

**EL2-copper interaction in heat-treated GaAs**

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Heating semi-insulating GaAs in the presence of copper produces conversion to  $p$  type with the low-temperature Fermi level located on carbon at 26 meV above the valence band. As the  $EL2$  concentration is much larger than the shallow-donor concentration in these samples, this decompensation by Cu could not occur unless copper interacts with  $EL2$  to render the  $EL2$  electrically inactive. Copper complexing with  $EL2$  or copper replacement of the  $As_{Ga}$  component of  $EL2$  are possible mechanisms. The data are consistent, within the expected error, with complete passivation of all the  $EL2$ . It is proposed that the most likely mechanism is Cu complexing with  $EL2$  to form electrically inactive  $As_{Ga}-Cu_{Ga}$  next-nearest-neighbor double-donor-double-acceptor complexes.

Many semiconductor device production techniques include high-temperature processing of bulk substrate materials. Examples include molecular-beam epitaxy growth at elevated temperatures on GaAs substrates, and postimplant annealing of ion-implanted layers in bulk semi-insulating wafers. Anomalous behavior under high-temperature processing can produce unpredictable and undesired consequences for the resulting structures. The literature on high-temperature processing of GaAs includes many anomalous characteristics such as unexplained cyclical high and low conductivity states<sup>1</sup> and  $p$ -type conversion attributed to As out diffusion.<sup>2</sup> Compounding the uncertainty is the published work on copper in GaAs, which was described as "complex and confusing" in 1984,<sup>3</sup> and is not significantly clearer today. Copper is known to be a fast diffuser in GaAs and many other semiconductor materials. It is a pervasive contaminant which is present in all but the most carefully controlled experiments. A better understanding of the role played by copper in GaAs could substantially improve GaAs processing technology.

Copper is widely believed to complex with a number of impurities and defects in GaAs to produce a variety of electronic levels in the forbidden gap.<sup>4-9</sup> There is strong evidence that copper complexes exist and some of them, e.g., Cu-Te complexes,<sup>4</sup> are strongly supported by experiment. Other Cu complexes have been proposed with atomic structures only weakly supported by the experiment.

In this paper we present evidence that copper interacts

with  $EL2$ , preventing  $EL2$  from carrying out its usual role as the deep donor which compensates accidentally introduced acceptors to pin the Fermi level near midgap in semi-insulating GaAs. Copper, then, can be considered to be an impurity which decompensates acceptors in semi-insulating material. Copper complexing with  $EL2$  and copper replacement of the  $As_{Ga}$  component of  $EL2$  are two possible mechanisms; the first mechanism can have the symmetry of centers previously observed in Cu containing GaAs (Refs. 8 and 9) and is therefore preferred. We suggest that some previous studies of heat-treated GaAs should be reassessed to eliminate the possibility that the observed effects were caused by copper decompensation of acceptors.

The experiments reported here used GaAs wafers approximately 0.6 mm thick, from bulk crystals grown by the liquid encapsulated Czochralski (LEC) and vertical zone melt<sup>10,11</sup> (VZM) methods. Diffusions were performed as summarized in Table I. Two GaAs wafers, one LEC and the other VZM, were dipped in a  $CuSO_4-H_2O$  solution, dried and heated in a flowing helium atmosphere to approximately 750°C, one for 2 h and one for 4.5 h. Another VZM GaAs wafer was sputtered with Cu, then heated in an evacuated quartz ampule with elemental arsenic at 775°C for 4 h. One VZM GaAs control wafer was cleaned in bromine methanol, rinsed in methanol, and heated, without Cu, in the flowing-He atmosphere at 750°C for 4.5 h. In all cases the quartz tube containing the GaAs was removed from the furnace after diffusion and allowed to cool to room temperature in air. No rapid

TABLE I. Experiments performed.

Sample growth method	Cu deposition method	Temperature (°C)	Diffusion time (h)	Atmosphere
LEC	CuSO <sub>4</sub>	750	2	Flowing He
VZM	CuSO <sub>4</sub>	750	4.5	Flowing He
VZM	Sputtering	775	4	Sealed + As
VZM	No Cu	750	4.5	Flowing He

quenches were used. Some differences in copper behavior have been observed for diffusions at low ( $< 800^\circ\text{C}$ ) and high ( $> 800^\circ\text{C}$ ) temperature.<sup>4</sup> All experiments reported here were done in the lower-temperature range. After the diffusion all wafers were polished on all sides with a coarse polish to remove residual deposits and surface regions from which As may have out diffused.

All samples were measured in infrared transmission at 4.2 K in the spectral range from  $80\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  with a Bomem DA3.02 Fourier-transform infrared spectrometer. Thermal contact between the sample and the helium bath was provided by a low-pressure He gas. This thermal contacting method ensures good cooling without the stress usually produced by mechanical clamping or gluing.

Before Cu diffusion, electrical conductivity measurements indicated that all wafers were semi-insulating so had Fermi levels near midgap and near *EL2*. The neutral *EL2* concentration of the VZM samples was determined from near IR absorption.<sup>12</sup> The fraction of ionized *EL2* was determined from the free-electron concentration<sup>13</sup> at 300 K. Typical values for an as-grown VZM wafer are as follows: total *EL2* concentration in the mid- $10^{15}\text{ cm}^{-3}$  range, ionized (positive) *EL2* concentration in the mid- $10^{14}\text{ cm}^{-3}$  range. Infrared absorption measurements of the as-grown samples were consistent with the Hall effect and conductivity measurements since there was no significant free carrier absorption and no absorption due to electronic  $1s-2p$  transitions at uncompensated acceptors in the spectral regions in which these transitions are known to occur.

Samples heated in the presence of Cu were very different from the control sample. All Cu diffused samples became *p* type with the low-temperature Fermi level pinned on carbon acceptors at 26 meV. The presence, in the IR transmission spectrum of Fig. 1(b), of  $1s-2p$  transitions at neutral carbon with no lower-energy  $1s-2p$  transitions observable establishes that the Fermi level is on

carbon at low temperature. In addition, the well-known Cu level at 155 meV above the valence band was clearly observed above  $1150\text{ cm}^{-1}$ , producing absorptions due to  $1s-2p$  and  $1s$ -continuum transitions. Absorption lines in Fig. 1(b) are denoted by the conventional letter designations (*G*, *D*, *C*) of the strong, easily resolved resonant acceptor transitions.<sup>14</sup> If Cu entered GaAs only as an uncomplexed substitutional acceptor on the Ga site, then one would expect the Fermi level to become pinned at the 155 meV level, not at 26 meV.

Arsenic out diffusion has been proposed as a cause of *p*-type conversion in GaAs.<sup>2</sup> In that earlier study, the samples became *p* type with an activation energy near that of the 155-meV Cu level after heat treatment. The effect was attributed to As out diffusion rather than Cu in diffusion, since liquid-phase epitaxy (LPE) GaAs free of Cu contamination could be made with a similar technique. However, since gallium getters Cu,<sup>15</sup> and gallium was present during the LPE growth but not during the heat treatment, the possibility of Cu contamination during the heat treatment cannot be excluded. We believe that As out diffusion is not producing the *p*-type conversion we observe based on identical behavior after diffusing Cu in a flowing-He atmosphere and sealed with an As atmosphere. In addition, heating a control sample without Cu in a flowing-He atmosphere produced no observable change. It is possible that some As out diffusion occurred near the surface after heating in the flowing atmosphere. Changes near the surfaces would be removed by the polish after diffusion, and our observational method (IR transmission) averages the entire sample, and so limited surface As depletion would not be observed.

There are five types of Cu interaction which should be considered as possible origins of the observed behavior: (1) Cu interacts with something other than *EL2* to produce an acceptor shallower than carbon. (2) Cu interacts with (and removes from the compensation process) some donor other than *EL2*. (3) Cu complexes with *EL2* to produce an acceptor shallower than carbon. (4) Copper replaces  $\text{As}_{\text{Ga}}$ , forcing the As from its substitutional position rendering *EL2* inactive. (5) Cu complexes with *EL2* to remove it from the compensation process. Only the last two possibilities are consistent with expectations for this material. The first possibility would require the presence of some center at concentrations always less than but within  $1 \times 10^{15}\text{ cm}^{-3}$  of the *EL2* concentration in all GaAs samples. This requirement is necessary because no acceptor shallower than carbon has been seen in any Cu-doped samples. The second cannot be the case as there is enough *EL2* in all samples to compensate all the carbon several times over. The third would require that Cu complexing occurs only at two-thirds (assuming *EL2* is a double donor) of the *EL2*. The remaining one-third would compensate the complexed two-thirds. There is no basis for such a partitioning. The last possibility appears to be the most likely source of decompensation since  $\text{As}_{\text{Ga}}\text{-Cu}_{\text{Ga}}$  next-nearest-neighbor pairs have the  $C_s$  symmetry of Cu-related centers seen in optically detected magnetic resonance<sup>8</sup> and photoluminescence<sup>9</sup> studies of GaAs.

An independent determination of the concentration of carbon on the arsenic site was made by measuring the

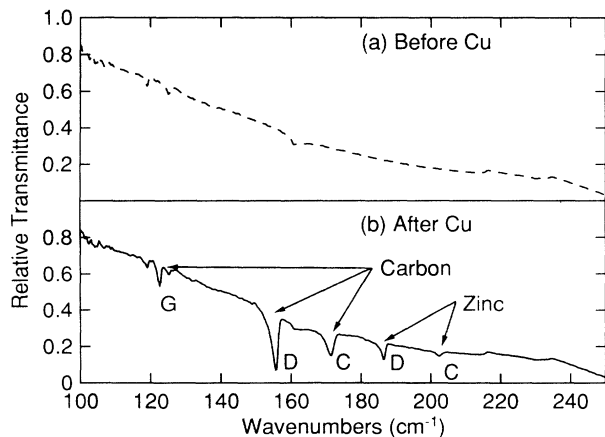


FIG. 1. Far-infrared transmittance of a VZM GaAs wafer (a) as grown and (b) after Cu diffusion. The resonant absorptions after Cu diffusion are due to electronic  $1s-2p$  transitions at neutral carbon and zinc shallow acceptors. Line positions observed here for carbon *G*, *D*, and *C* lines and for zinc *D* and *C* lines are, respectively, 122.5, 155.7, 171.4, 186.6, and  $202.5\text{ cm}^{-1}$ .

strength of its local vibrational mode absorption. This measurement, with the low-temperature calibration of Sargent and Blakemore,<sup>16</sup> gave a carbon concentration of  $9.3 \times 10^{14} \text{ cm}^{-3}$  in the as-grown material. From the strength of the  $1s$ - $2p$  transitions of carbon and the known carbon IR absorption cross section<sup>17,18</sup> we determine the concentration of neutral carbon after Cu diffusion to be  $1.2 \times 10^{14} \text{ cm}^{-3}$ . Therefore, no more than  $8.1 \times 10^{14} \text{ cm}^{-3}$  donors compensate carbon after the Cu diffusion. As carbon is the shallowest known acceptor in bulk GaAs it is reasonable to conclude that the total electrically active donor concentration in these Cu-doped samples is  $8.1 \times 10^{14} \text{ cm}^{-3}$ . All the remaining shallow donors and *EL2* have become inactive. The concentration of electrically active donors after Cu diffusion is, within the error in the measurement, equal to the initial shallow donor concentration. Thus it seems probable that all the *EL2* has become electrically inactive. As a check on any remaining presence of (ionized) *EL2* in Cu-diffused samples, near-IR absorption spectra were taken for them, at a temperature high enough to preclude any complications involving the "metastable" *EL2*\* state. These spectra showed only featureless free hole absorption, with no trace of the  $0.95 \pm 0.15 \text{ eV}$  photoneutralization band of *EL2*<sup>+</sup>.

Some uncertainty is expected in the accuracy of these numbers. The uncertainty in concentration is at least as large as the uncertainty in cross section for measured electronic  $1s$ - $2p$  transitions or LVM, of the order of  $\pm 50\%$ . A large contribution to this uncertainty is the accuracy of the primary standards used to establish concentrations in calibration samples. For instance, the Hall effect is one of the standards for determining IR cross sections. It is arguably the best standard, as it measures the concentration of defects of the desired type, not the total concentration including interstitials as is the case with secondary-ion-mass spectroscopy. A common uncertainty in Hall effect defect concentration measurements is the Hall factor which is typically taken to be in the range 1.0–1.4, although its true value may well be as large as 2 at some temperatures.<sup>19</sup> Since shallow acceptors such as C and Mg are measured in the Hall effect in temperature ranges

TABLE II. Concentrations of electrically active centers.

Center	As grown ( $\text{cm}^{-3}$ )	After Cu ( $\text{cm}^{-3}$ )
Shallow donors (all ionized)	$5.9 \times 10^{14}$	$5.9 \times 10^{14}$
Total <i>EL2</i>	$7.3 \times 10^{15}$	0?
Neutral <i>EL2</i>	$6.7 \times 10^{15}$	0
Total copper	0	$3.5 \times 10^{17}$
Neutral copper	0	$3.5 \times 10^{17}$
Total zinc	$2.6 \times 10^{14}$	$2.6 \times 10^{14}$
Neutral zinc	0	$2.6 \times 10^{14}$
Total carbon	$9.3 \times 10^{14}$	$9.3 \times 10^{14}$ ?
Neutral carbon	0	$1.2 \times 10^{14}$

in which ionized impurity scattering is significant, we have used a Hall factor of 1.5 for our calibration standards.<sup>18</sup>

The measurements reported here give, within the  $\pm 50\%$  uncertainty, an essentially complete tally of the electrically active impurities and defects in these samples. Results for a VZM wafer are given in Table II.

In summary, copper diffused into LEC or VZM GaAs moves the Fermi level to the level of carbon, the shallowest known acceptor in these materials. In order for Cu to effect this Fermi-level shift it must render inactive approximately 90% or more of the *EL2* in the as-grown wafer. We propose that Cu complexes with *EL2* to produce an electrically inactive complex center. Previous studies of heat-treated GaAs which show similar *p*-type behavior after heating should be reassessed to determine the role played by Cu in those studies.

These experiments do not uniquely determine the atomic structure of this *EL2*-Cu complex. One possible candidate is a  $\text{As}_{\text{Ga}}\text{-Cu}_{\text{Ga}}$  next-nearest-neighbor double-donor-double-acceptor complex. This complex would appear to have the correct electrical behavior and also has the  $C_s$  symmetry of the Cu-related centers seen in optically detected magnetic resonance<sup>8</sup> and photoluminescence.<sup>9</sup>

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<sup>1</sup>D. C. Look, W. M. Theis, P. W. Yu, J. R. Sizelove, W. Ford, and G. Mathur, *J. Electron. Mater.* **16**, 63 (1987).

<sup>2</sup>R. K. Boncek and D. L. Rode, *J. Appl. Phys.* **64**, 6315 (1988).

<sup>3</sup>J. S. Blakemore and S. Rahimi, *Semiconductors and Semimetals* (Academic, New York, 1984), Vol. 20, p. 233.

<sup>4</sup>C. S. Fuller, K. B. Wolfstirn, and H. W. Allison, *J. Appl. Phys.* **38**, 2873 (1967).

<sup>5</sup>F. Willmann, M. Blätte, H. J. Queisser, and J. Treusch, *Solid State Commun.* **9**, 2281 (1971).

<sup>6</sup>H. J. Guislain, L. DeWolf, and P. Clauws, *J. Electron. Mater.* **7**, 83 (1978).

<sup>7</sup>H. P. Gislason, A. G. Wang, and B. Monemar, *J. Appl. Phys.* **58**, 240 (1985).

<sup>8</sup>T. A. Kennedy and N. D. Wilsey, *Phys. Rev. B* **32**, 6942 (1985).

<sup>9</sup>B. Monemar, H. P. Gislason, W. M. Chen, and Z. G. Wang, *Phys. Rev. B* **33**, 4424 (1986).

<sup>10</sup>E. M. Swiggard, *J. Cryst. Growth* **94**, 556 (1989).

<sup>11</sup>R. L. Henry, P. E. R. Nordquist, R. J. Gorman, and S. B. Qadri, *J. Cryst. Growth* **109**, 28 (1991).

<sup>12</sup>G. M. Martin, *Appl. Phys. Lett.* **39**, 747 (1981).

<sup>13</sup>J. S. Blakemore, *J. Phys. Chem. Solids* **49**, 627 (1988).

<sup>14</sup>A. K. Ramdas and S. Rodriguez, *Rep. Prog. Phys.* **44**, 1297 (1981).

<sup>15</sup>C. S. Fuller, K. B. Wolfstirn, and H. W. Allison, *J. Appl. Phys.* **38**, 4339 (1967).

<sup>16</sup>L. Sargent and J. S. Blakemore, *Appl. Phys. Lett.* **54**, 1013 (1989).

<sup>17</sup>W. J. Moore, R. L. Hawkins, and B. V. Shanabrook, *Physica B* **146**, 65 (1987).

<sup>18</sup>W. J. Moore (unpublished).

<sup>19</sup>N. Apsley, D. A. Anderson, and J. B. Morrison, *Semicond. Sci. Technol.* **2**, 44 (1987).