Observation of Metastable and Stable Energy Levels of EL2 in Semi-insulating GaAs

D. Kabiraj* and Subhasis Ghosh†

* Nuclear Science Centre, New Delhi 110067 and
† School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067

By using combination of detailed experimental studies, we identify the metastable and stable energy levels of EL2 in semi-insulating GaAs. These results are discussed in the light of the recently proposed models for stable and metastable configurations of EL2 in GaAs.

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Physics of metastable point defects is one of the most fascinating problems in contemporary condensed matter physics. Over the years several metastable defects in both covalent and ionic solids have been discovered, but for technological reasons, EL2 in GaAs is the most intensely studied yet least understood, metastable defect. It is believed[1] that bond-breaking mechanism (BBM), in which defects change lattice position is universally responsible for all the metastable defects in solids. The EL2 defects[2], responsible for semi-insulating (SI) properties of GaAs by compensating residual acceptors, can exists in two different atomic configurations. The first one is the well characterized normal configuration (EL2n) and the second one is the metastable configuration (EL2m) in which all the optical, electrical and magnetic properties of EL2 disappear when SI-GaAs is illuminated with a subband gap light \( \sim 1.1eV \) at low temperature \( (\leq 150K) \), known as phoquenching (PQ). EL2m is metastable because all the properties can be recovered either by heating the sample, or by photorecruitment at low temperature, known as photo-recovery (PR). Though, a great deal of attention has already been paid to understand the physics of this defect, but the microscopic origin of EL2 remains illusive till today. In particular, the most important issues remained to be resolved are, (i) atomic configuration of EL2 in both normal and metastable configurations, (ii) driving mechanism for EL2n to EL2m transition and, (iii) compensation mechanism after PQ, since free holes with concentration same as that of EL2 will be available when EL2s are in photoquenched state. There are some efforts[2][3][4][5] to explain some of these issues by postulating the existence of actuator levels which trigger the metastable transition by capturing photoexcited holes from EL2s. But, this actuator level is characterized by the absence of any direct experimental observation. In addition to this, interest in EL2 has been revived for two reasons, first: an increasing interest in defect engineering using this defect and second: the role of this defect on the properties of low temperature grown GaAs.

Several models[2] based on either isolated native point defect or defect complex comprising of arsenic antisite (AsGa), gallium antisite (GaAs), arsenic vacancy (VAs), gallium vacancy (VGa), arsenic interstitial (Asi) have been proposed, but very little is known about the electrical properties and defect energy levels of EL2m. Recently, two models, for the first time, proposed correlation between electrical activity and the defect energy level related to metastable configuration of EL2. Fukuyama et al[7] have proposed a BBM-based model and shown that a three-center-complex \( V_{As}-As_{Ga}-Ga_{As} \) is the atomic origin of EL2 with specific predictions of different defect energy levels related to EL2 in normal and metastable configurations and their role on PQ (EL2n \( \rightarrow \) EL2m) and PR (EL2m \( \rightarrow \) EL2n). Chadi[8] has also proposed a BBM-based model and reaffirmed that atomic origin of EL2 is the isolated \( As_{Ga} \) which can exist in eight charge states giving rise to two energy levels for EL2n and EL2m. It is only known that EL2 introduces a mid-gap level. There is no experimental investigations on the normal and metastable levels proposed in Ref.[7] and Ref.[8]. Identification of these levels will help immensely to resolve a long standing controversy regarding the microscopic origin of EL2n and EL2m and mechanism behind the EL2n \( \rightarrow \) EL2m transition. In this letter, we report an experimental observation of the energy levels directly related to EL2 in normal and metastable states using different spectroscopic techniques suitable for highly resistive materials like, SI-GaAs.

**Experiment.** The photo-current (PC), thermally stimulated current (TSC), photo-Hall-voltage (PHV) and thermally stimulated Hall voltage (TSHV) measurements on both unirradiated and irradiated SI-GaAs samples obtained from two different sources were carried out. The observation of TSC and TSHV spectra with the signature of trap levels requires enough carriers be available for capture and finally for emission and is achieved by the photoexcitation at low temperature prior to heating cycle. Three monochromatic sources, 1.16eV and 1.37eV (which cause PQ) and 2.54eV (which does not cause PQ) were used for this purpose. In order to perform the TSC and TSHV measurements under identical initial condition, following sequence was used, (i) the sample was cooled to 10K in dark and equilibrated for two hours and then photoexcited for PC growth and finally illumination was terminated at different times for obtaining the TSC spectra from 10K to 300K by heating the sample at the rate of 0.1K/sec, (ii) the sample temperature was raised to 320K and equilibrated for two hours to avoid any resid-
ual metastability, (iii) the sample temperature was again brought down to 10K and step (i) was followed. To support the microscopic identification, 48MeV Li ions, obtained from the Pelletron accelerator at Nuclear Science Centre, New Delhi, was used to create and annihilate the intrinsic point defects in SI-GaAs. The energy is chosen such a way that the range of the ions is larger than the thickness(∼ 100µm) of the sample, so that the damage of the sample due to the creation of extended defects by nuclear collision can be avoided and the intrinsic defects are created only by electronic excitation 10.

Fig.1(a) shows the PC growth at 10K under the excitation of 1.16eV and 2.54eV lights. As expected there is no PQ of EL2 in case of 2.54eV light, but strong PQ has been observed after 50sec of photoexcitation in case of 1.16eV light and subsequently PC is saturated to a steady state value, which depends on the intensity of the photoexcitation. Fig.1(b) shows the comparison of TSC spectra taken after 20sec exposure with 1.16eV and 2.54eV lights, respectively. The most interesting feature is the completely different TSC spectra in these two cases. The peaks at 26K and 140K are absent in TSC spectra taken with 2.54eV light and peak at 75K, 240K and 260K are absent in the TSC spectra taken with 1.16eV light. Fig.1(c) shows the comparison of TSC spectra taken after 600sec exposure with 1.16eV and 2.54eV lights. In contrast to previous case, TSC spectra are almost identical in this case. Hence, there is no difference in TSC spectra taken with 2.54eV light for different exposure times, but TSC spectra taken with 1.16eV light are completely different for different exposure times.

To study the PQ and change in conduction type during quenching, time evolution of PC and PHV growth has been studied under the photoexcitation with two different quenching lights(1.16eV and 1.37eV), which are shown in Fig.2 and Fig.3. It is known 7 that SI-GaAs is very weakly n-type. The temporal evolution of PC and PHV can be divided into two regimes, regime I: a steep rise followed by decrease towards a minimum due to PQ of EL2(EL2 → EL2m) and conduction is p-type in this regime, regime II: PC and PHV reach a minimum, conduction type changes from p-type to n-type, followed by a very slow increase due to PR of EL2(EL2m → EL2n) and finally conduction type returns to weakly n-type. In case of 1.16eV light(Fig.2), PQ is over after 50sec, followed by PR which restores initial PC and conduction type after 550sec, but in case of 1.37eV light(Fig.3), it takes longer time(∼1500sec) for PQ and efficiency of PR is very low compared to 1.16eV light. This is due to strong dependence quantum efficiency of PQ and PR on the wavelength of photoexcitation 11. 9. To investigate the evolution of TSC spectra at different stages of quenching and recovery of EL2, light exposure was terminated at different stages of PQ and PR and the corresponding TSC spectra show how the different energy levels evolve with quenching and recovery of EL2. Fig.2 and Fig.3 show similar TSC spectra irrespective of wavelength of initial photoexcitation. It is clear from Fig.2 and Fig.3 that energy levels at 26K and 140K are disappearing as EL2n → EL2m, so these energy levels must be related to metastable configuration of EL2. After PR, these metastable levels are not recovered, instead, a new set of levels at 75K, 240K and 260K are appeared, so these energy levels are observed as EL2m → EL2n. Similar metastable TSC peak at around 140K has been previously observed 11, 12, but not the other metastable TSC peaks. As shown in Ref. 9, we have also observed two step PQ(shown in Fig.2 and Fig.3) which will be subject of our future investigation.

Fig.4 shows the TSC and TSHV spectra taken after 100sec exposure(during PQ) with of 1.16eV light. By comparing the TSHV and TSC spectra, we observe, (i) the metastable TSC peaks at 26K and 140K are present in TSHV spectra and hence these are hole traps 13, (ii) the TSC peaks at 65K, 90K and 120K are absent, instead a dip at their positions and these should be due to electron traps 12, which should give rise to negative peak in TSHV spectra.

The irradiation induced modifications in PC and TSC measurement results are shown in Fig.5, which provide useful information regarding the role of the levels at 26K and 140K observed during EL2n → EL2m transformation. Fig.5(a) shows how efficiency of PQ is reduced compared to that in control sample in samples irradiated with a fluence of 1×1012ions/cm2 and 1×1013ions/cm2. Corresponding TSC spectra in Fig.5(b), clearly show that the heights of the metastable peaks at 26K and 140K responsible for PQ and EL2n → EL2m transition reduced in sample irradiated with a fluence of 1×1012ions/cm2 and finally TSC peak at 26K disappeared and the peak height of TSC peaks at 140K reduced further in samples irradiated with a fluence of 1×1013ions/cm2. Hence, there is correlation between the reduction of efficiency of PQ i.e. EL2 concentration and reduction of the peak heights of the metastable peaks at 26K and 140K related to EL2m.

Origin of TSC/TSHV peaks in SI-GaAs when EL2s are in normal state. The TSC spectra obtained either after photoexcitation of 2.54eV light or after photoexcitation of 1.16eV(or 1.37eV) for long duration(after PR) are the energy levels in SI-GaAs when EL2s are in normal state. The origin of weak TSC peak at 40K is not known much, recently it has been shown 14 that it may be due to complex related to VGa and GaAs. The strong peak at 65K and 120K(as shown in Fig.1, Fig.2 and Fig.3) are due to two energy levels of double donor VAs(+0 and 2+/+) 11, 12. We have shown 10 that the strong peak at 90K may be due to OAs. This identification is corroborated by the annihilation of this peak under ion irradiation with 50MeV Li, as shown in Fig.5. Based on earlier published data 11, 12, 15 and energetic positions, the TSC peaks at 150K, 200K and 215K are attributed
Origin of metastable levels of EL2. All these findings indicate that the metastable TSC peaks at 26K($\sim$0.035eV), 132K($\sim$0.27eV), which are observed during EL2$^m$ $\rightarrow$ EL2$^m$, i.e. EL2 in metastable configuration, because of the (i) observation of these levels when EL2s are in metastable state, (ii) disappearance of these levels when EL2s are in normal state, (iii) gradual disappearance of these levels when the concentration of EL2 are reduced in irradiated samples, (iv) similar electrical property of all these levels, which are hole-traps, and (v) absence of these levels in Cr-doped SI-GaAs(not shown). These results can be interpreted by both the models discussed in Ref. 7 and Ref. 8. But, to put our experimental results on more rigorous basis we now discuss the three-center-complex model based on the proposal of V$_{As}$-As$_{Ga}$-Ga$_{As}$, as atomistic origin of EL2. According to this model, (i) As$_{Ga}^- - V_{As}$ pair is responsible for metastability while Ga$_{As}$ controls the transition between the normal and metastable state, (ii) the Columbic interaction between Ga$_{As}$ and As$_{Ga}^-$ pins the As atom at its Ga-site. PQ starts with the photoionization of hole from As$_{Ga}^-$(As$_{Ga}^- \rightarrow$ As$_{Ga}^0 + h$) and subsequent capture of hole by Ga$_{As}$, which is supported by the p-type conductivity during PQ, as shown in Fig.2 and Fig.3. This results the neutralization of Ga$_{As}^-$ and As$_{Ga}^+$ to Ga$_{As}^0$ and As$_{Ga}^0$, respectively, leading to (i) switching off the Columbic attraction and breakage of the bond between As$_{Ga}$ and Ga$_{As}$ and (ii) As atom moves towards the V$_{As}$ due to BBM until the formation of metastable complex. Movement of As atom from As$_{Ga}$ site towards the interstitial site gives rise to V$_{Ga}$ and As$_i$. The role of As$_{Ga}$ and movement of As$_i$ by few angstroms on the EL2$^m$ $\rightarrow$ EL2$^m$ transition has also been established theoretically. Hence, as EL2$^m$ $\rightarrow$ EL2$^m$, these metastable point defects(V$_{Ga}$ and As$_i$) should give rise to TSC peaks, which should be hole traps. The metastable defect energy levels at 0.035eV and 0.27eV from valence band minimum(VBM) are attributed to As$_i$ and V$_{Ga}$, respectively. Similar ionization energies of V$_{Ga}$ and As$_i$ have been predicted by calculating local atomic structure with lattice relaxation. The existence of V$_{Ga}$ in the metastable configuration of EL2$^m$ has been argued by positron annihilation experiment.

The recovery of EL2 according to this three-center-complex model would be [V$_{As}$ - (As) - V$_{Ga}$] $\rightarrow$ [V$_{As}$ - As$_{Ga}^+$ - Ga$_{As}$], and the excess electrons in the conduction band during this process is consistent with experimentally observed(Fig.2 and Fig.3) conduction type conversion from p-type during PQ to n-type during recovery of EL2$^m$. According to this model, three processes: (1) ionization of deep donor V$_{As}^0$, which is supported by the enhancement of TSC peaks at 65K and 120K during PR, as shown in Fig.2 and 3, (2) ionization of deep acceptor Ga$_{As}^0$, which should result a new metastable peak during PR and is attributed to the TSC peak at 75K($\sim$0.13eV), similar ionization energy of Ga$_{As}$(0/-) has also been predicted theoretically, and (3) movement of As atom towards the antisite position resulting annihilation of As$_i$ and V$_{Ga}$, which is supported by the disappearance of TSC peaks at 26K the 140K during PR.

Origin of stable levels of EL2. As the recovery process proceeds with prolonged photoexcitation with sub band gap light, we observe the disappearance of metastable levels related to EL2 and appearance of new peaks at 240K($\sim$0.49eV) and 260K($\sim$0.56eV). These peaks are always observed when TSC is taken with above band gap light. These levels are related to the normal state of EL2. Based on their energetic positions, these levels are attributed to double acceptor Ga$_{As}$(-/2-) and double donor As$_{Ga}$(2+/+) [21, 22]. To have EL2s in normal state, Columbic interaction is required between Ga$_{As}$ and As$_{Ga}$, so they should be either in Ga$_{As}^-$ and As$_{Ga}^-$ or Ga$_{As}^0$ and As$_{Ga}^0$ states. Recently, similar ionization energy, 0.47eV from VBM, which should be equivalent to TSC peak at 240K, has been observed by excitation photocapacitance method. Lastly, we would like raise a issue regarding the observation of these stable levels only when EL2s are always in normal state i.e. never photoquenched at low temperature. Once the temperature is raised beyond 150K, they should be observed always. Is the thermal recovery not complete beyond 150K? Self promoted behavior of EL2 and temperature dependent incubation time have been observed during recovery and explained by some kind of correlation among EL2s, but more experimental and theoretical studies are required for the ascertainment of this speculation. It has been shown that correlated defects are required for consistent description of experimental results in highly compensated Ge[24] and magnetic semiconductor (Ga,Mn)As.

In conclusion, we have identified the defect energy levels related to normal and metastable configurations of EL2 in SI-GaAs by using different spectroscopic techniques and PC growth during PQ and PR under different initial conditions. A three center model for microscopic structure of EL2 has been discussed in the context of the origin of these metastable and stable levels and their role on PQ and PR of EL2 in SI-GaAs.

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Figure Captions

Figure 1. (a) PC growth in SI-GaAs with 1.16eV light(solid line) and 2.54eV light(dashed line). Photoex-

citation terminated at different times(shown by ↑ in (a)) and corresponding TSC spectra taken with 1.16eV and
2.54eV lights for (b) 20sec and (c) 500sec exposure at 10K. Light was switched on at t=10sec.

Figure 2. (a) Comparison of temporal evolution of PC growth and photo Hall voltage(PHV) under the pho-
toexcitation of 1.16eV light. Light was switched on at t=10sec. (b) Evolution of TSC spectra under the differ-
ent dose of initial photoexcitation(shown by ↑ in (a)). TSC peaks observed during PQ(EL2n → EL2m) and
PR(EL2m → EL2n) are indicated by ↑ and ↓, respectively. TSC spectra(except the bottom one) are shifted up for clarity.

Figure 3. (a) Comparison of temporal evolution of PC growth and photo Hall voltage(PHV) under the pho-
toexcitation of 1.37eV light. Light was switched on at t=10sec. (b) Evolution of TSC spectra under the differ-
ent dose of initial photoexcitation(shown by ↑ in (a)). TSC peaks observed during PQ(EL2n → EL2m) and
PR(EL2m → EL2n) are indicated by ↑ and ↓, respectively. TSC spectra(except the bottom one) are shifted up for clarity.

Figure 4. Comparison of TSC(solid line) and
TSHV(dotted line) spectra during PQ i.e. when EL2s are in metastable states. The peaks related to EL2m are
indicated by arrow(↑).

Figure 5. (a) PC growth in irradiated SI-GaAs samples with 1.37eV light. Light was switched on at t=10sec. (b) Evolution of TSC spectra in irradiated SI-GaAs samples, with 20sec initial photoexposure.
Figure 1
Figure 3
Figure 5