The transformations of the EL6 deep level defect in n-GaAs : Is EL6 a DX-like center?

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ABSTRACT

Based on the charge redistribution effect, as observed by the present authors, and the earlier reported large lattice relaxation and persistent photoconductivity phenomena associated with the EL6 defect seen in doped, undoped, semiinsulating(SI) and low temperature grown GaAs (LT-GaAs), it is suggested that this defect be classified as a DX-center. A tentative unified atomic model is proposed for all the native defects EL2, EL3, EL5, and EL6 observed in GaAs.

INTRODUCTION

The electronic level 2 (EL2) in GaAs and the DX-centers observed in III-V alloy semiconductors are the most widely studied defects because of their technological significance [1,2]. While EL2 is known for its metastability and photocurrent quenching phenomena, DX-centers are known for their large lattice relaxation (LLR), persistent photoconductivity (PPC), shallow-to-deep transition, negative-U ordering and charge redistribution effects[2]. It has been widely accepted that EL2 is responsible for the semiinsulating (SI) behavior of GaAs, through the compensation of all the free charge carriers. This property has allowed SI-GaAs to be widely used as the substrate material for epitaxial growth of optoelectronic devices such as LEDs and laser diodes. Interestingly, thermally stimulated current (TSC) and photoinduced current transient spectroscopy (PICTS) measurements performed on SI-GaAs have revealed that medium-deep levels, in particular, a defect level at around E_C- (0.33 ± 0.02) eV also plays a significant role in the compensation mechanism and thus bringing the SI character[3,4]. The medium-deep level at E_C- 0.33 eV, may be identified with EL6 native defect, from the classification scheme of Martin, Mitonneau, and Mircea [5]. Such occasional observations have left an uncertainty among researchers as to whether EL2 is alone responsible for the compensation mechanism or any other deep level defect is equally capable of doing this. Further support for the involvement of EL6 has come from low temperature (~300°C) grown GaAs (LT-GaAs), which when annealed at 300-350°C, becomes more highly resistive than the as-grown state. Here, the interesting observation is that the as-grown material showed EL2 related emission, while the annealed material exhibited EL6 defect related emission by completely quenching the EL2 defect emission [6,7]. These observations questioned the role of EL2 in SI and LT-GaAs and raised considerable interest in the EL6 deep level. Such observations could be quite significant in view of the reports claiming that there is a strong interaction between these two defects [6-10].

Deep level optical spectroscopy (DLOS) measurements performed on GaAs have revealed that the EL6 defect level possesses an unusually large Franck-Condon shift (d_{FC} = ~0.6 eV) [11]. It is thus EL6 level may be classified as a DX-like center in GaAs based on the following reasoning. d_{FC} is defined as the difference in thermal and optical ionization energies of a given defect level. Large lattice relaxation (LLR) effects of a defect atom are usually revealed through this parameter. The bigger the d_{FC} value, the larger the lattice relaxation. Besides, LLR is proposed as the mechanism for the observation of PPC in AlGaAs [2]. It is thus of interest to know whether such PPC phenomena are associated with the EL6 defect level. However, the strong photocurrent quenching (PCQ) phenomena associated with EL2 undermined such an observation for a long time. Recently, however, a systematic study by Mitchel and Jimènez revealed that PPC is indeed observed, following the PCQ, and it is strongly argued that this be attributed to EL6 defect level in GaAs [12].

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It is well known that the DX-centers always display a multiple-peak DLTS signature (four components) corresponding to the two-electron occupancy state. Su and Farmer unveiled the mystery behind such a complex signature by observing the charge redistribution among the different components of DX-level [13], through a careful analysis of the isothermal capacitance transients of these defects. The splitting is now understood as being caused by the donor impurity under the deeply relaxed (bond rupture) position, entering into a four-bond axes interaction with the nearest neighbour atoms. ***It is from this same view point that our present interest arises on the EL6 defect level, which always appears with a left and right shoulders*** [8,11,14,15]. The present work also attempts to propose a unified defect model for all the major native defects observed in GaAs.

EXPERIMENT

The samples used in this study are cut from a horizontal gradient freeze (HGF) grown, undoped GaAs wafer with a carrier concentration of the order of 10^{16} cm^{-3}. After degreasing in alchohol, the samples are subjected to an acid etch in H_2SO_4:H_2O_2:H_2O (1:1:20) for two minutes to remove the native oxide. A 10 minute rinse in deionised water followed by a blow in dry N_2 gas left clean surfaces for metallization. Schottky contacts of 1mm diameter are prepared by thermal evaporation of silver through a metal mask. Au:Ge (88:12) alloy is used for the Ohmic contacts. The DLTS measurements are carried out with a home built system, whose details are published elsewhere [16]. A standard DLTS measurement performed on a Ag/n-GaAs Schottky with a reverse bias of -2V, and a filling pulse of +2V height and 10 ms duration, revealed the presence of two dominant levels (peaks D and G), located at 0.375 eV and 0.827 eV below the conduction band, as seen in Fig.1(a). These two levels are identified with EL6 and EL2 respectively [5]. Of particular interest is the multiple peak structure, consisting of peaks C, D and E. Though a similar DLTS signature has been observed in GaAs grown by a variety of techniques such as HB[14], LEC[17], and vapour-phase epitaxy[11], the left (peak C) and right (peak E) shoulder peaks were not given due consideration because of their relatively low concentration and the complexity involved in determining their activation energies, and cross-sections. However, by carefully resolving the shoulder peaks from the main peak through a non-linear curve fitting program, we have estimated the activation energies for C, D and E peaks as E_C-(0.278 ± 0.008) eV, E_C-(0.375 ± 0.010) eV, and E_C-(0.403 ± 0.007) eV, allowing their identification with EL7, EL6 and EL5 respectively [5].

RESULTS AND DISCUSSION

DLTS measurements are systematically carried out on this particular defect family (EL5/6/7) by varying the filling pulse duration from as short as 10 ns to the maximum permissible 1000 ms. Two such spectra recorded with different rate-window time constants are shown in Fig.2. For all the spectra, the three components are resolved through a computer simulation and the corresponding peak amplitudes are plotted as a function of the filling time, as shown in Fig.3. For clarity of discussion, a few spectra from Fig.2(a) are separately shown in Fig.4.

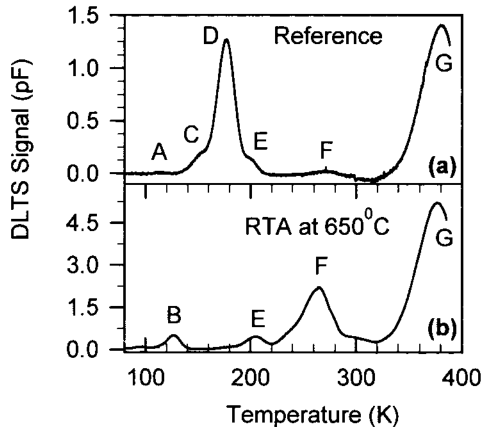

Fig.1. DLTS spectra recorded on a Ag/n-GaAs Schottky diode for 10 ms trap filling time.

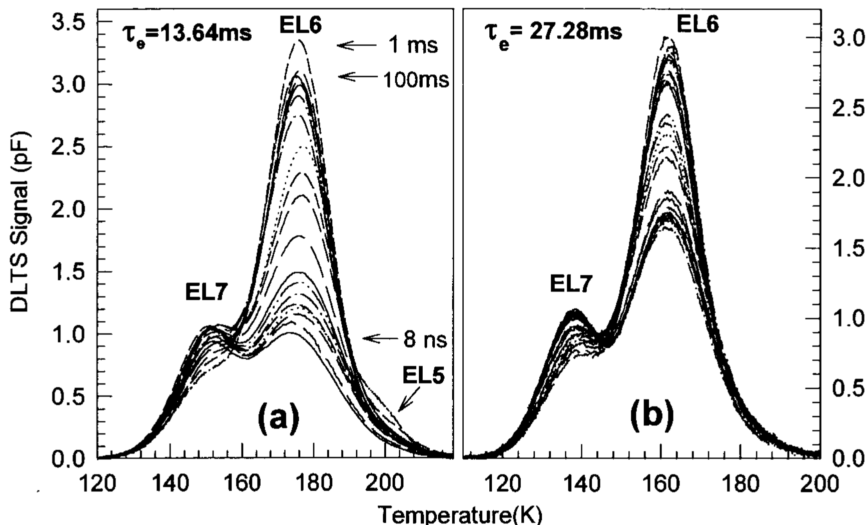

Fig.2. DLTS spectra recorded on Ag/n-GaAs diodes with a reverse bias of -2V.

Fig.3. Peak amplitudes of EL5,EL6,and EL7 defects as a function of filling time

As seen from Fig.4(a), for trap filling times of 10 ns duration, EL7 and EL6 peaks are clearly observed. Interestingly, EL7 is dominating over the EL6 deep level, while there is no sign of EL5 peak. For filling times of 10 μs duration, the EL6 level intensity is seen to rise dramatically by a factor of three followed by a sharp decrease in the EL7 defect concentration. For filling times of 100 ms duration, the EL5 peak seen to rise with a correlated decrease in the EL6 defect concentration, as seen from Fig.4(c).

The latter transformation EL6→EL5, has been seen in a more elegant by Shiraki *et al* [17], since they could employ still longer filling pulses. However, the EL7→EL6 transformation was not observed by these workers. Thus by varying the trap filling pulse from a minimum to the maximum permissible duration, the EL7 defect can be transformed into EL6 (EL7→EL6) and EL6 into EL5 (EL6→EL5), thus making the redistribution transformation EL7→EL6→EL5 clear.

The physical explanation can be offered as follows. If the defect is a DX-like center, it must be able to capture two electrons at the same defect site (negative-U ordering). Since our C-V data showed that the free carrier concentration is slightly greater than the defect concentration, it will be difficult to fill all the defect states with two electrons. Hence, there will be a number of unfilled states available. In such a case, these unfilled states are ready for capture, if any free charge carrier is available. In other words, the possibility exists for the recapture by these empty states, through the conduction band, if there is any emission from the filled states. The question still remains as to why the charge redistribution is a filling time dependent process?

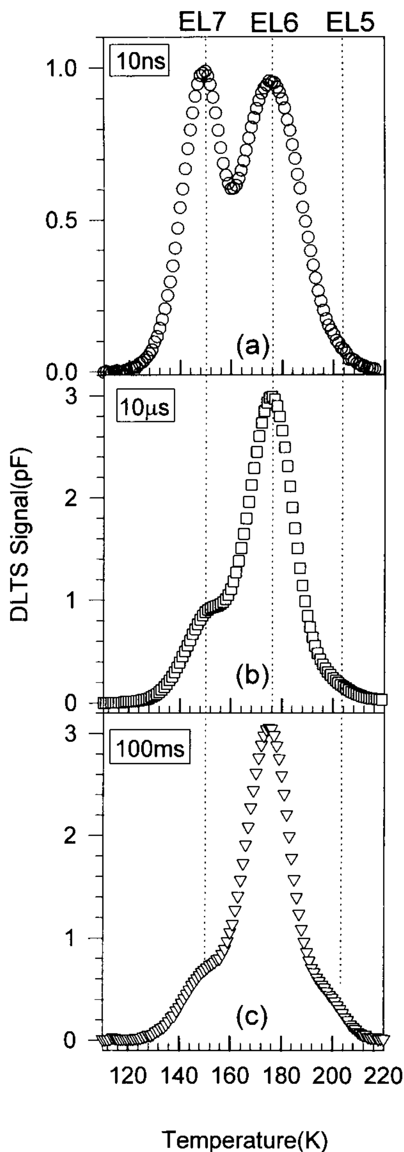

Fig.4. Transformation of the EL7 defect into EL6, and EL6 into EL5 as a function of the trap filling time.

One favored explanation for the DLTS signature of the EL6 defect family, as shown in Fig.2., is that based upon the deeply relaxed configuration of the arsenic atom. In other words, the arsenic atom, after the two electron capture, deeply relaxes from its antisite (As_{Ga}) position to an unknown interstitial position (As_i) leaving behind a gallium vacancy (V_{Ga}). In this interstitial position, the arsenic atom enters into a multi-coordinated interaction with the nearest neighbouring atoms. Since the atomic lengths between the arsenic and its neighbouring atoms will be different (under the bond-ruptured configuration), the corresponding cross-sections (σ_n) would also be expected to be different for capture and emission rates from each site will be different. The nearest sites would be expected to have the maximum σ_n, while the more distant ones the least σ_n.

When the arsenic atom emits its charge, the fact that through which one of the neighbouring atoms, this emitted charge is being transferred to the conduction band, determines the relative intensity of the peak in the DLTS spectrum. During short fillings, the nearest neighbouring atom will capture the charge because of its relatively higher cross-section, leaving no chance for the distant neighbouring atoms either to capture directly or to recapture from the conduction band. Thus the EL7 peak appears dominant at short filling times. For longer fillings, the capture probability of the distant ones is also increased and in addition, more time is allowed for recapturing the charge which is emitted into the conduction band by the nearest neighbouring atoms. Hence,the EL6 level begins to raise with a correlated decrease in EL7 for moderate filling times, and subsequently, EL5 begins to raise with a corresponding reduction in EL6, and EL7 peak amplitudes at longer fillings. Thus the charge redistribution among the different components of the EL6 defect family occurs, similar to the DX-centers in AlGaAs:Si [13], as the filling time is increased.

The present result, however, only accounts for three components, while DX-center in AlGaAs exhibits four components. The explanation may be found in the commonly seen native defect level EL3, which could possibly be the fourth component. The validity of this statement arises from the fact that there is some kind of interaction between EL6 and EL3, as shown in Fig.1(b). By rapid thermal annealing the sample at $650^{o}C$, the EL5/6/7 defect structure is almost totally quenched, while the EL3 concentration is increased by a factor of ~100. This suggests that the majority of the EL6 converted into EL3. In this context, we note that EL3 has been observed while transforming EL5 into EL6 by suitably varying the growth conditions [18]. The EL3 level has been attributed to the two-electron occupancy state of a negative-U defect, which locks the Fermi level exactly at E_C-0.36 eV, which corresponds to the EL6 defect level position [19]. Based on this evidence, it is believed that EL3 defect level may be a part (fourth component) of the EL6 defect family.

In view of the above mentioned interactions among the native defects in GaAs, it is interesting to discuss the possible atomic configurations of these defects. The most widely discussed models for EL2 defect are As_{Ga}, and As_{Ga}-As_i [20,21]. Though a number of models such as As_{Ga}-V_{Ga}-V_{Ga}, As_{Ga}-V_{Ga}-V_{As}, As_{Ga}-As_i- V_{Ga}-V_{As}, have been proposed, there is a common consensus that As_{Ga} is certainly involved in giving rise to the EL2 defect level [22]. On the other hand, models such as (V_{Ga}-V_{As})-As_i [14], and V_{Ga}-As_i for EL6, V_{Ga}-As_i , and the Frenkel pair V_{As}-As_i defects for EL5 [18], have been suggested. Similarly, with all permutations and combinations of gallium and arsenic vacancies as well as interstitials, atomic configurations for defects such as EL7, EL8, EL3 and so on have been proposed. However, the present work, we believe has made a significant breakthrough in understanding the nature of the defects EL5, EL6, EL7 and possibly EL3. Essentially, the same atomic species are involved in giving raise to all these defects. This explains why these native defects are commonly seen in GaAs, irrespective of the growth technique employed. Since most of these materials are grown under arsenic rich conditions, it is reasonable to believe that arsenic may be playing a crucial role in the appearance of these defects.

A unified atomic model for all the native defects in GaAs may be proposed as the As_i in the deeply relaxed mode enters into a multi-axis interaction with the nearest neighbouring atoms and thus gives rise to the EL5/6/7 defects along with possibly EL3, while in the antisite position As_{Ga}, it gives rise to EL2. This postulate is consistent with the widely accepted model, $As_i + V_{Ga}$ (EL6) $\Leftrightarrow$ As_{Ga} (EL2) [6]. Since there is ample evidence to find one to one relationship between the commonly seen native defects in GaAs, it is strongly believed that the arsenic antisite with its metastable properties is largely responsible for the origin of all the defects.

Conclusion

In summary, we have presented evidence for the charge redistribution among the EL7, EL6 and EL5 deep donor levels. Since the filling time dependent transformations of the defect levels (i) EL7 into EL6 and (ii) EL6 into EL5 are quite similar to the behavior of the DX-center in AlGaAs, coupled with its likely involvement in low temperature PPC, EL6 defect family has tentatively been classified as a DX-center in GaAs. The metastability of the arsenic atom in the interstitial, and antisite positions is proposed as being largely responsible for the occurrence of a number of native defects, which are very commonly seen in GaAs, irrespective of the growth technique employed.

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