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Ultrasound regeneration of EL2 centres in GaAs

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Abstract. The new effect of ultrasound-stimulated regeneration of the ground state of EL2 centres is observed and investigated. A regeneration transition, metastable (EL2*)-to-ground (EL2^0), is caused by ultrasound vibrations induced in a GaAs wafer at a temperature 105–120 K after bleaching of EL2 centres with 1.2 eV light. The EL2-related absorption band and the luminescence band with a maximum of 0.64 eV are examined. The kinetics of the ultrasound EL2 regeneration and the dependence of the number of regenerated EL2 centres on ultrasound strain are measured at different temperatures. Relevant mechanisms for the regeneration are discussed, and the arguments in favour of the dislocation model are presented.

1. Introduction

The properties of EL2 centres in semi-insulating GaAs are still the subject of current physical and technological interest. EL2 centres are recognized by the effect of the low-temperature metastability, which is attributed to their transition from the ground state, EL2^0, to the metastable state, EL2*, under the illumination of a sample with monochromatic light within the spectral range of 1.0–1.4 eV ($T < 140$ K). This EL2^0 to EL2* transition is accompanied by a large lattice relaxation and leads to the photoquenching of the capacitance signal as well as a quenching of intensity for EL2-related bands in spectra of the optical absorption, photoluminescence (PL), ESR and DLTS [1]. The regeneration of the ground state, i.e. the metastable to stable transition (EL2* to EL2^0) can occur in three different ways:

(i) thermally, due to the heating up of a sample in the dark above 130 K, which is specified by an activation energy $e_{th} = 0.34$ eV [2];

(ii) using free electron injection, which provides an enhanced rate of regeneration and relevant reduction for the activation energy down to 0.107 eV [3];

(iii) by illuminating a crystal with monochromatic light in the range 1.30–1.50 eV [4] or 0.80–1.0 eV [5, 6].

The optical regeneration process can be also thermally activated. The activation energy depends upon the regeneration wavelength varying in the range 0.035–0.10 eV [7].

In this paper the effect of the ultrasound (US) stimulated regeneration of EL2 photoluminescence is observed for the first time†. A new mechanism for the reduction of a thermal regeneration barrier caused by the interaction of EL2 centres with dislocations is proposed. It consistently accounts for the experimental data.

2. Experimental details

A Czochralski-grown undoped semi-insulating GaAs wafer ($\rho = 10^8$ Ω cm (100) orientation) with a dislocation density of the order of 10^5 cm^{-2} was studied. Meanwhile, the In-doped GaAs wafer with a suppressed density of dislocations down to 10^2 cm^{-2} was also investigated. The concentration of the EL2 centres according to both the capacitance measurements and the intensity of the EL2-related optical absorption band with the threshold at 0.8 eV is found to be of the order of 10^{16} cm^{-3}. The samples had a parallelepiped shape of $1 \times 2 \times 10$ mm^3 and were tightly bound by the (100) plane to the surface of a circular piezoceramic transducer using acoustic glue (epoxy compound). It is worth mentioning that the acoustic strain and stress generated by a transducer in a crystal are critically dependent on the quality of the acoustic contact between the two constituents of such a vibrating system. The US vibrations of a crystal were generated by the US transducer at its resonance frequency in the range $f = 80$–250 kHz. These vibrations are specified by the amplitude of the acoustic strain generated by a transducer, U_{us}, the temperature, T_{us}, and the duration time, t_{us}, of the US treatment of a sample. The usual set-up was utilized for the absorption and the PL measurements [5].

† The results were presented at ICDS'17 (Austria, 1993).

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3. Results

The well documented PL band with a maximum at 0.64 eV caused by the free-to-bound recombination between a conduction band and the $EL2^0$ state [8], is observed. The intensity I of this band is quenched from the initial value, I_0, to a stationary level, I_{st}, under crystal illumination in the 1.0–1.4 eV spectral range (figure 1, curve A). The bleached PL intensity, $I_0 - I_{st}$, is proportional to the number of EL2 centres in the ground state [5]. It is worth mentioning here that the EL2-related 0.64 eV PL band usually strongly overlaps with the oxygen-related luminescence [9], and, as a result, its connection with the EL2 centre may be ambiguous. In fact, the intensity of the PL transition even unrelated to the EL2 centre can be quenched due to the shift of the Fermi level governed by the bleaching of the EL2 centre. However, even in this case the intensity of such a PL band can be used as a quantitative test for the ground/metastable transformation of the EL2 centre. Independent verification of the ground/metastable state of the EL2 centre is provided by the optical absorption measurements. The relevant absorption band with the threshold at 0.8 eV attributed to the $EL2^0$ to conduction band electron transition can be examined.

The heating of a sample in the dark to more than 130 K and the subsequent holding at this temperature for longer than 60 s leads to the complete regeneration of the initial intensity for the 0.64 eV PL band. This is a consequence of the $EL2^*$ to $EL2^0$ transition. This observation is consistent with the recovery of the EL2 absorption band possessing a threshold at 0.8 eV (inset in figure 1, curve 2). The rate of thermal regeneration decreases exponentially when the recovery temperature is lowered. The relevant activation energy is estimated as 0.3 eV, which is consistent with known data [2]. As a consequence, thermal regeneration of the $EL2^0$ state is negligible at $T < 120$ K. This is shown in figure 1 (curve B) as the PL kinetics measured after the bleaching of the EL2 centre with 1.2 eV light (curve A) and following holding a sample in the dark for as long as 70 s at 105 K.

It was found by measuring the intensity of the EL2 absorption band that a regeneration transition can be stimulated at temperatures $T_{us} = 105$–120 K, if after the EL2 bleaching the thermal regeneration is accompanied by the US vibrations. This is shown in figure 1 (inset) as two temperature scans with ultrasound (1) and without ultrasound (2). This observation is approved by the US regeneration of the 0.64 eV PL band shown in figure 1 (curve C). We point out that the US vibrations are applied between B and C kinetics at the same temperature and the same time interval as for a sample held between A and B kinetics.

We define as the regeneration ratio, $\delta I = N_{us}/N_0$, the number of EL2 centres returned to the ground state after the US vibrations (N_{us}) with respect to the total number of EL centres undergoing the metastable to stable transition (N_0). The regeneration ratio can be measured using the intensity of the 0.64 eV PL band as follows

$$\delta I = \frac{I(t_{us}) - I_{st}}{I_0 - I_{st}} \tag{1}$$

where $I(t_{us})$ is the maximum PL intensity after US regeneration for a time of t_{us}; I_0 and I_{st} are defined above and shown in figure 1. The value of δI is measured as a function of US parameters t_{us}, T_{us} and U_{us}, which provide the relevant kinetic, temperature and amplitude dependences respectively for the US-enhanced regeneration.

The kinetics of isothermal US regeneration, i.e. the dependence of δI on t_{us}, at two different temperatures are shown in figure 2. The curves can be fitted well by the following relations:

$$\delta I = 1 - \exp[(t_{us} - t_0)/\tau_{us}]. \tag{2}$$

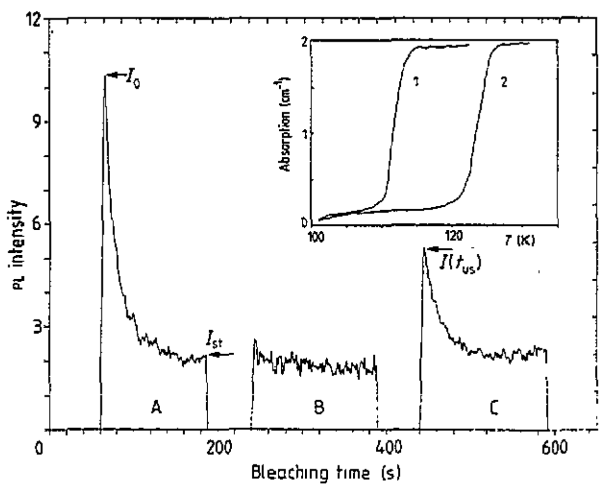

Figure 1. The bleaching kinetics of the 0.65 eV PL band under $h\nu = 1.2$ eV illumination: A, after cooling down a sample in the dark; B, after holding a sample for as long as 70 s at 105 K; C, after the US regeneration with $t_{us} = 70$ s, $T_{us} = 105$ K, $U_{us} = 7.5 \times 10^{-6}$. Inset: thermal regeneration of EL2 absorption band ($h\nu = 1.2$ eV) with (1) and without (2) ultrasound.

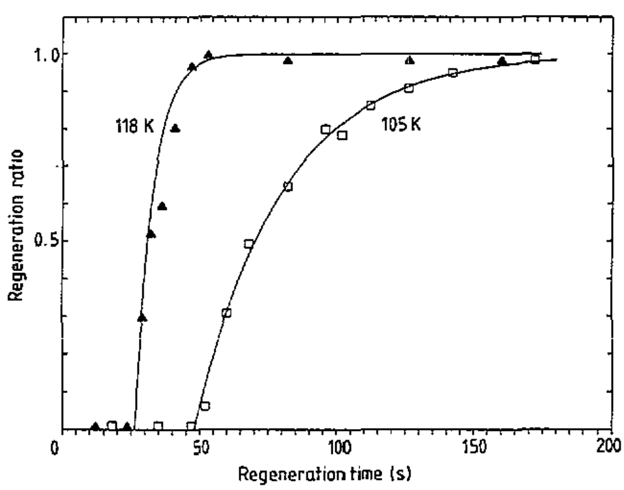

Figure 2. Kinetics of the isothermal US regeneration. Points are the experimental data, full curves correspond to the fitting curves using equation (2) with parameters $t_0 = 26$ s and $t_{us} = 6.5$ s (curve 1), $t_0 = 48$ s and $t_{us} = 32$ s (curve 2).

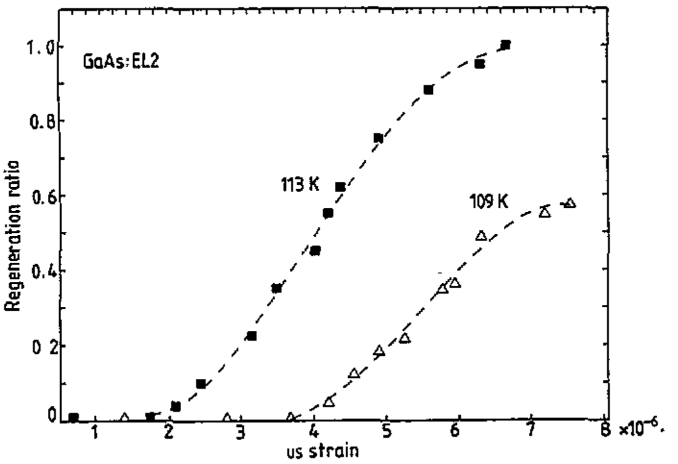

Figure 3. Dependence of the regeneration ratio versus amplitude of the US strain on the transducer.

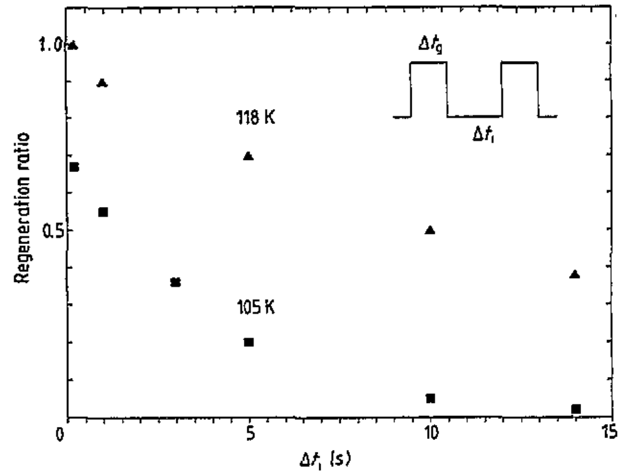

Figure 4. Dependence of the regeneration ratio versus time interval between two subsequent US gates. Inset: the experimental scheme for the gate-modulated US regeneration.

A peculiarity of the kinetic curve is the delay time, t_0, which is attributed to the initial time of the regeneration process. This initial time is increased when either temperature, T_{us}, or the amplitude of an acoustic strain, U_{us}, are decreased. We emphasize that complete US regeneration of EL2 centres is independent of both T_{us} and U_{us}, and is equal to the total number of EL2 centres regenerated into the ground state. This fact shows that the US vibrations effectively transfer all EL2 centres in a sample into the ground state.

The characteristic time of the kinetics curve, τ_{us}, given by equation (2), depends on temperature, T_{us}, as depicted in figure 2. The activation energy for the US regeneration, ε_{us}, has been evaluated from the Arrhenius plot of log τ_{us} versus T_{us}^{-1}. The value of ε_{us} varies as a function of U_{us}, and can be suppressed from its regular value of 0.3 eV down to 0.09 eV under the maximum available value of $U_{us} = 7.5 \times 10^{-6}$.

In figure 3 the amplitude dependences of δI versus U_{us} are shown at two temperatures. We point out that they are specified by a 'threshold amplitude', U_{th}, which is decreased with the increase of temperature for US regeneration†.

At this step the ordinary thermal regeneration of the EL2^0 state due to the ultrasound vibrations can account for the observed US recovery process. Actually, it could be caused by a local release of the heat due to the absorption of US vibrations by some lattice defects associated with EL2 centres. This would provide the appearance of local regions overheated with respect to the lattice, and due to this thermal recovery of EL2 centres. A temperature of such overheated volumes is controlled by the balance of a heat supply due to US vibrations and a cooling process via thermoconductivity of the crystal lattice. A characteristic cooling time, τ_c, can be estimated from the relation:

$$\tau_c = \alpha^2/\pi^2\chi \tag{3}$$

† The 'threshold behaviour', in fact, may correspond to an exponential function of the regeneration ratio versus U_{us}, which shows a sharp initial step due to the limited accuracy of the experiment.

where χ is the coefficient of thermal diffusivity for GaAs, which is equal to 3–4 cm^2 s^{-1}, and $\alpha = 0.1$ cm specifies the minimum sample dimension. This gives a value of 3×10^{-4} s for τ_c. We will show now that this time is inconsistent with the result of the following experiment.

The US regeneration has been studied using low-frequency gate modulation of the ultrasound as shown in figure 4 (inset), which is specified by the duration of a single gate, Δt_g, and by the time interval between two subsequent modulation pulses, Δt_i. If one adjusts the value of Δt_g to be shorter than t_0 (the delay time for US regeneration), then the recovery of the EL2^0 state occurs after a definite number of modulation pulses (n), as soon as the following inequalities hold true: $n\Delta t_g > t_0$ and $\Delta t_i < \tau_c$. Hence, varying a time for Δt_i and holding Δt_g and n the same, one can measure the characteristic time of the assumed cooling process which has to be checked with the value estimated above. The results for such an experiment are shown in figure 4. The calculated values for τ_c are 20 s ($T_{us} = 118$ K) and 5 s ($T_{us} = 105$ K). They are in evident contradiction with the expected cooling time of 10^{-3}–10^{-4} s attributed to lattice thermoconductivity. This contradiction shows the inconsistency of the local heating model with the experimental data depicted in figure 4. We point out that τ_c is less than t_0 at each temperature. This fact along with other results for US regeneration will be discussed in the next section.

4. Discussion: the model for ultrasound regeneration of EL2 centres

To interpret the new effect of EL2 regeneration stimulated by the US vibrations of a crystal we propose a model that utilizes the dislocation concept. It was observed that the distribution of EL2 centres is similar to the profile of the dislocation density in the same GaAs wafer [10]. In terms of US vibrations, the interaction of the ultrasound wave with dislocations can be considered using the string model [11]. The US vibrations of a crystal force the oscillation of dislocation lines which are fixed at pinning points by various crystal defects. With the increase of the amplitude for US vibration the amplitude of dislocation oscillations is increased as well, and under some threshold value of U_{us} the break of a dislocation from a pinning point occurs. The number of such breaks increases with time, which leads to the increase of crystal volume, which is affected by oscillation of dislocations. These dislocation oscillations induce in a crystal the alternate strain field, which gives rise to the lattice regions of local tension and compression, in particular, near the EL2 centre. The compression half-period of US treatment provides the reduction of the regeneration barrier. This suggestion is consistent with the hydrostatic pressure experiments [12] as well as with the study of the regeneration process under uniaxial strain [13], where the suppression of the energy barrier for EL2 regeneration was observed.

Within the dislocation model we can qualitatively account for specific features of the US regeneration kinetics (figure 2), as well as the amplitude dependence (figure 3) as a function of T_{us}. We take into account that the probability of a single dislocation break is given by the relation

$$W = W_0 \exp[-(E - U_{us}V)/kT_{us}] \tag{4}$$

where E is the binding energy of a dislocation to the lock, $V = b^2/L$, b is the Burgers vector and L is the average distance between pinning points on a dislocation [11]. Hence, the threshold behaviour of the amplitude dependence for the US regeneration is caused by that of a dislocation break from the pinning points, which, according to equation (4), is an exponential function of T_{us}. Consequently, U_{th} has to decrease with increasing temperature. This is consistent with our experiment (figure 3). Concerning the kinetics for US regeneration, the observed delay time, t_0, is related to the probability of release of a dislocation from a definite number of pinning points, and, consequently, $t_0 \sim W^{-1}$ defined by equation (4). This consideration is also consistent with the observed temperature dependence t_0 (figure 2).

As a consequence of the dislocation model it is reasonable to interpret the time t_c (figure 4) as being attributed to the process of recapture of a dislocation by pinning points. The probability of such recapture is decreased, and consequently t_c is increased, with the increase of T_{us}, which is consistent with experimental data shown in figure 4. The inequality $t_c < t_0$ also favours this conclusion, since in order to minimize the total energy of a system, the probability of breaking off a dislocation, t_0^{-1}, has to be lower than that of dislocation recapture given by t_c^{-1}.

The US regeneration was checked in GaAs:In samples with a density of dislocations reduced to 10^2 cm^{-2}. The effect of the US-stimulated recovery for EL2 centres is well observed in these samples. This is presumably a consequence of the space correlation of EL2 centres with respect to the dislocation [10]. However, the activation energy for the relevant US regeneration process is smaller than that in semi-insulating GaAs. This can be explained as the variation of the mutual interaction between dislocations. Special experiments to establish the relation between dislocation density and recovery of the EL2 centres are required.

We would like to analyse several known mechanisms which could account for the effect of US regeneration of the EL2 ground state:

(i) The observed process could be attributed to free electrons released by US vibrations of a crystal. This would provide reduction for the regeneration barrier in accordance with [3]. However, the measurement of the conductivity in our samples during the time of US influence clearly shows that the free carrier concentration is held constant.

(ii) The US-enhanced regeneration can be a consequence of the optical process if the acoustic vibrations excite sufficiently strong acoustoluminescence [14]. We were unable to detect any optical emission of a sample stimulated by ultrasound in the spectral range 0.5–1.5 eV with a density of power higher than 1 mW cm^{-2}. Meanwhile, the optical recovery of the EL2^0 state requires an incident light intensity of 2 mW cm^{-2} for 20 min [4].

(iii) Another possibility is the US induced transfer of the metastable to stable EL2 centre caused by resonant absorption of acoustic vibrations by the EL2 centre. This process needs the resonance condition for the frequency of ultrasound:

$$f = n_0 \exp(-\varepsilon/kT_{us}) \tag{5}$$

where $n_0 = 10^{13}$ s^{-1} is the effective frequency of lattice vibrations and f is the operating frequency of the US transducer. Following (5), we estimated the value of $\varepsilon = 0.150$–0.185 eV for $T_{us} = 105$–120 K and $f = 10^5$ s^{-1}. The minimal activation energy for the US recovery observed in our experiments (0.09 eV) is beyond this interval. Consequently, this mechanism can also be ruled out.

(iv) It is worth mentioning the recent data for uniaxial stress-induced EL2 regeneration in semi-insulating GaAs [13]. The authors had observed the additional low-temperature step for a temperature recovery process under uniaxial stress applied to a crystal. This was found when a stress of 200–600 MPa was applied along the ⟨111⟩ crystal direction. We can estimate the upper limit of the stress introduced into a lattice by the maximum amplitude for US vibrations available in our experiment. (This stress should not be confused with the local periodic compression field due to dislocation oscillations as discussed above.) Using the characteristic value of the elastic constant for GaAs of 1.02×10^5 MPa and the maximum amplitude of acoustic strain on the transducer of 7.5×10^{-6}, the relevant stress is given as 0.8 MPa. This value is much less than that in both the hydrostatic pressure [12] and the uniaxial stress experiments [13]. This estimation shows the difference between the ultrasound and pressure-induced mechanisms for EL2 regeneration.

5. Conclusions

Calculations based on the density-function theory [15] show that the probability of the optically induced transition $EL2^0$ to $EL2^*$ within the As_{Ga} defect strongly depends on the mutual arrangement of the total energy curves for the ground state and the excited state of the EL2 centre. It seems reasonable to assume that mechanical strains in a lattice generated, in particular, by ultrasound oscillations can vary this arrangement noticeably and, hence, affect the probability of the metastable to stable transition of the EL2 centre. Furthermore, one can explain by the effect of a local strain the reason why an isolated antisite atom, As_{Ga}, is related to the centre without metastable behaviour, while participating in a complex with As_i it demonstrates EL2-like properties [16]. In the latter case, an As_i atom presumably provides the elastic strain which disturbs the total energy curves of the As_{Ga} in a proper way.

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