Verification of *EL2* electronic absorption effect on charge transfer in semi-insulating GaAs

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The electronic absorption of *EL2* centers has been clarified to be related to the electron and hole photoionizations, and the transition from its ground state to metastable state, respectively. Under an illumination with a selected photon energy in the near infrared region, these three processes with different optical cross sections will show different kinetics against the illumination time. It has recently been shown that the photosensitivity (measured under 1.25 eV illumination) of the local vibrational mode absorption induced by some deep defect centers in SI-GaAs is a consequence of the electron and hole photoionizations of *EL2*. This paper directly measures the kinetics of the electronic transition associated with *EL2* under 1.25 eV illumination, which implies the expected charge transfer among different charge states of the *EL2* center. A calculation based on a simple rate equation model is in good agreement with the experimental results.

INTRODUCTION

The effect of near infrared (NIR) illumination on charge transfer of (O- V_{As}) centers, represented by the interconversion among the three local vibration modes (LVM) *A*, *B*, and *C*, in SI-GaAs has been studied by several groups.¹⁻⁵ In our previous work,⁵ this photosensitive behavior has been observed in conjunction with the dynamic behavior of a large number of H-related LVM lines and the electronic transition absorption of Fe centers in SI-GaAs material under 1.25 eV illumination. The kinetic processes of LVM absorption in the middle infrared region from different centers show a different time dependence. The three LVM absorption bands *A*, *B*, and *C* of (O- V_{As}) correspond to three charge states (O- V_{As})⁰, (O- V_{As})²⁻, and (O- V_{As})⁻ respectively. The time dependence of the intensity interconversion of *A*, *B*, and *C* consists of two parts: I and II. They have different time scales. In contrast, the photoquenching or intensity decreasing of all H-related lines and Fe intracenter transitions take place only during the illumination time of part II. The relative intensity variation among the three absorption bands, associated with (O- V_{As}) in part I, i.e., $A \rightarrow C \rightarrow B$, is interpreted as a process mainly related to the electron photoionization of *EL2* [from the ground state *EL2*⁰ to the positively charged *EL2*⁺, with a cross section σ_n^0 (1.25 eV)], which provides excess electrons for charge transfer (electron capture) from (O- V_{As})⁰ to (O- V_{As})⁻, and to (O- V_{As})²⁻. On the other hand, the variation in part II, namely $B \rightarrow C \rightarrow A$, is explained to be mainly related to the hole photoionization of *EL2* (from *EL2*⁺ to *EL2*⁰, with a cross section of σ_p^0), which provides excess holes for the charge transfer from (O- V_{As})²⁻ to (O- V_{As})⁻ and to (O- V_{As})⁰, which is consistent with the fact that the quenching of Fe²⁺ in this part can only result from a charge state change of Fe²⁺ to Fe³⁺ by capturing holes. Meanwhile, the photoinduced transition from *EL2*⁰ to the metastable state *EL2** (with a cross section of σ^*) keeps occurring under the illumination and, finally, all

the *EL2* centers should approach their metastable state *EL2**. Simultaneously, the circle of the charge transfer of the (O- V_{As}) centers, represented by the absorption intensity variation in the form of $A \rightarrow C \rightarrow B \rightarrow C \rightarrow A$, will be completed during this process. It was also pointed out⁵ that this happens for samples in which the Fermi level is pinned to the *EL2*⁰/*EL2*⁺ level. In order to check the above assumption, it is therefore essential to investigate directly the *EL2* charge state transfer induced by 1.25 eV illumination, by measuring the electronic absorption variation at various wavelengths in the near infrared region, as the difference of the three optical cross sections will result in different consequence of the illumination.

EXPERIMENT

The measurements were performed on a Fourier-transform spectrometer IFS120HR (Bruker) with a close cycle cryostat (APD) to maintain the sample temperature at 13 K. A neutral density filter (N4) was put in front of the sample to reduce the excitation effect of the probe beam. A monochromator with a tungsten lamp tuned at 1.25 eV (0.995 μm) was positioned by the side of the sample chamber being used as the light source of illumination, which induces charge state transfer of *EL2*, so that this is a kind of pump-probe experiment where the probe beam for measuring the absorption is assumed to play no role in the charge state transfer process of *EL2*. The pumping light source intensity can be varied by a tunable power supply. In order to establish an illumination condition for this measuring system similar to the one used in the previous work, the intensity interconversion of $A \rightarrow C \rightarrow B \rightarrow C \rightarrow A$ of (O- V_{As}) center has to first be realized, then the same illumination condition has to be adopted to measure the *EL2* electronic absorption at different wavelengths.

EXPERIMENTAL RESULTS

First, the interconversion of three LVM absorption bands *A*, *B*, and *C* of the (O- V_{As}) center induced by 1.25 eV illu-

FIG. 1. Interconversion reproduced in this work among the three local vibration mode absorption bands A, B, and C associated with the (O-V_{As}) centers under 1.25 eV illumination. A1, B1, and C1 corresponds to the isotopic component from (⁶⁹Ga-O-⁶⁹Ga) of (O-V_{As}) center. (a) shows the A → C → B fast process (part I), (b) gives the B → C → A slow process (part II). The solid lines are guide for the eye.

mination was reproduced and shown in Fig. 1. It is similar to the one reported in our previous work. Part I [Fig. 1(a)] is a fast process (A → C → B), and part II [Fig. 1(b)] is a slow process (B → C → A). This measurement sets up an illumination time scale for EL2 electronic absorption in NIR region.

The electronic absorption of EL2 under 1.25 eV illumination (pump light) was measured between 0.7 and 1.4 eV (probe beam). Figure 2 gives two absorption difference spectra, which show the changes of absorption by the end of the illumination in part I and part II (Fig. 2), respectively. It can be seen that the 1.25-eV illumination reduces absorption of higher-energy photons, which is dominated by σ_n^0 ; but, meanwhile, increases the lower-energy photon absorption, which is mainly due to EL2⁺ absorption with a cross section of σ_p^0 . Since σ_n^0 is about one order of magnitude larger than σ_p^0 at 1.25 eV, the electron photoionization is faster than hole photoionization. This is evidenced by the fact that in part I, the decrease of high-energy photon absorption is greater than the increase of low-energy photon absorption. However, in part II, the enhancement of low-energy photon absorption becomes greater. This is due to the increasing concentration of EL2⁺ as a result of the fast photoionization of EL2⁰. According to the photoionization cross sections known in literature,^{6,7} while the absorption at 1.36 and 1.20 eV is

FIG. 2. The absorption differences between the absorption spectra, measured before illumination and at the end of the 1.25 eV illumination, obtained by subtracting the initial spectrum from the end one, in part I and part II, respectively.

mainly contributed from electron photoionization absorption of EL2⁰, the absorption at 0.9 and 0.8 eV is from the hole photoionization of EL2⁺. Electronic absorption at four-photon energies, i.e., 1.36, 1.20, 0.90, and 0.80 eV against illumination time was chosen to investigate the EL2 charge state transfer kinetics. The results given in Fig. 3 indicate that in part I, within illumination time about $t < 40$ min, the absorption at 1.36 and 1.20 eV decreases quickly with illumination time, the absorption at 0.9 and 0.8 eV do not change much. The scattered data points may come from the time-dependent fluctuation of background during measurements. In part II, when illumination time $t > 40$ min, the high-energy photon absorption at 1.36 [Fig. 4(a)] and 1.20 eV [Fig. 4(b)] keeps decreasing, but the low-energy photon

FIG. 3. Absorption variation of EL2 centers at 1.36, 1.20, 0.9, and 0.8 eV, measured within illumination time $t < 40$ min, which corresponds to the time period of part I, i.e., A → C → B fast process of (O-V_{As}) center. The lines are guide for the eye.

FIG. 4. Illumination time dependence of the electronic absorption of *EL2* measured (a) at 1.36, (b) at 1.20, (c) at 0.9, and (d) at 0.8 eV, the points are experimental results, the solid lines are calculation curves. The part II slow process $B \rightarrow C \rightarrow A$ of the interconversion of ($O-V_{As}$) center took place about $t > 40$ min. The unit of absorbance is arbitrary.

absorption at 0.9 [Fig. 4(c)] and 0.8 eV [Fig. 4(d)] starts increasing. These observations can be well understood from a rate equation calculation as discussed below.

DISCUSSION

In order to explain the whole kinetic process of the *EL2* electronic absorption and its relationship with the photosensitivity of the relevant defect absorption, the effect of the 1.25 eV illumination on the charge transfer of different *EL2* states was calculated by using a model of Vincent, Bois, and Chantre,⁶ which has successfully been used to explain the *EL2* center absorption kinetics.⁶ At low temperature, the thermal processes, including the thermal recovery from *EL2*^{*} to *EL2*⁰ can be ignored, hence the rate equations become:

$$\begin{aligned} \frac{dN}{dt} + (\sigma_n^0 \phi + \sigma^* \phi) N - \sigma_p^0 \phi N^+ &= 0, \\ \frac{dN^+}{dt} + \sigma_p^0 \phi N^+ - \sigma_n^0 \phi N &= 0, \end{aligned} \quad (1)$$

where N and N^+ are the relative concentrations, or the proportions of the ground and positively charged *EL2* states, respectively, ϕ is the photon flux. The solution of above equation is

$$N = A' \exp(-\beta_1 t) + B' \exp(-\beta_2 t),$$

$$N^+ = A \exp(-\beta_1 t) + B \exp(-\beta_2 t), \quad (2)$$

with

$$\beta_1 + \beta_2 = (\sigma_n^0 + \sigma_p^0 + \sigma^*) \phi,$$

$$\beta_1 \beta_2 = \sigma_p^0 \sigma^* \phi^2. \quad (3)$$

A , B , A' , and B' are determined by the initial condition. In our case, the Fermi level was pinned at the *EL2* level, whence $N(0) = N^+(0) = \frac{1}{2}$, and we find that

$$A = \{[(\sigma_p^0 - \sigma_n^0) \phi - \beta_2] / 2(\beta_1 - \beta_2)\},$$

$$B = \{\beta_1 - [(\sigma_p^0 - \sigma_n^0) \phi] / 2(\beta_1 - \beta_2)\},$$

$$A' = A(\sigma_p^0 \phi - \beta_1) / \sigma_n^0 \phi, \quad (4)$$

$$B' = B(\sigma_p^0 \phi - \beta_2) / \sigma_n^0 \phi.$$

For calculating N and N^+ as a function of time, we need the photoionization cross sections for 1.25 eV (the illumination photon energy), namely $\sigma_n^0(1.25 \text{ eV})$, $\sigma_p^0(1.25 \text{ eV})$, and $\sigma^*(1.25 \text{ eV})$. For calculating the electronic absorption variation at the four-probe photon energies, we also need the cross-sections parameters. The value of the corresponding cross sections can be found in Table I.

TABLE I. Photoionization cross sections at the illumination photon energy 1.25 eV and the four-probe photon energies (Refs. 6 and 7).

Photon energy (eV)	1.25	1.36	1.20	0.90	0.80
Wave number (cm^{-1})	10 081	11 000	9700	7258	6452
$\sigma_n^0 (10^{-16} \text{ cm}^2)$	1.31	1.313	1.21	0.07	0
$\sigma_p^0 (10^{-16} \text{ cm}^2)$	0.08	0.07	0.08	0.33	0.02
$\sigma^* (10^{-16} \text{ cm}^2)$	0.035	0.007	0.065	0	0

An effective absorption coefficient $\alpha(h\nu)$ against illumination time is proportional to

$$[\sigma_n^0(h\nu) + \sigma^*(h\nu)]N(t) + \sigma_p^0(h\nu)N^+(t), \quad (5)$$

where $N(t)$ and $N^+(t)$ are the results of Eq. (2), in which the photon flux is determined as $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ from fitting the experimental data, and it is the only fitting parameter in this work. Note that in Eqs. (1)–(4), the cross sections are those for 1.25 eV, but in Eq. (5), the cross sections are those for the corresponding photon energies of the probe beam.

For the sake of observing the complete effect of the illumination, a long-time period of about 100 000 minutes was used in the calculation shown in Fig. 5, which shows the variation of the $EL2$ population at different charge states as a function of illumination time. It can be seen that eventually all of the $EL2$ centers will convert to the metastable state. The ground state starts from a half occupied condition, and decays monotonously down with different rates in different time domains. The positively charged state also starts from a half occupation, passing through a maximum at about 700 min, where the experimental measurement finishes, and decays down towards zero when the illumination time is close to 10^5 min. It suggests that in the measurements, if the illumination keeps much longer beyond the time we used, one should expect a decrease of $EL2^+$ absorption.

FIG. 5. Calculated relative concentrations N^0 , N^+ , and N^* , corresponding to $EL2^0$, $EL2^+$, and $EL2^*$ states, respectively, as a function of the illuminating time according to Eq. (2).

FIG. 6. The absorption variations at 1.36, 1.20, 0.9, and 0.8 eV calculated by Eq. (5), supposing that the concentrations N^0 and N^+ are in an order of 10^{17} cm^{-3} .

The calculated absorption variation of $EL2$ at the four energy positions, as a function of time, is shown in Fig. 6, in agreement with the experimental result, i.e., in part I, as shown in Fig. 3, the decrease of the absorption at 1.36 and 1.20 eV is dominant, and in part II, as shown in Fig. 4, the absorption at 1.36 and 1.20 eV keeps decreasing, the absorption at 0.9 and 0.8 eV shows clearly an increase. Actually, the calculated absorption variations in part II have been shown in Fig. 4 as a solid line. Therefore, the calculation result clarifies well the whole kinetic process of the absorption of $EL2$ centers under 1.25-eV photon illumination. Moreover, since the absorption at low energy, which is supposed to be mainly due to $EL2^+$ absorption, did not start decreasing until the end of illumination of part II as depicted in calculation (Fig. 6), it suggests that in our measurement, if the illumination keeps much longer beyond the time we used, one should expect a decrease of $EL2^+$ absorption and the complete conversion of $EL2$ centers to the metastable state.

As a consequence, a large amount of photoionized electrons into conduction band from $EL2^0$ assure $(O-V_{As})^-$ center of a charge transfer from $(O-V_{As})^0$ to $(O-V_{As})^-$ and then to $(O-V_{As})^{2-}$ in part I of the interconversion. In part II of the 1.25 eV illumination, increased photoionized holes from $EL2^+$ into valence band can be captured again by $(O-V_{As})^-$ center to reverse the charge states from $(O-V_{As})^{2-}$ to $(O-V_{As})^-$ and then to $(O-V_{As})^0$. As a matter of fact, the hole capture process on the H-related centers and Fe center can be observed only in part II of the illumination.

CONCLUSION

By directly measuring the electronic absorption of the $EL2$ center, we can conclude that the 1.25-eV illumination induced photosensitivity of various defect centers in SI-GaAs is indeed due to the charge state transfer of the predominant deep center $EL2$. The charge transfer among dif-

ferent states of *EL2* provides excess free carriers in the conduction band and/or valence band, and their concentrations are dependent on the illumination time period. Consequently, the charge state of other multicharged centers will be affected by the existence of these free carriers. This model is well consistent with the experimental observation of the charge state transfer of *EL2* centers, reported in the present paper. This result is also a further confirmation of the photo-

sensitive nature of those multicharged defects, such as the (O-V_{As}) center, the H-related centers, and the Fe center.

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