

**Characterization of nanometer As-clusters in low-temperature grown GaAs by transient reflectivity measurements**

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We report a systematic experimental study of the transient reflectivity of low-temperature grown GaAs as a function of excitation wavelength, excitation density and lattice temperature. We observe that the reflectivity decay is temperature independent for excitation energies between 20 and 70 meV above the band gap of GaAs. Under this condition the reflectivity increases linearly with excitation density and is in very good quantitative agreement with the Drude model. Subsequently, we present a model which allows the extraction of the diameter and density of As-clusters in low-temperature grown GaAs from the reflectivity decay.

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## **I. INTRODUCTION**

Low-temperature grown gallium arsenide<sup>1</sup> (LT-GaAs) is an important material for the fabrication of photoconductive THz-sources<sup>2,3</sup>, ultrafast detectors or ultrafast saturable absorber mirrors<sup>4</sup>. Its unique electrical properties are subpicosecond carrier lifetimes, good carrier mobility and high dark resistivity.

GaAs grown by molecular beam epitaxy (MBE) at low temperatures ( $< 300$  °C) incorporates 1 – 2 % arsenic excess which depends on the growth temperature  $T_g$  and on the arsenic pressure during the deposition<sup>5,6</sup>. As a result a high density of antisite defects  $As_{Ga}$  as well as Ga vacancies is produced. The arsenic antisite defects  $As_{Ga}$  form a donor miniband close to the centre of the band gap<sup>1,7</sup>. The concentration of  $As_{Ga}$  increases with decreasing  $T_g$  and can reach  $10^{19} - 10^{20}$  cm<sup>-3</sup>. The subpicosecond carrier trapping is attributed to ultrafast trapping by  $As_{Ga}^+$  donors. For device applications the as-grown samples are usually thermally annealed. The excess arsenic precipitates into metallic clusters surrounded by depleted regions of As/GaAs. In annealed samples the As-cluster replace the point defects as ultrafast trapping centres. Furthermore, annealing recovers the mobility of the material and results in the desired high resistivity<sup>8</sup>.

Particular with respect to device application a complete characterisation of the electrical properties and a comprehensive understanding of As-cluster properties is important. Devices fabricated from LT-GaAs rely on ultrafast transient currents. The generation and decay of these currents depend on the interplay of carrier mobility and carrier lifetime<sup>9-11</sup>. While the temperature dependence of the mobility and conductivity of LT-GaAs has been studied extensively<sup>12,13</sup>, little consideration has been given to the temperature dependence of the carrier lifetime, particular of annealed LT-GaAs<sup>14</sup>. Commonly carrier lifetimes are determined by femtosecond optical pump-probe reflectivity or transmittivity measurements<sup>1</sup>.

However, in the past it has been observed that the determination of the carrier lifetimes from the pump-probe signal is difficult because the signal depends significantly on the excitation density and on the pump-probe wavelength<sup>16-18</sup>.

In this article we report the results of a systematic investigation of the femtosecond reflectivity decay in annealed low-temperature grown gallium arsenide (LT-GaAs) at excitation wavelengths between 780 and 820 nm, excitation densities of  $10^{16} - 10^{17} \text{ cm}^{-3}$  and sample temperatures between 30 and 300 K. We demonstrate that the experimental conditions can be tuned such that the reflectivity decay is dominated by free carrier trapping. We develop a model which calculates the As-cluster radius and density from measured decay time constants.

## **II. EXPERIMENT**

The samples investigated in this study were grown by molecular beam epitaxy on a semi-insulating GaAs substrate: first, a 72.5 nm GaAs buffer layer was deposited at 600 °C, subsequently, a 1.3  $\mu\text{m}$  layer was grown at a temperature  $T_g$ . Three samples were prepared with  $T_g = 200, 225$  and 250 °C. The samples were then annealed in the MBE chamber during 10 min at 600 °C.

We have investigated the transient reflectivity change of our samples with femtosecond optical pump-probe reflectivity measurements<sup>19</sup>. Figure 1 shows a schematic of our experimental arrangements. A Ti:sapphire laser generates 80 fs pulses with wavelengths  $\lambda_c$  tunable between 780 nm and 820 nm. The laser power  $P$  is 500 mW and the pulse repetition rate  $f_r$  is 82 MHz. The pulse train is split in pump and probe beams with a ratio of 10 : 1. The pump pulses are delayed with respect to the probe beam by a motorized translation stage and are modulated by an optical chopper at 3.5 kHz. The two laser beams are focused on

the sample with a lens of focal length of 250 mm. The reflected probe beam is detected by a photo diode and a lock-in-amplifier (LIA). Reference frequency for the LIA is the chopper frequency so that only the pump-induced reflectivity change is detected. The sample is mounted in a He-flow cryostat which allows continuous change of the sample temperature. With this setup a sensitivity of  $\Delta R / R = 10^{-6}$  is obtained.

### **III. RESULTS AND DISCUSSIONS**

#### **A. Excitation wavelength**

Firstly, we discuss the influence of the excitation wavelength on the reflectivity transient. The excitation wavelength determines the excess energy of the photoexcited carriers. The excess energy is the difference between the photon energy and the band gap of the GaAs. The results of the measurements are displayed in fig. 2. The sample temperature has been set to 30 K and the excitation density to  $N_e = 1.3 \times 10^{17} \text{ cm}^{-3}$ . We observe that the reflectivity transients exhibit a complex temporal shape under the condition that the excitation wavelength is resonant with the band gap of GaAs,  $E_g = 1.519 \text{ eV}$  ( $\equiv 816 \text{ nm}$ ) at  $T = 30 \text{ K}$ . In addition, this shape is very sensitive to small variations of the experimental parameters. Since the spectral width (full width half maximum) of the 80 fs laser pulses is  $\Delta E = 16.3 \text{ meV}$  ( $\Delta\lambda = 6 \text{ nm}$ ) the laser spectrum overlaps with the bottom of the conduction band of GaAs. The complex and sensitive shape of the reflectivity transients for excitation wavelength close to the band gap is therefore primarily attributed to the influence of excitons. The binding energy of an exciton in GaAs is  $5 \text{ meV}$ <sup>20</sup> ( $\equiv 58 \text{ K}$ ). The band edge in LT-GaAs is significantly smeared out. Sub-band gap states up to 40 meV below the unperturbed band

edge have been observed <sup>21</sup>. These sub-band gap states exhibit no sharp excitonic features. This has been attributed to a large inhomogeneous distribution of excitonic transitions.

At excitation wavelengths significantly above the band edge however, the reflectivity transients are easily reproduced. At excitation wavelengths  $\lambda_c = 780 - 805$  nm which correspond to excess energies between 20 meV to 70 meV, we do not observe a dependence of the reflectivity transient on excitation wavelengths. Under this experimental condition, the maximum of the relative transient reflectivity also linearly increases with pump laser power P (fig.3).

### **B. Drude Model**

We assume that the reflectivity change is caused by free carriers. In order to prove this assumption we have calculated the relative transient reflectivity(  $\Delta R / R$  ) as a function of pump laser power P with the Drude model. In equation (1) n is the refractive index and d the absorption length of GaAs at  $\lambda \approx 800$ nm <sup>22</sup>,  $\epsilon = n^2 \epsilon_0$  the dielectric constant, and  $m_r^*$  the conduction band effective mass <sup>20</sup>, by r we denote the radius of the laser focal spot on the sample surface.

$$\frac{\Delta R}{R} = \frac{n}{n^2 - 1} \cdot \frac{P \epsilon^2}{e m_r^*} \cdot \frac{P I_c^3}{2 \hbar P^4 c^3 f_r r^2 d} \quad (1)$$

Our calculations are in very good quantitative agreement with the experiment. The small differences between the measurements are attributed to slight variations of the beam diameter  $2 r$  and indicated by the shaded cone. From this analysis we conclude that for excitation energies between 20 meV and 70 meV the change of reflectivity is dominated by free carriers.

### **C. Temperature dependence**

Next, we consider the transient reflectivity of the LT-GaAs for various lattice temperatures (fig. 4). We observe that the transient reflectivity consists of a temperature dependent and a temperature independent part.

$$\Delta R(t, T) = R_0(T) + R(t) \quad (2)$$

We start with the discussion of the temperature dependent contribution  $R_0(T)$ . This signal strongly decreases at lower temperatures. The background  $R_0(T)$  is present before and after zero time delay and is therefore a cumulative effect of subsequent laser pulses. Due to the lock-in technique this signal can only be caused by the laser pump beam. Scattering of pump laser light into direction of the probe beam is excluded because it is expected to be temperature independent. The temperature dependent but time independent background  $R_0(T)$  is attributed to a thermomodulation of the refractive index of the LT-GaAs due to local heating by the pump laser beam. From the temperature dependence of the refractive index  $n$ , we can estimate the local temperature change to be approximately 10 K and the thermalization time of the local heating process to be about 600 ns. The thermomodulation is proportional to the change of the refractive index with temperature  $\sim (dn / dT)$ . The background  $R_0(T)$  is smaller at lower temperatures because the temperature dependence of the refractive index is weaker at low temperatures than at room temperature<sup>23</sup>. The long thermalization times are in agreement with the observation that the background  $R_0(T)$  is a cumulative effect of the incident laser pump pulses.

Following, we focus on the discussion of the reflectivity decay  $R(t)$ . Our measurements reveal that the decay of the reflectivity  $R(t)$  is independent of temperature between 30 K and 300 K. We observe that the reflectivity transients decay exponentially. By

fitting according to eq. (3) we find decay times of  $\tau = 250, 500$  and  $950$  fs for growth temperatures of  $200, 225$  and  $250$  °C.

$$R(t) \propto \exp\left(-\frac{t}{\tau}\right) \quad (3)$$

Since the reflectivity linearly increases with laser pump power  $P$  and subsequently with the number of generated photocarriers, the decay time is considered as the lifetime of free carriers.

#### **D. Characterization of As-cluster size and density**

As outlined in the beginning, due to the low growth temperature of LT-GaAs an excess of As is incorporated in the lattice that causes a high point defect density ( $N_D > 10^{19}$  cm<sup>-3</sup>). During the subsequent annealing process, As microclusters are formed within the LT-GaAs layer which are responsible for the ultrafast carrier trapping. The engineering of the As precipitates for device applications has received considerable attention recently. It has been demonstrated that the diameter of the As-cluster can be controlled between  $1 - 10$  nm through the annealing temperature<sup>24</sup>. The in-plane as well as lateral distribution of the As-cluster can be controlled through incorporation of compositional or doping variations as well as an external strain field<sup>25</sup>. By this patterned self-assembled arrays of metallic nanoparticles with regular spacing of a few  $10$  nm have been demonstrated<sup>26</sup>.

We now demonstrate that the density  $N_{CL}$  and diameter  $2r_{CL}$  of the As cluster can be extracted from the measured decay times using a simple model. For the calculation the following six assumptions are made: (i) The in situ annealing process does not change the amount of intrinsic arsenic. (ii) The point defect diameter is given by the GaAs lattice constant. (iii) The arsenic point defects migrate to form As microclusters which are spherical. (iv) These clusters dominate the trapping processes. (v) The product of defect density and

defect volume is constant during the change from point defects to microclusters. (vi) The capture cross section of the clusters is given by their geometrical cross section.

$$N_{T_g} \cdot V_D = N_{CL} \cdot V_{CL} = N_{CL} \frac{4}{3} \boldsymbol{p} \cdot r_{CL}^3 \quad (4)$$

The cluster density  $N_{CL}$  is related to the photocarrier lifetime by Shockley-Read-Hall theory:

$$\boldsymbol{t}_c = \frac{1}{N_{cl} \boldsymbol{S}_{cl} v_{th}} \quad (5)$$

with a thermal velocity of  $v_{th} = 2.5 \cdot 10^5$  m / s for GaAs. The amount of excess arsenic  $N_{T_g}$  incorporated during growth is described by an exponential function [1]:

$$N_{T_g} = N_{T_{g0}} \exp \frac{-T_g}{T_{g0}} (3) \quad (6)$$

The empirical parameters are  $N_{T_{g0}} = 5.2 \cdot 10^{22}$  cm<sup>-3</sup> and  $T_{g0} = 30$  °C. Under these assumptions, we obtain as our results:

$$r_{CL} = \frac{3N_{T_g} V_D}{4} \quad (7)$$

$$N_{CL} = \frac{3N_{T_g} V_D}{4\boldsymbol{p}_{CL}^3} \quad (8)$$

The values of  $r_{CL}$  and  $N_{CL}$  calculated from the measured lifetime  $\tau$  and growth temperature  $T_g$  are listed in table 1. They are compared to measurements of the cluster radius and cluster density by transmission electron microscopy<sup>23, 27, 28</sup> (TEM) and theoretical calculations of the cluster size based on an analysis of the temperature dependence of the kinetics of As-cluster formation<sup>29</sup>. The cluster radii and cluster density obtained with our model exhibit very good agreement with TEM measurements. Thus, we have demonstrated that it is possible to characterize the size and distribution of As nanoparticles in LT-GaAs by the analysis of the transient reflectivity.

#### **IV. CONCLUSIONS**

In summary, we have experimentally investigated the reflectivity of annealed LT-GaAs grown at temperatures between 200 and 250°C. We observe that the change in reflectivity upon femtosecond optical excitation is dominated by the free carrier response for excitation energies 20 to 70 meV above the band edge of GaAs. The transient reflectivity is temperature independent under this condition. In addition, we observe a background reflectivity which linearly decreases if the sample temperature is lowered from room temperature to 30 K. The background reflectivity is attributed to thermomodulation of the refractive index of the LT-GaAs due to local heating by the pump laser beam. Since the transient reflectivity is dominated by the free carrier response it is possible to extract the size and distribution of the As-clusters from the measured reflectivity transients by a simple model.

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$T_G$ (°C)	radius $r_{CL}$ (nm)	density $N_{CL}$ ( $10^{18}\text{cm}^{-3}$ )
200	1.75	1.54
225	1.44	1.15
250	1.15	1.03
TEM data		
200 (ref. 24)	2.17	
200 (ref. 28)	1.85	$0.1\pm 0.02$
250 (ref. 27)	1-5	0.1-1

Table 1

Figure captions

Fig.1 Schematic of the experimental arrangements.

Fig. 2 Reflectivity change of the LT-GaAs sample grown at 200 °C measured at 30 K for two different excitation wavelengths. The excitation density has been  $N_e = 1.3 \times 10^{17} \text{ cm}^{-3}$ . Measurements no. 3 and no. 4 (lines) have been performed 4 months after measurements no. 1 and no. 2 (symbols). At 30K the band gap of GaAs is  $E_g = 1.519 \text{ eV}$  ( $\lambda_g \equiv 816 \text{ nm}$ ). If the photon energy of the exciting laser pulse is resonant with the band edge of GaAs the reflectivity change is highly nonlinear and difficult to reproduce. If the electrons are excited above the band edge ( $\lambda_c = 800 \text{ nm}$ ,  $\Delta E = hc / (\lambda_c - \lambda_g) = 31 \text{ meV}$ ) the measurements are reproduced with high accuracy.

Fig. 3 Maximum of the relative transient reflectivity as a function of incident pump laser power for LT-GaAs samples grown at 200, 225, 250 °C. The excitation density is calculated from the laser power under the assumption that each photon absorbed excites one electron – hole pair in the LT-GaAs. For all three samples the maximum of relative transient reflectivity linearly increases with laser power. The shaded cone indicates the transient reflectivity calculated according to the Drude model. The size of the cone is determined by the error of the calculation which is dominated by the 10 % error in the determination of the radius of the laser focal spot on the sample surface.

Fig. 4 Transient reflectivity measured for various temperatures. The reflectivity is displayed in percentage of the 10 mV sensitivity range of the LIA. The temporal shape of the

reflectivity transient is independent of temperature. The background  $R_0$  linearly increases with temperature (inset).

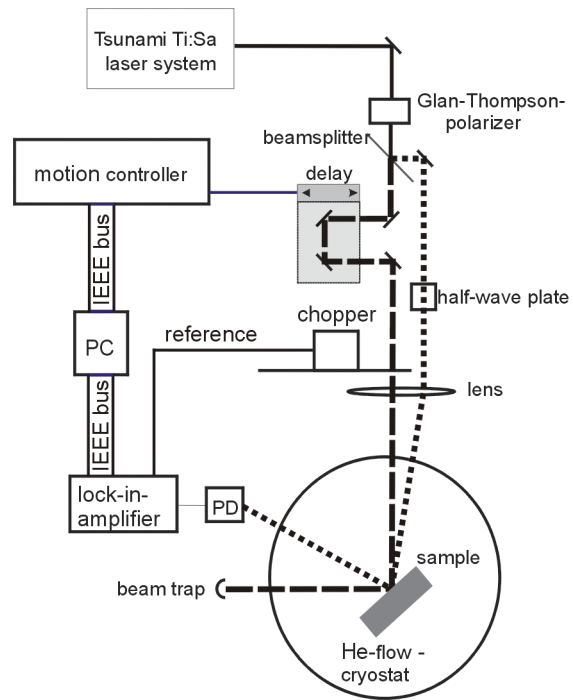


Fig. 1 T. Korn et al. Characterization of nanometer As-clusters in low-temperature grown GaAs by transient reflectivity measurements

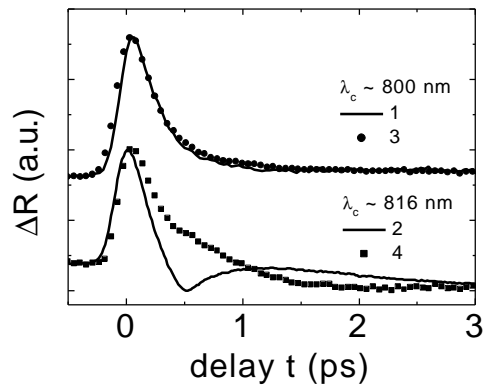


Fig. 2 T. Korn et al. Characterization of nanometer As-clusters in low-temperature grown GaAs by transient reflectivity measurements

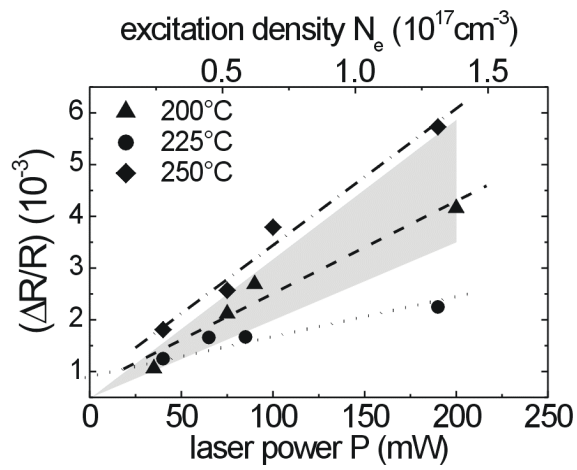


Fig. 3 T.Korn et al. Characterization of nanometer As-clusters in low-temperature grown GaAs by transient reflectivity measurements

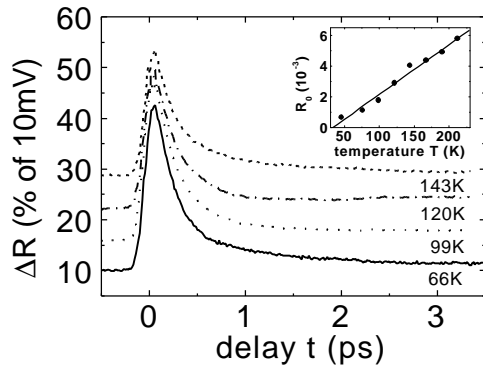


Fig. 4 T. Korn et al. Characterization of nanometer As-clusters in low-temperature grown GaAs by transient reflectivity measurements