ELECTRONIC PROPERTIES OF SEMI-INSULATING GaP:Cu

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Theoretical calculations which model the influence of Cu precipitates on the behavior of free carriers in Cu diffused GaP are compared with experimental results obtained in earlier studies. We come to the conclusion that the large reduction of carriers seen in n-type GaP is mostly governed by a compensation mechanism. At high temperatures the mobility, however, is mainly reduced by scattering of free carriers from space charge regions surrounding metallic precipitates and is found to be dominated by a term $\propto T^{1/2}$.

Introduction

Semi-insulating (SI) III-V materials have gained increased interest over the last few years[1]. Besides the well known explanation of the SI behavior of these materials by a compensation mechanism a 'buried Schottky contact' model was proposed which explained SI properties of LT GaAs:As[2] (Low Temperature GaAs, MBE grown at 200°C) and InP:Cu[3,4,5] by overlapping space charge regions resulting from precipitate-matrix transitions, which deplete the material of free carriers. This model might be of significant influence for GaP:Cu, too. Copper, which is a common impurity in GaP, has been investigated for several decades[7-17]. Clear results, however, are scarce, as no definite defect level energy could be detected, but a whole set of acceptor levels, ranging from E_V+0.55eV to E_V+0.82eV were measured with different experimental techniques. Especially the question, whether Cu introduces simply a substitutional acceptor level could not be answered until today.

Only recently a discussion has emerged if the density of deep defect levels in GaAs:As might be high enough to accomplish a similar SI behavior[6]. New experimental results for Cu diffused, initially n-type LEC GaP obtained by our group including investigation of concentration limits, lattice site determination and high temperature Hall measurements (300K-550K) indicated that the concentration of Cu in GaP can be high enough to introduce both a high level of substitutional acceptors as well as metallic precipitates[18].

The task of this work was to investigate the electronic properties of GaP:Cu more precisely. Theoretical calculations on the influence of metallic precipitates on free carrier mobility were compared with experimental results. From these data it was tried to decide whether the transport properties of GaP:Cu are dominated by deep defects which pin the Fermi level or by the existence of space charge regions around metallic precipitates.

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Mobility Component μ_s

The calculation of the mobility component induced by metallic precipitates was treated by several authors[19,20]. Here, we follow the ideas of McNichols and Berg[19]. This approach is sufficiently sensitive to differences of the thermal energy of free carriers which is of particular importance for comparison with Hall data extracted over a wide temperature range. In addition to the former calculations, we too included the possibility of Fermi level pinning thus being able to model the effect of deep defects with rather large concentrations.

To compute the precipitate induced mobility component we considered scattering of free carriers from non-overlapping, isolated spherical depletion regions. Due to the dominance of the space charge region for the potential geometry, the assumption of spherical depletion zones remains valid even if the precipitate itself has a differnt structure[20].

Solving Poisson's equation, one finds for the three dimensional potential near a metallic cluster

$$\phi(r)=\frac{qN_dR^3}{3\varepsilon_s r}\left(\frac{3}{2}\frac{r}{R}-\frac{1}{2}\frac{r^3}{R^3}-1\right) \tag{1}$$

where q is the electron charge, N_d the doping concentration, ε_s the semiconductor dielectric constant and R the radius of the depletion zone given by

$$R=\frac{a}{2}+\frac{a}{4\eta}+\eta \tag{2}$$

$$\text{with}\quad \eta=\frac{a}{2}\sqrt[3]{2\alpha\left(1+\sqrt{1-\alpha^{-1}}\right)-1} \tag{2a}$$

$$\text{and}\quad \alpha=\frac{6\varepsilon_s\phi_{bi}}{qN_da^2} \tag{2b}$$

if a is the radius of the precipitate and ϕ_{bi} the built-in potential.

Given Eq. (1), an effective scattering radius r_{eff}, which takes into account the temperature dependent penetration of free carriers into the space charge region, can be modeled by that radius, where the potential equals $k_BT/2$, k_B being Boltzman's constant. Using this and a classical approach for the calculation of the mean collision time, which yields $\mu=(2k_BTm^*)^{-1/2}q/(N_s\pi r r_{eff}^2)$, the mobility component μ_s induced by non-overlapping, isolated depletion zones can be computed to

$$\mu_s=\frac{q}{4\pi\left(2m^*k_B\right)^{1/2}N_s\gamma R^2T^{1/2}}\cos^{-2}\left[\frac{\pi}{3}+\frac{1}{3}\arccos\left(\gamma^{-3/2}\right)\right] \tag{3}$$

$$\text{with}\quad \gamma=1+\left(L_D/R\right)^2 \tag{3a}$$

where m^* is the effective mass, N_s the density of the scatterers and L_D the Debye-Hückel length.

Temperature Dependence

Fig. 1 shows the calculated mobility μ_s for four different doping concentrations N_d and a Cu concentration of $C_{Cu}=10^{18}cm^{-3}$. The parameters used in the computation were chosen to be typical for n-type GaP. A barrier height of 1.6eV[21] was used for the calculation of the built in potential. A possible Fermi level pinning and thus a constant depletion zone radius is included, too. The radius of the precipitates was assumed to be 3nm which is a typical size found in InP:Cu as well as in GaAs:As.

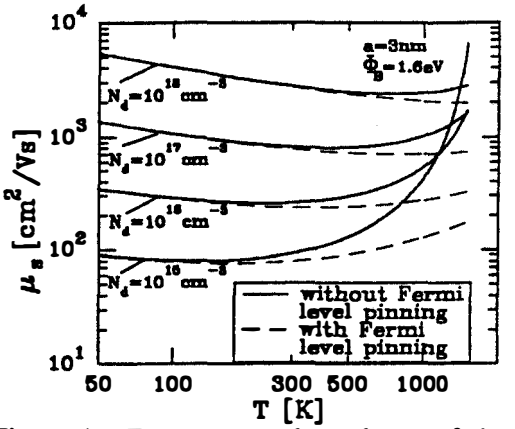

Figure 1. Temperature dependence of the mobility component μ_s induced by metallic precipitates and their associated space charge regions.

The temperature dependence of μ_s is governed by three factors: A decreasing depletion zone radius R as well as a higher thermal energy of the free carriers at high temperatures tend to enhance μ_s with temperature. On the other hand, the collision time is decreased, favouring a reduction of mobility $\propto T^{-1/2}$. It can be seen that the latter term is of significant influence up to very high temperatures, being even more important, if the Fermi level is pinned. Only at very high temperatures, the influence of the effective radius starts to dominate, increasing μ_s again. As a minimum of mobility is reached in the range between 300K and 600K, one should expect that if such a component were present, it would be relevant in this temperature regime.

Experimental Results

From our earlier studies we obtained that Cu can reach concentrations as high as $1x10^{-19}cm^{-3}$ in GaP, with a considerable amount located at metallic clusters randomly distributed in the semiconductor matrix[18]. On the other hand, investigating carrier concentration and Fermi level position indicates that Cu forms deep defects, too, with concentrations high enough to account for a conversion from n- to p-type material even for initial shallow donor concentrations of up to $1.3x10^{18}cm^{-3}$. The Fermi level is effectively pinned at E_V+0.55eV.

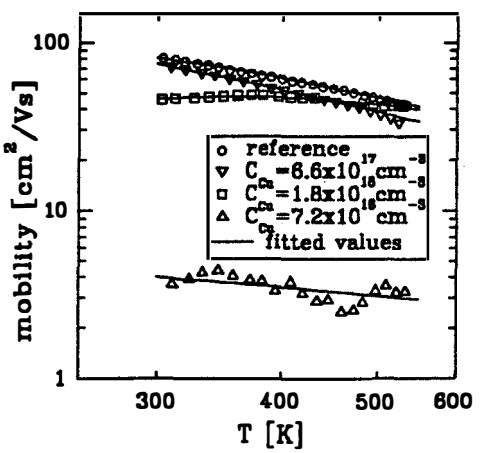

Figure 2. Experimental mobility data and fitted values for one set of samples with the same initial doping concentration, but different Cu concentration.

By fitting the experimental Hall data with an ansatz $\mu^{-l} = \Sigma\mu_i^{-1}$ where μ_i^{-1} is given by $m_i^{-l} \cdot T^{-ni}$ the mobility especially for SI samples was found to be dominated by a term $\propto T^{-1/2}$. Figure 2 shows the results for one set of samples. For a more detailed discussion of the experimental data please refer to Ref. 18.

Discussion

The temperature dependence of the Cu induced mobility component reveals that scattering from depletion zones is of considerable relevance for GaP:Cu as a term $\propto T^{-1/2}$ influences the behavior of μ very strongly. Such a view is confirmed by a closer investigation of the experimental results. Samples with the same concentration of Cu, but smaller initial doping concentration, thus yielding a higher net acceptor concentration, show a larger mobility component μ_s, as expected from theoretical results. On the other hand, samples with the same initial doping concentration, but a larger amount of Cu have a decreased mobility μ_s. However, a quantitative analysis of the experimental data with the mobility given in Eq. (3) is not very useful, as there are too many dependent parameters such as precipitate size, density and Cu concentration involved in forming the metallic clusters. Another uncertainty arises from the effective barrier height for the metal-semiconductor transition, which can be inherently different from the values found for planar, 2-dimensional metal-semiconductor contacts[3].

Summary

It was shown that the behavior of the mobility in SI GaP:Cu can be described by scattering of free carriers from non-overlapping, isolated space charge regions. This confirms the picture that Cu forms metallic precipitates as well as electrically active acceptor levels. The precipitates dominate the mobility but have a rather small influence on the carrier concentration, which is mainly governed by the deep acceptors through a compensation mechanism. The theoretical model presented in this paper should be of considerable interest for materials where the involved parameters are well determined.

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