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Light-induced relaxing dipoles in n-type $Al_xGa_{1-x}As$

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Thermally stimulated depolarization-current measurements with monochromatic light excitation are applied to $Al_xGa_{1-x}As$. We obtain conclusive evidence that electric-dipole relaxation occurs in this alloy. Light-induced relaxation of depolarization-current measurements show that relaxing dipoles have characteristics that are influenced by the wavelength of the monochromatic light. We associate these dipoles with a negatively charged DX-center ground state, since charge-relaxation currents are destroyed by photoionization of $Al_{0.50}Ga_{0.50}As$ using either 647-nm Kr^+ or 488-nm Ar^+ laser lines. Correlation may exist among charged donor states, DX^--d^+. Ionization at the DX-center threshold photoionization energy, $\cong 0.8$ eV, leads to a striking current-peak shift, which can be explained using a model that involves As vacancies.

It is well known that the DX center is the dominant deep level in $Al_xGa_{1-x}As$ and the cause of persistent photoconductivity (PPC) observed in this alloy at low temperatures. In Chadi and Chang's negative-U model,[1] the substitutional impurity traps two electrons concomitant with lattice distortion, generating an interstitial negatively charged impurity (DX^-). Since electrons come from the dopant, when DX^- are generated, charge balance assures that the same amount of d^+ centers (substitutional donor after releasing one electron) are created in the $Al_xGa_{1-x}As$ sample. A few years ago O'Reilly[2] stated that mobility data in GaAs under hydrostatic pressure can only be explained with dipole scattering by DX^--d^+ pairs, since the extra electrostatic energy gained by placing a d^+ center close to a DX^- center is significant. Although, under regular doping concentrations, the probability that a d^+ center is the nearest neighbor to a DX^- center is negligibly small, correlation among DX^--d^+ charged donors has provided an explanation for some phenomena in $Al_xGa_{1-x}As$-based structures.[3,4]

Thermally stimulated depolarization-current (TSDC) measurements have given us conclusive evidence of the presence of the electric dipoles in both direct[5] and indirect[6] band-gap $Al_xGa_{1-x}As$. The results are modeled under O'Reilly's DX^--d^+ picture. In this paper we present results of a modified TSDC experiment, to verify the DX^- participation in the TSDC bands observed. In this procedure, an indirect band-gap sample is illuminated with monochromatic light at low temperature in order to remove electrons from DX centers. Such a treatment does not produce PPC in this material. Then, monochromatic light will not photoinduce an electronic current, due to the absence of PPC, and there is no depolarization current as well, because DX-center-related dipoles are destroyed by such a procedure.

Lang, Logan, and Jaros[7] proposed a DX model in which the defect is a complex involving a donor and an As vacancy (V_{As}). The attractive donor potential would lower the symmetry of V_{As} and split the triply degenerate t_2 state, but the overall properties would be determined by the vacancy potential itself.[8] Although it is claimed by Van Vechten[9] that there are more than sufficient vacancies in all types of GaAs and thus they should be taken into account in a DX-center model, the presence of vacancies to explain DX-center properties is no longer considered in most models in the past decade. It is generally accepted that the transport properties are dominated by the donor charge states (d^+,d^0,DX^-); however, vacancies can be responsible for some carrier trapping, which becomes very important in creating a dipole system and a TSDC measurable signal, since vacancies do exist in the sample, as assured by Van Vechten.

The samples used in this work were grown by molecular-beam epitaxy on an undoped, semi-insulating GaAs substrate. The direct band-gap $Al_xGa_{1-x}As$ sample has $x\cong 0.32$ and a Si impurity donor concentration of 1×10^{18} cm^{-3}. The indirect band-gap sample has $x\cong0.50$ and a Si doping of 5×10^{17} cm^{-3}. In order to prevent a two-dimensional electron-gas formation at the interface, since we are interested in the bulk properties itself, samples have the following structure: 0.25 μm of undoped GaAs buffer layer plus 0.25 μm of undoped $Al_xGa_{1-x}As$ that is compositionally graded from $x=0$ to $x\cong0.32$ (or $x\cong0.50$), 0.25 μm of undoped $Al_{0.32}Ga_{0.68}As$ (or $Al_{0.50}Ga_{0.50}As$), and the 2.0-μm active layer.

In usual TSDC experiments, a voltage is applied to the sample at room temperature in the dark while the temperature is decreased to about 10 K. Then the polarization voltage is removed, the temperature is allowed to increase at a

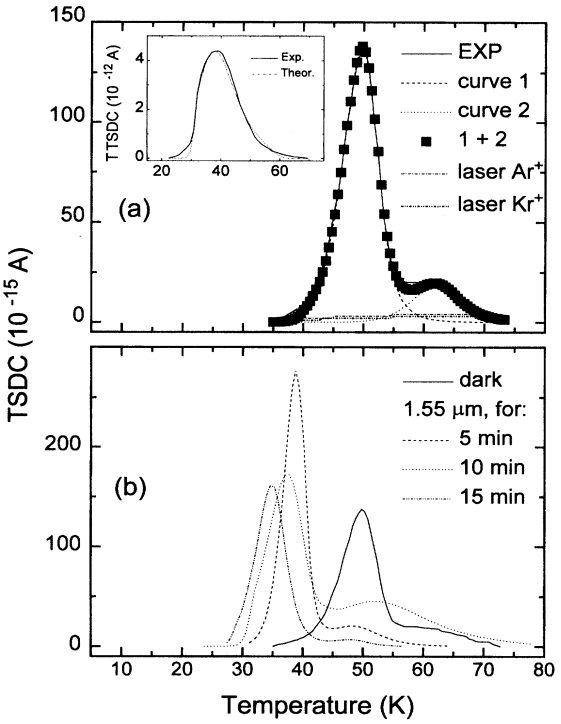

FIG. 1. (a) Thermally stimulated depolarization current in the darkness for $Al_{0.50}Ga_{0.50}As$ and influence of monochromatic light in TSDC bands. Broken line: Kr^+-laser excitation line (647 nm). Dotted line: Ar^+-laser excitation line (488 nm). Inset: TSDC in the darkness for $Al_{0.32}Ga_{0.68}As$. (b) Recorded TSDC bands after irradiating 1.55-μm excitation line for 5, 10, and 15 min in the indirect band-gap sample.

fixed rate, and the current is measured with an electrometer and recorded. The same contacts are used to measure the depolarization current. Dipoles present in the sample are polarized during cooldown and relax to their original random distribution as the temperature is increased.[5] Since no light reaches the sample, no electron is photoexcited to the conduction band when the temperature increases.

Figure 1(a) shows recorded TSDC bands for direct and indirect band-gap $Al_xGa_{1-x}As$. The inset in Fig. 1(a) is a usual TSDC result for the direct band-gap sample, which is about 30 times higher than the current of the indirect band-gap sample, which is shown in the major part of Fig. 1(a). The measured current of Fig. 1(a) is clearly not electronic,[5] considering its order of magnitude. Besides, there is no voltage applied to the sample when the temperature is increased. No known process could cause the release of a few electrons to the conduction band at low temperature and recapture at higher temperature in the dark. Our interpretation is that the observed current is due to electric-dipole reorientation.[5,6] The fitted curves are obtained using Havriliak-Negami relaxation-time distribution approach.[10] A distribution of relaxation times and activation energies is needed in order to fit the data, since we have a dipole-length distribution and the Al atoms are randomly distributed around the defect.[5] The obtained average activation energies are $E_a \cong 0.108$ eV for direct band-gap and $E_a \cong 0.132$ eV for indirect band-gap material, respectively. These values are both very close to the DX-center binding energy.[11] There is another peak in the $Al_{0.50}Ga_{0.50}As$ TSDC curve, with activation energy $E_a \cong 0.165$ eV and lower intensity. Since we have many vacancies in the $Al_xGa_{1-x}As$ sample,[9] we expect that they could trap electrons to become V_{As}^-. The 30-times-higher depolarization current in the direct band-gap sample is reasonable, since there are many more DX^--related dipoles even though the Si doping is only twice as high. The V_{As} unoccupied level is resonant with the conduction band, while the occupied level relaxes to a bound state in the gap.[7] In an As vacancy there are three "dangling" electrons;[8] two of them populate the s-like (a_1) state and the third one belongs to the threefold degenerate t_2 state. The extra electron of the charged vacancy (V_{As}^-) would also belong to this state. A ground state of t_2 symmetry is a candidate for a Jahn-Teller distortion.[8,12] This distortion in the V_{As}^- ion position could be responsible for the dipole system that relaxes at higher temperature, as shown by the smaller TSDC band in Fig. 1(a).

In our indirect band-gap $Al_xGa_{1-x}As$ sample, when monochromatic light is used to excite electrons from the DX center to the conduction band (X valley) at temperatures below $\cong 60$ K, the sample does not exhibit the PPC phenomenon. Electrons are immediately captured metastably by the X-valley effective-mass state.[13,14] Hence indirect band-gap material is suitable for testing the origin of TSDC bands by illuminating the sample with monochromatic light at low temperature in combination with regular TSDC. Since no electronic current is photogenerated in the indirect band-gap sample, it assures that the measured thermally stimulated current comes from relaxing dipoles.

Here we summarize our ideas before going any further: In the direct band-gap sample, as the temperature is lowered to 10 K in the dark, there is an electron freezeout at DX centers, and the TSDC band seen in the inset of Fig. 1(a) is observed. In the indirect band-gap sample, there are three states responsible for trapping the electrons: the X-valley effective mass, the DX center, and the As vacancy. Their occupation obeys some statistical distribution. The first is a neutral state (d^0), which cannot generate a TSDC band. The other two give rise to electric dipoles, which generate the two peaks shown in Fig. 1(a). This is quite consistent with the much lower current magnitude in the indirect band-gap sample depolarization, if compared to the direct band-gap sample.

Figure 1(a) also shows the effect of monochromatic light of two distinct wavelengths in the TSDC band. Light is applied as follows: The sample is electrically biased at room temperature by applying an electric field of 15.7 V/cm (the same as used in the regular TSDC procedure). Then the temperature is decreased slowly to about 10 K, when monochromatic light irradiates the sample for 5 min. The sample is returned to darkness and the electric field is removed. Then the temperature is increased at a fixed rate. The only modification to what we call here regular TSDC is the light excitation of the sample at the lowest temperature. We use $\lambda = 488$ nm from an Ar^+ laser line, which is above the band-gap transition or $\lambda = 647$ nm from a Kr^+ laser line, which is below the band-gap energy but well above the DX-center threshold photoionization energy (about 0.8 eV independent of aluminum mole fraction).[15] Either laser line destroys the TSDC bands obtained in the dark [Fig. 1(a)]. This is a very

TABLE I. Parameters for TSDC data fitting in $Al_xGa_{1-x}As$ using the Havriliak-Negami asymmetric relaxation-time distribution approach.

x	Temperature main peak (K)	E_a (eV)	τ (10^{-14} sec)	Temperature sec. peak (K)	E_a (eV)	τ (10^{-14} sec)	Obs.
0.32	39.0	0.108	90				dark
0.50	49.8	0.132	92	62.1	0.165	97	dark
	39.4	0.121	0.5	48.6	0.132	97	λ=1.55 μm, 5 min
	37.7	0.114	0.75	52.7	0.143	97	λ=1.55 μm, 10 min
	34.6	0.110	0.59	47.7	0.129	97	λ=1.55 μm, 15 min

good indication that the main electric-dipole relaxation is actually DX-center related, and that the DX-center ground state is negatively charged, since no neutral state could be responsible for the dipole relaxation current obtained in both samples in the dark. The current peak at 62 K is also destroyed by each laser line. Although by convenience we use laser lines, the same effect is obtained using a tungsten lamp and a monochromator.

In order to fully understand the photoionization influence on TSDC bands, light at the DX-center threshold photoionization wavelength (1.55 μm) is applied to the sample for 5 min. Such a wavelength is obtained from a monochromator with a tungsten lamp source and a filter which cuts off wavelengths below $\cong$800 nm. This monochromatic light does not destroy the TSDC band but induces a shift of the main current peak from 50 K (regular TSDC) to 39 K (light induced), corresponding to an average activation energy for dipole relaxation of 0.121 eV. There remains some dipole relaxation current with average activation energy of 0.132 eV, caused by a relaxing dipole system of reduced concentration (proportional to the area under the curve). This is seen in Fig. 1(b). For 5 min of illumination, the main peak becomes much narrower and higher, meaning that the dipole distribution is not as wide as in the darkness, but concentrated around a specific dipole system. Illuminating the sample at this wavelength for longer times gives results also shown in Fig. 1(b). All the parameters used to fit these data are given in Table I. The longer the illumination time, the lower the peak temperature and the lower the average activation energy of the main peak. It is interesting to notice that independent of illumination time, there is always a secondary peak that remains in a position very close to the TSDC band obtained in the dark, which means that some portion of the original dipole system distribution has not been completely destroyed after 15 min of illumination. Another feature is that τ_0, the average constant relaxation time has the same order of magnitude ($\cong 10^{-12}$ sec) for the measurements in the dark in both samples and for all the secondary bands in the experiments using 1.55-μm monochromatic light (Table I). Main bands obtained after light irradiation for different exposure times also have τ_0 with the same order of magnitude ($\cong 5\times 10^{-15}$ sec), which is more than two orders of magnitude lower than the bands obtained in the dark. Mooney *et al.*[15] show that although 0.8 eV is the DX-center threshold photoionization energy, there is a variation of several orders of magnitude in the photoionization cross section when the photon energy changes from 0.8 to 2.0 eV, depending on the alloy composition. Then we do not expect the TSDC band to be destroyed when the sample is illuminated with 1.55-μm monochromatic light. However, the shift in the current peak is rather unexpected and suggests that the influence of monochromatic light of this wavelength is not only depleting electrons from DX^- centers. Actually, we believe that vacancies are very important to understanding the recombination process that takes place in our modified TSDC experiment.

In Fig. 2, we present a sketch of a configurational coordinate diagram proposed for the DX-center transition. Illuminating the sample with 0.8-eV monochromatic light, the DX^- center is taken to a postulated activated state (denoted as DX^* in Fig. 2). This state can release electrons to the X valley (conduction-band minimum) due to its parabolic potential. Such a possibility is in agreement with Mooney *et al.*,[15] since 0.8 eV is too low to completely photoexcite the DX center, particularly at $x\cong 0.50$, where the photoionization cross section increases over six orders of magnitude when the excitation light energy goes from 0.8 to 2.0 eV. Some electrons can populate the conduction band and be metastably trapped by the X-valley effective-mass state. The 1.55-μm wavelength also depletes occupied vacancies since the peak obtained at 62 K is destroyed. Lang, Logan, and

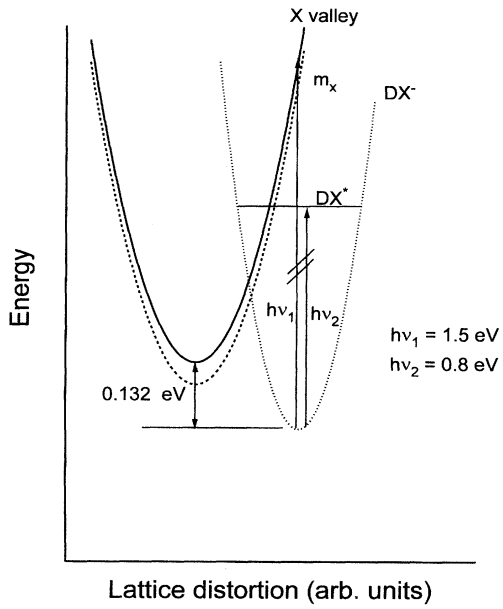

FIG. 2. Sketch of the configurational coordinate diagram involving DX^- electron thermal ionization and optical excitation to the conduction band in the indirect band-gap $Al_xGa_{1-x}As$ (X valley), also showing the X-valley effective-mass state (m_X) and the DX^* activated level.

Jaros[7] suggest a Franck-Condon shift of about 0.8 eV for their DX-center model transition. In this model, the DX center is basically an As vacancy, since the overall properties of the defect, such as energy and wave function, are quite similar to an isolated vacancy. Then, we believe that a transition to an unoccupied vacancy level is observed. However, the most important effect observed in the TSDC spectrum is the generation of a much more defined dipole system, concentrated around a specific system. Van Vechten[9] claims a tendency for a V_{As} center to be formed close to a donor in well-annealed samples. If such is the case, we believe that our excited DX center (DX^*) is able to give electrons to vacancies located close to a d^+ center and a more localized d^+-V_{As}^- dipole system is generated, being responsible for the peak observed in Fig. 1(b) after 5 min of illumination with 1.55-μm monochromatic light. This assumption is reinforced by the fact that light is applied in conjunction with the electric field, which could drive the electrons from DX centers to vacancies. As the illumination time increases, electrons populate more vacancies, leading to a broader TSDC band, since the dipole-length distribution and aluminum neighborhood widens the distribution. We should also mention that there are two possible kinds of V_{As}-related dipoles: V_{As}^--d^+ and distorted V_{As}^-, since the occupied As vacancy state is subject to a Jahn-Teller distortion.

Another possibility is that the activated DX^* state is frozen in this metastable configuration, giving rise to a dipole system such as DX^*-d^+, which is also helped by the electric field maintained during the sample illumination. It would also decrease the depolarization energy, as observed by the TSDC spectrum. We shall notice that this activated state must have a negative charge, since a neutral state would not lead to any measurable current, for there would not be a charge dislocation when it relaxes to a more stable configuration. Besides, the increase in the area under the TSDC curve assures that the transition via a DX^0 intermediate state is improbable, because fewer dipoles would be expected, and a DX^0 state, although still placed in an interstitial site, does not lead to any depolarization current when the temperature is increased, since there is no ion movement. The increase in the area under the curve means that charged states are being created and more dipoles are generated.

In conclusion, electric dipoles present in $Al_xGa_{1-x}As$ have relaxing characteristics that are strongly influenced by monochromatic light. The way wavelength affects the TSDC band is in close relation with photoionization cross-section curves as obtained by Mooney *et al.*[15] In other words, in the saturation region of DX center photoionization, light destroys the dipole current, which does not happen when the monochromatic light wavelength is near the DX-center photoionization threshold energy. Although we cannot assure that the dipoles are O'Reilly's DX^--d^+ pairs, our results strongly suggest that a DX^- ground state is responsible for the main dipole relaxation current peak obtained in the dark. The presence of vacancies in $Al_xGa_{1-x}As$ is also verified, since a secondary peak is always present in the TSDC spectrum, either in the dark or after illumination with 0.8-eV monochromatic light.

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