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NEW ASPECTS OF (SEMI-INSULATING) GaP:Cu

C. Eder[1], V. Schlosser[1], R.P. Leon[2], K.M. Yu[3], E.R. Weber[2,3]
[1]Institut für Festkörperphysik, Universität Wien, Strudlhofg. 4, A-1090 Wien and
Ludwig Boltzmann Institut für Festkörperphysik, Kopernikusg. 15, A-1060 Wien, Austria
[2]Department of Materials Science, University of California, Berkeley, CA 94720, USA
[3]Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

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ABSTRACT

Experiments were performed to investigate the possible relevance of the buried Schottky contact model for the complex behavior of Cu in GaP. PIXE studies show that Cu can reach very high concentrations in that material. Channeling indicates that a part of the Cu forms precipitates. Hall measurements on sets of samples were made to examine the electrical transport coefficients. The mobilities of the samples with the most abundant concentration of Cu were found to be dominated by a term $\propto T^{-0.5}$ which was identified as a component induced by metallic spikes with non-overlapping depletion zones. We come to the conclusion that Cu introduces an acceptor like defect as well as precipitates. For high initial carrier concentrations, however, the depletion widths are probably too small for the buried Schottky contact model to apply. For doping concentrations lower than $5x10^{16}cm^{-3}$ the model might be of considerable relevance.

INTRODUCTION

Copper is a common impurity in GaP which has been under investigation for several decades now. Its ability to render GaP semi-insulating has been reported [1-3] as well as the fact that both electronic particles can be trapped in samples diffused with copper [3]. Many experiments were carried out. They revealed several defect levels, ascribed to the presence of Cu. Most authors report defect levels of 0.55eV, 0.68-0.75eV and 0.82eV above the valence band [1-7], some also detected a level at 0.6eV below the conduction band [3].

Despite all this effort, however, a clear defect identification could not be given until today and it seems that a number of different Cu-related defects is present in GaP. Especially the question, whether Cu introduces simply a substitutional acceptor level could not be answered until today. On the one hand, data from Raman scattering confirm just that view [8]. On the other hand, the characteristic orange luminescence (COL) emission could be ascribed to an exciton bound to an isoelectric Cu_{In}-Cu_{Ga}-Cu_{In} defect [9].

Recently, a new mechanism - the buried Schottky contact model- able to deplete semiconductors of free carriers of both signs has been found for InP:Cu [10] and low temperature MBE GaAs:As [11]. This model explains the trapping of carriers by the presence of Cu-In and As precipitates, respectively. These cause depletion zones due to precipitate matrix transitions. If the density of the precipitates is high enough, those zones overlap and thereby deplete the whole semiconductor of free carriers.

In this work the relevance of such a mechanism for Cu diffused GaP is studied. The experiments involved studies of concentration limits, lattice site determination and electrical measurements. Hall measurements were mostly performed at high temperatures. Thus, being close to the intrinsic region of GaP, the influence of shallow dopants on the temperature dependence of electrical transport coefficients was greatly reduced.

EXPERIMENTAL

Starting material were 2-inch LEC GaP single crystal wafers of both signs, Si and S doped to $5.1 \times 10^{17} cm^{-3}$ and $1.3 \times 10^{18} cm^{-3}$ for n-type, C doped and compensated by P antisite defects to $1 \times 10^{15} cm^{-3}$ for p-type samples. The samples were cut, degreased with aceton and methanol and etched in a solution containing HNO_3:HCl:CH_3OOH (1:1:1, stabilized for 30 min.). Cu was evaporated on one side of the samples using a thermal evaporator. For the diffusion process the samples were sealed in evacuated quartz ampules with a measured amount of P to prevent sample surface decomposition at higher temperatures. Diffusions were performed at temperatures from 600°C to 1300°C for each set of samples, for times long enough to saturate all of the sample volume with Cu. After diffusion, the samples were rapidly cooled to room temperature by dropping them from a vertical furnace directly into an oil bath. Mechanical and chemical polishing removed any residual Cu at the sample surface.

Ohmic contacts for Hall measurements were prepared for both n- and p-type samples. After etching the surface a Ni/Au-Ge structure was evaporated for n-type, a Au/Zn/Au structure for p-type material. All contacts were tempered at 550°C for 3 minutes.

Particle Induced X-ray Emission (PIXE) using 1.4 MeV protons for the ion beam was performed to determine the concentration of Cu for different diffusion temperatures. The samples with the highest amount of Cu were used for channeling. Temperature variable Hall measurements mostly in the range from 300K to 550K were made to examine electrical transport coefficients. The temperature dependence of the mobility of all samples was analyzed and fitted

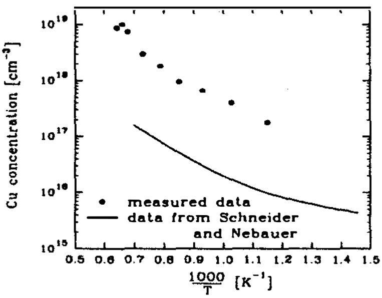

Figure 1. Cu concentration in GaP after rapid cooling. The maximum concentration appears at 1250°C. The solid line represents data measured by Schneider and Nebauer with radioactive tracers [12].

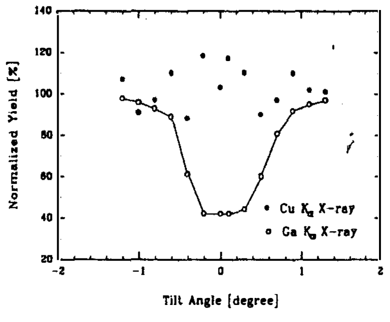

Figure 2. 1.4 MeV proton channeling along ⟨110⟩ for a sample diffused at 1200°C. The Cu K_α signal does not follow the Ga K_α signal.

with the ansatz $\mu^{-1} = \Sigma\mu_i^{-1}$ where μ_i^{-1} is given by $m_i^{-1} \cdot T^{-n_i}$, in order to extract a possible mobility component induced by copper.

RESULTS

The PIXE results show that Cu in GaP can reach very high concentrations, if the sample is rapidly quenched to room temperature, -figure 1. A maximum concentration of $1 \times 10^{19} cm^{-3}$ occured at 1250°C. This lies far above the equilibrium solubility limits measured by Schneider and Nebauer [12]. It indicates that Cu can introduce another component than one of purely substitutional character. The concentration in p-type material seems to be somewhat reduced, as a check with a p-type sample revealed.

From the channeling scan it can be seen that the Cu K_α x-ray does not follow the host signal but is rather close to the value for the crystal being in random position -figure 2. This is commonly observed for precipitates.

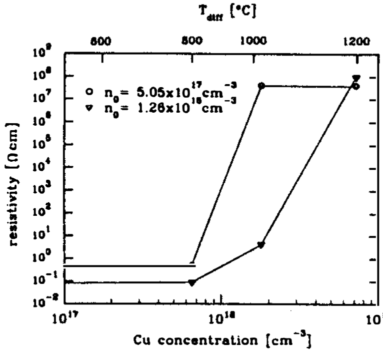

Figure 3. Resistivities at 300K for two sets of samples with initial doping levels n_0. Even samples with a very high initial doping level can become semi-insulating ($\rho > 10^7 \Omega$ cm), if the copper concentration is high enough.

The Hall measurements show that even samples with a high initial doping concentration of $n_0 = 1.26 \times 10^{18}$ cm^{-3} become semi-insulating ($\rho > 10^7 \Omega cm$), provided that the diffusion temperature and hence the copper concentration is high enough -figure 3. Initially p-type material, however, shows only a slight increase in resistivity.

It was also observed that the carrier concentrations of all semi-insulating samples were reduced to about $1 \times 10^{10} cm^{-3}$ at 300K -figure 4. The activation energies deduced from Arrhenius plots were in the range of 0.55eV to 0.64eV. Semi-insulating samples also showed a conversion from n- to p-type material. This conversion indicates that Cu compensates the shallow donors by an acceptor like level. Comparing the difference in carrier concentration $\Delta n = n_0 - n(C_{Cu})$ confirms that picture -table 1. It can be seen that for both n-type sets the reduction in free carriers for a Cu concentration of $6.5 \times 10^{17} cm^{-3}$ is about the same, indicating a limit of the substitutional solubility. The otherwise large reduction prohibited the same analysis for other Cu concentrations.

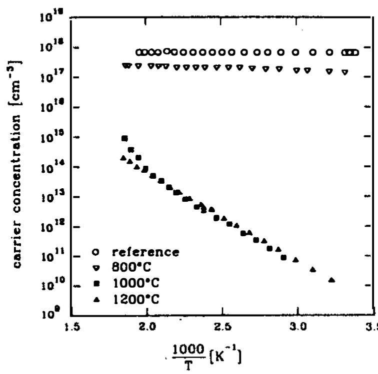

Figure 4. Carrier concentration for a set of samples with initial concentration $n_0 = 5 \times 10^{17} cm^{-3}$ and different diffusion temperatures. N is reduced to $\sim 1 \times 10^{10} cm^{-3}$ for samples diffused at 1000°C and higher. The other set of samples showed the same reduction for T_{diff}=1200°C. Filled symbols indicate p-type material.

Table 1. Carrier concentration n and difference Δn to initial doping level n_0 for different Cu concentrations. The sign indicates the type of carrier.

	n_0=5.05x10^{17}cm^{-3}		n_0=1.26x10^{18}cm^{-3}	
C_{Cu} [cm^{-3}]	n(C_{Cu}) [cm^{-3}]	Δn [cm^{-3}]	n(C_{Cu}) [cm^{-3}]	Δn [cm^{-3}]
6.5x10^{17}	-1.54x10^{17}	3.51x10^{17}	-8.99x10^{17}	3.61x10^{17}
1.8x10^{18}	+2.88x10^{9}	> n_0	-3.26x10^{16}	1.22x10^{18}
7.2x10^{18}	+4.83x10^{9}	> n_0	+1.58x10^{10}	> n_0

However, Δn is found to be smaller than the concentration of Cu observed by PIXE. This also indicates that Cu introduces another, additional component. An analysis of the measured mobilities for the two n-type sets shows that in addition to terms propotional to $T^{-1.5}$ and $T^{+1.5}$ a term proportional to $T^{-0.5}$ is needed to fit the data. Figure 5 shows the measured data and the fits. McNichols and Berg have shown that the importance of a term $\propto T^{-0.5}$ for a mobility component introduced by metallic spikes with non-overlapping depletion zones increases with temperature [13]. Table 2 gives a summary of the parameters found to fit the mobilities. The exponentials needed for the fits were ascribed to a phonon, an impurity and a copper induced component.

Table 2. Preexponentials and exponentials found to fit the measured mobilities. Mobility components are given in units of cm^2/Vs.

	n_0=5.05x10^{17}cm^{-3}			n_0=1.26x10^{18}cm^{-3}		
C_{Cu}[cm^{-3}]	μ_{ph}	μ_i	μ_{Cu}	μ_{ph}	μ_i	μ_{Cu}
reference	5.5x10^{5}T$^{-1.5}$	-	-	5.6x10^{5}T$^{-1.5}$	6.3x10^{-2}T$^{1.5}$	-
6.5x10^{17}	10.7x10^{5}T$^{-1.5}$	-	2578T$^{-0.5}$	4.4x10^{5}T$^{-1.5}$	10.9x10^{-2}T$^{1.5}$	-
1.8x10^{18}	9.0x10^{5}T$^{-1.5}$	-	1027T$^{-0.5}$	6.6x10^{5}T$^{-1.5}$	1.4x10^{-2}T$^{1.5}$	-
7.2x10^{18}	5.0x10^{5}T$^{-1.5}$	-	853T$^{-0.5}$	4.5x10^{5}T$^{-1.5}$	1.4x10^{-2}T$^{1.5}$	77T$^{-0.5}$

DISCUSSION

Comparing the data from PIXE with Hall measurements it can be seen that only a part of the Cu is electrically active. This part probably forms an acceptor like level, compensating shallow donors.

The channeling results suggest that most or all of the inert Cu forms precipitates. This is supported by the high Cu concentration measured, as Cu would not be stable in a purely interstitial form. The mobility component that was found to be induced by copper has the same temperature dependence as it would be expected for metallic spikes and their depletion zones.

From these results we deduce that Cu forms acceptor like levels as well as precipitates in GaP. However, depletion zones do probably not overlap at least for high doping concentrations, i.e. small widths. An estimation of the range of such zones in three dimensions from calculating the potential around a spherical metallic precipitate supports this view. Using published values for the barrier height of Cu on GaP and a precipitate diameter ≤10nm, we find that

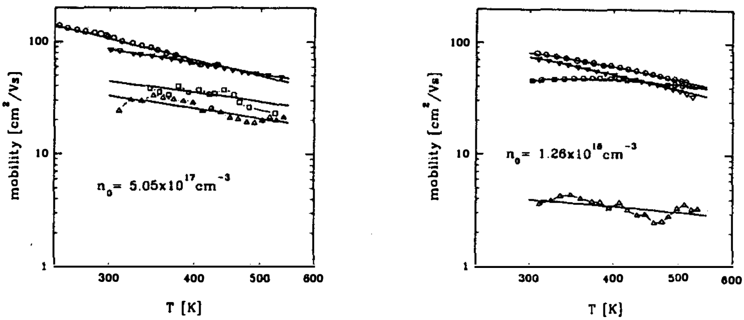

Figure 5. Mobility data for samples with $n_0=5.05\times10^{17}cm^{-3}$ and $n_0=1.26\times10^{18}cm^{-3}$. The solid lines show the fits. The curves were fit with the parameters given in table 2.
(o reference, $\nabla C_{Cu}=6.5\times10^{17}cm^{-3}$, $\Box C_{Cu}=1.8\times10^{18}cm^{-3}$, $\Delta C_{Cu}=7.2\times10^{18}cm^{-3}$)

for carrier concentrations larger than $5\times10^{17}cm^{-3}$ a Cu concentration of at least $5\times10^{19}cm^{-3}$ would be needed for overlapping depletion zones. This is certainly not fullfilled. For carrier concentrations of about $10^{16}cm^{-3}$, however, the required amount of Cu decreases to $5\times10^{16}cm^{-3}$. This opens the possibility that the buried Schottky contact model applies for lower doped sampled.

Further investigations will be necessary to confirm this thesis. TEM analysis should reassure the presence of precipitates. Further mathematical calculations will be made to calculate the temperature dependence of the mobility in case of overlapping depletion zones.

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