a sample having an atomic carbon and dimer concentrations of $7 \times 10^{19} \text{ cm}^{-3}$ and $1.2 \times 10^{19} \text{ cm}^{-3}$.

anneal temperature of 500 °C. As seen, for all the samples, as the thermal treatment goes on the carrier concentration increases exponentially as a function of thermal treatment duration, with an annealing time constant, $\hat{\delta}_h$, ~ 1200 s, reaching a first maximum. This first exponential reactivation kinetics, clearly corresponds to the one due to the decomposition of CH complexes[8]. Then, as the annealing continues, the hole concentration decreases reaching a minimum and finally increases anew, following clearly a different kinetics from that due to the CH decomposition, reaching hole concentration values higher than the earlier maximum becoming equal, between the experimental error, to the carbon concentration obtained by SIMS. Let us discuss first the "as grown" hole p_0 , atomic carbon [C], CH and C_2 concentrations whose respective values, for all type of samples, are summarized in Table I. As seen hole concentration ranges from 4.8 to $10 \times 10^{19} \text{ cm}^{-3}$. The CH concentration, is given by the hole concentration increase to the first p_0 maximum, as this first increase is due only to the decomposition of the CH complex [6]. The CH, as seen, ranged from 0.9 to $5.5 \times 10^{19} \text{ cm}^{-3}$. The as grown C_2 concentration, assuming that only inactive carbon is that being part of carbon dimers [6], is given by the difference between the atomic carbon concentration, measured by SIMS, and the hole concentration at, once again, the first maximum on the $p_0(t)$ curve, varies from ~ 0.1 to $1.2 \times 10^{19} \text{ cm}^{-3}$.

The hole concentration decrease between the first hole concentration maximum and the subsequent minimum can be explained as follows. The small size of the carbon atom produces an important lattice elastic stress around the carbon dimer inducing, at the anneal temperature, the site switch of one of the carbon atoms. The first carbon site switch takes place to an interstitial position where carbon behaves like a double donor, producing the observed hole decrease [3]. As the anneal treatment goes on the interstitial carbon site switches a second time to an As substitutional site farther away from the first one where the switching carbon was initially located. Such process might occur according to the reactions below

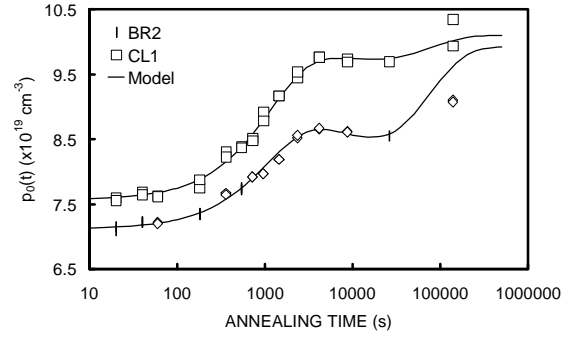
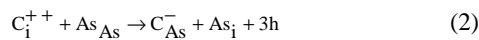
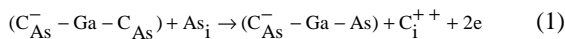


Figure 2. Room temperature hole concentration as a function of anneal time at a temperature of 500°C for samples having an atomic carbon and dimer concentrations of $10 \times 10^{19} \text{ cm}^{-3}$ and $1.0 \times 10^{19} \text{ cm}^{-3}$, sample BR2 and $0.3 \times 10^{19} \text{ cm}^{-3}$ sample CL1.

and considering that no dimers are reformed and that they are first order processes, their continuity equations are given by

$$\frac{d[C_2]}{dt} = -k_i[C_2] \quad (3)$$

$$\frac{d[C_i]}{dt} = -k_s[C_i] \quad (4)$$

where k_i and k_s are the kinetic coefficients of the reactions that produce the interstitial carbon from the initial carbon dimer and the substitutional final, from the interstitial produced in the step before. These two successive reactions just relocate the carbon atom involved in reactions (3) and (4).

Solution to Eq. (3), considering a dimer initial concentration of $[C_{20}]$ and that after the anneal treatment all the dimers have been decomposed, is given by

$$C_2(t) = C_{20} \exp(-k_i t) \quad (5)$$

where, according to reaction stated by Eq. (1) each decomposed carbon dimer produces an interstitial carbon. Then, each interstitial carbon will, according to Eq. (2), relocate. Solving the continuity equation of this relocating process, i.e., Eq. (4), the interstitial concentration as a function of the anneal time is obtained, if it is considered that $k_i \ll k_s$, and that the anneal process is continued until the dimer and interstitials are completely annealed off, the solution is given by

$$C_i(t) = C_{20} [1 - \exp(-k_i t)] \exp(-k_s t) \quad (6)$$

The change on the hole concentration produced by these processes is just given by the concentration of carbon that being part of a dimer has switched site to an As site, and is given by

$$\Delta p_0(t) = [C_{20}] - [C_2(t)] - [C_i(t)] \quad (7)$$

Finally, the hole concentration evolution as a function of the anneal time is obtained

Table 1. Fitting parameters used in Eq. (8) to fit hole concentration data during the thermal annealing at a temperature of 500°C, concentrations are in 10^{19} cm^{-3} and time constants are in 10^3 s .

Sample	Dopant	[C] SIMS	p_{00}	CH_0	C_{20}	$\hat{\sigma}_h (=1/k_h)$	$\tau_i (=1/k_i)$	$\hat{\sigma}_s (=1/k_s)$
BR1	CBr ₄	7.0	4.8	0.9	1.2	1.2	20	70
BR2	CBr ₄	10.0	7.1	1.7	1.0	1.15	20	70
CL1	CCl ₄	10.0	7.5	2.2	0.3	1.0	20	70
CL2	CCl ₄	15	10.0	5.0	0.1	2.0	20	70

$$p_0(t) = p_{00} + CH_0(1 - \exp(-k_h t)) + C_{20}(1 - \exp(-k_i t)) - 2C_{20}(1 - \exp(-k_i t))\exp(-k_s t) \quad (8)$$

where p_{00} and CH_0 are the "as grown" hole and CH complex concentrations respectively and k_h is the kinetics coefficient of the reaction that produces the carbon reactivation through the decomposition of the CH complex[8,10]. The experimental data of Figs. 1, 2 and 3 have been fitted using Eq. (8), fitting parameters are given in Table I, too. As seen from the values for k_i and k_s , both site switch process are independent from both the C_2 and the atomic carbon concentrations.

To assess the carbon site switch that we propose here we used low temperature infrared absorption as it allows the identification of CH and C_2H complexes. The 10 K infrared absorption spectra for the "as grown" samples, contain the absorption peaks produced by the C-H complex at 2635 cm^{-1} and that produced by the C_2-H complex at 2688 cm^{-1} . However, as the thermal heat treatment goes on, the spectra show first the disappearance of the CH complex, then that of C_2H . If after reaching the final hole concentration, the samples are rehydrogenated, the absorption peak produced by the CH complex is anew present in the low temperature infrared absorption spectra but not at all the one

corresponding to C_2H . This clearly indicates that the CH complex is, as expected, recomposed by the hydrogen indiffusion, but the C_2H complex is not present proving that the carbon dimer has been decomposed by the thermal anneal and does not exist any more[9].

4. Conclusions

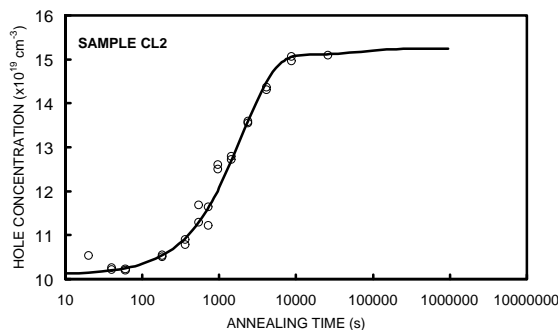
In conclusion, it has been shown that the processes present in the double site switch of one carbon in the C_2 dimer, often present in carbon doped GaAs epitaxial layers, are independent of the C_2 and atomic carbon concentration.

Acknowledgements

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**Figure 3.** Room temperature hole concentration as a function of anneal time at a temperature of 500°C for a sample having an atomic carbon and dimer concentrations of $15 \times 10^{19} \text{ cm}^{-3}$ and $0.1 \times 10^{19} \text{ cm}^{-3}$.