X-ray induced persistent photoconductivity in Si-doped $Al_{0.35}Ga_{0.65}As$

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We demonstrate that x-ray irradiation can be used to induce an insulator–metal transition in Si-doped $Al_{0.35}Ga_{0.65}As$, a semiconductor with *DX* centers. The excitation mechanism of the *DX* centers into their shallow donor state was revealed by studying the photoconductance along with fluorescence. The photoconductance as a function of incident x-ray energy exhibits an edge both at the Ga and As *K* edge, implying that core–hole excitation of Ga and As are efficient primary steps for the excitation of *DX* centers. A high quantum yield ($\gg 1$) suggests that the excitation is indirect and nonlocal, due to secondary electrons, holes, and fluorescence photons. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1410894]

I. INTRODUCTION

Understanding the microscopic mechanisms of deep-level traps is important to semiconductor technology, due to their inevitable presence in many semiconductors. Deep-level traps can degrade device performance by acting as recombination centers in optical devices, such as lasers and light-emitting diodes, or by giving rise to high resistivity.[1] Examples of deep-level traps are Si dopants in $Al_xGa_{1-x}As$, which act as *DX* centers when $x > 0.22$.[2] *DX* centers can be optically excited to a shallow donor state using visible light. At low temperatures, this state is metastable because of the resulting structural rearrangement (Fig. 1).[3] In the ground state, substitutional Si dopants in Ga sites are displaced from the tetrahedral site resulting in a large bond-rupturing displacement.[4,5] In the excitation process, the Si atom moves to the tetrahedral site, and two electrons are injected into the conduction band, increasing the conductivity.[4,5] At temperatures below ~ 80 K the induced photoconductivity is persistent.[6] Excitation of *DX* centers using visible light has been studied extensively in various semiconductor compounds over the last few decades.[7–10] Here, we demonstrate that irradiation by x rays can also induce persistent photoconductivity in Si-doped $Al_{0.35}Ga_{0.65}As$. While phenomenologically the persistent photoconductivity and its erasure upon annealing is similar to the x-ray induced metallization observed in a transition metal oxide,[11] the underlying mechanisms are quite different.

There have been several attempts to determine the local structure of *DX* centers using x-ray absorption fine structure (XAFS).[12–15] So far, the results have been inconclusive. Conventional XAFS, which monitored the Se fluorescence of Se-doped AlGaAs, failed to show the large lattice relaxation.[13] Recently, a new method for XAFS, which measures the energy-dependent x-ray induced photocapacitance, has been suggested to be site-selective, and therefore, to reveal the large lattice relaxation.[14] On the other hand, XAFS studies on CdTe:In claimed that x rays do not induce photoexcitation based on the observation that consecutive XAFS scans were reproducible.[15] In order to resolve this puzzle, we studied the mechanism of x-ray excitation of *DX* centers by measuring the energy dependence of x-ray induced photoconductance along with fluorescence. Our key finding is that x rays are efficient in inducing photoconductance by exciting the *DX* centers. However, the excitation process is indirect, i.e., core–hole excitation of host atoms not directly bonded to *DX* centers can lead to the excitation of *DX* centers. Thus, standard x-ray techniques for determining the local structure of *DX* centers are complicated by x-ray induced changes in their configuration. Unfortunately, methods relying on monitoring the ability to change their configuration, e.g., measures sensitive to the carriers liberated after x-ray photoexcitation, are unsuitable because of the nonlocality of the photoexcitation process.

II. EXPERIMENTAL RESULTS

The sample consisted of a Si-doped $Al_{0.35}Ga_{0.65}As$ film, grown using molecular beam epitaxy by Quantum Epitaxial Design. Over a semi-insulating GaAs substrate the following layers were grown: a 200 nm thick GaAs buffer layer, a 1.5 μm thick $Al_{0.35}Ga_{0.65}As$ spacer, a 1 μm thick $Al_{0.35}Ga_{0.65}As$:Si layer, and a 10 nm thick GaAs cap layer. The doping concentration is estimated to be 5×10^{19} cm^{-3}, which was extracted from temperature de-

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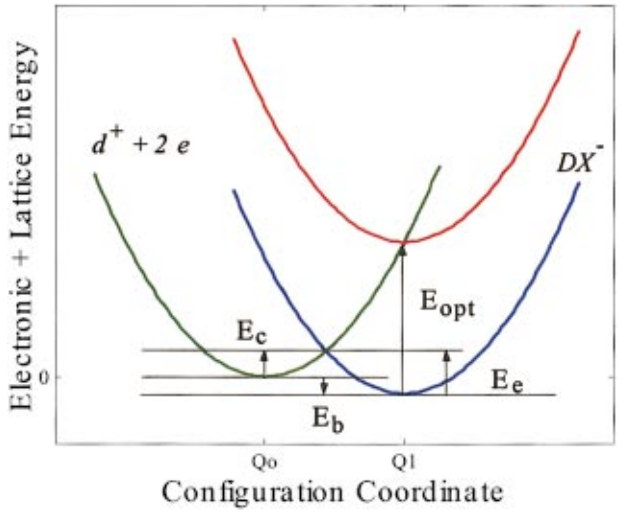

FIG. 1. (Color) Energy diagram for the large lattice relaxation model. The *DX* center in the ground state (configuration coordinate Q_1) can be optically excited to the metastable shallow donor state through an initial photon absorption E_{opt}, followed by lattice relaxation to configuration coordinate Q_0. The barrier E_c for the *DX* center to decay to the ground state, the binding energy E_b, and the barrier to excite the *DX* center E_e are shown in the diagram.

pendent Hall measurements.[16] The sample had a rectangular geometry with dimensions 5.2 mm×1.6 mm. Two ohmic contacts made of indium were separated by 4 mm. Conductance was measured using a lock-in amplifier in a two-terminal configuration. The excitation voltage was varied from 0.1 mV to 1 V (by 4 orders of magnitude) to cover the large range of conductance, which was independent of the excitation voltage.

Figure 2 shows the conductance measured as the sample was cooled in the dark. The warmup curve was almost the same, except for a small hysteresis, which exhibited a slightly lower conductance in the range $T \lesssim 150$ K. From 300 K down to 115 K, the conductance plotted on a logarithmic scale as a function of inverse temperature shows a linear

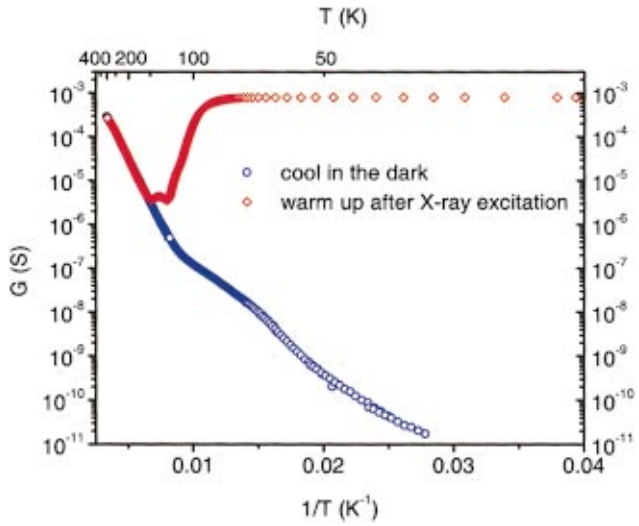

FIG. 2. (Color) Conductance as a function of temperature measured in the dark during the cooldown process plotted together with the conductance during warmup after persistent photoconductance was induced at 24 K.

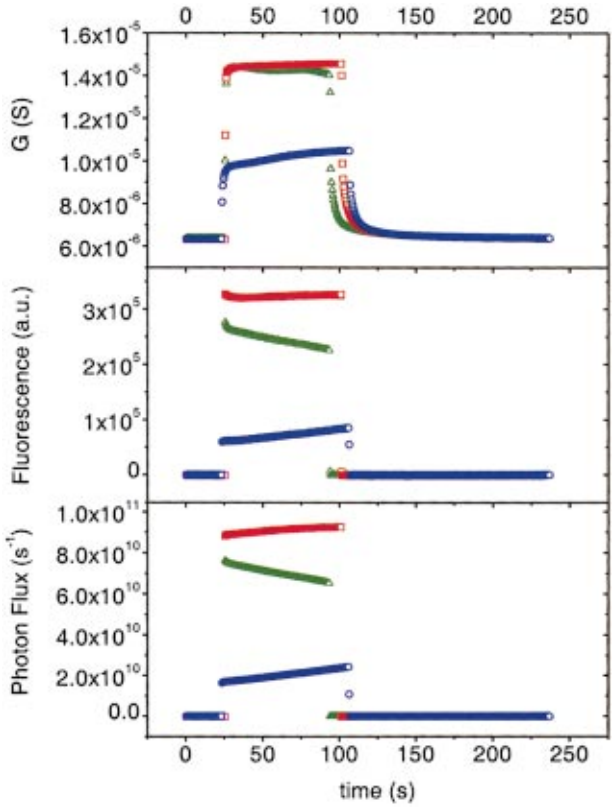

FIG. 3. (Color) Effect of x-ray irradiation on the photoconductance as a function of time at 160 K using a photon energy at the As *K* edge. The different curves correspond to different values for the photon flux. The fluorescence responds instantly to the x-ray irradiation and is proportional to the number of incident photons. The photoconductance responds with a time delay and is nonlinear in the photon flux, showing a saturation effect.

behavior. The steep decrease of the conductance is due to the trapping of electrons by *DX* centers. The slope corresponds to an activation energy of 0.118 eV for thermal carrier generation, which implies a *DX* center binding energy of 0.235 eV,[17] consistent with previously reported values.[18] In the range $70\text{K} > T > 50\text{K}$, we observe a much shallower slope, corresponding to an activation energy of 0.06 eV, which is due to traps associated with a different kind of impurity of very low concentration.

The x-ray experiments were conducted at beam line X16C at the National Synchrotron Light Source at Brookhaven National Laboratory. The x-ray beam was centered in the middle of the sample and was spread laterally to ~6 mm to illuminate the region between the two ohmic contacts. The vertical width of the beam was less than 1 mm. This is an improved beam geometry compared to our previous measurements in which we used a focused beam with a diameter on the order of 1 mm (much smaller than the distance between the ohmic contacts).[19] By illuminating the sample uniformly, we induce a uniform conductive channel between the ohmic contacts, resulting in a larger and faster response, and most importantly enabling the extraction of quantitative information. At 300 K, no photoconductivity was detected. The photoconductivity became noticeable around 210 K, where the effect was about 1%. Figure 3 shows the time-dependent response of the photoconductance

at 160 K to a varying incident photon flux together with the fluorescence. The energy of the incident x-ray beam was kept constant at the As *K* edge (11866 eV). In contrast to the fluorescence, which responds instantaneously to the incident x-ray flux, the photoconductance grows more gradually. In addition, while the fluorescence response is proportional to the incident flux, the photoconductance shows saturation. Both effects follow from the metastability of the photoexcited *DX* centers. As the beam is turned on, an excess population of donors in the shallow state builds up, and so increases the photoconductance. A finite time is required to reach the steady-state value for a given incident photon flux, and to decay thermally to the ground state when the beam is turned off.[20] The saturation effect arises due to the finite number of *DX* centers available for excitation, and becomes more pronounced at lower temperatures because the excited state becomes longer lived.

Energy scans of the photoconductance along with the fluorescence are plotted in Fig. 4 for both Ga and As *K* edges at 180 K. Here, the photoconductance was plotted after subtracting the dark current conductance. As depicted in both *K*-edge scans, the photoconductance closely follows the fluorescence scan, with steps in the photoconductance occurring at the same location as for the fluorescence. In addition, the step heights are similar for both *K* edges: 8.7×10^{-7} S for the Ga *K* edge (10366 eV) and 8.0×10^{-7} S for the As *K* edge with an incident flux of 4.2×10^{10} photons/s. This result has several significant implications. First, it demonstrates that core–hole excitation is an efficient primary step for the excitation of *DX* centers. Second, it suggests that the dominant mechanism for the x-ray excitation of *DX* centers is indirect. The fact that the additional photoconductance obtained by opening up a new core–hole excitation channel is similar for As and Ga shows that direct proximity of the absorber to the Si dopant is not required since the Si dopants are most likely directly bonded to As, not Ga.

As displayed in Fig. 5, persistent photoconductivity was induced at 24 K by illuminating the sample with both a defocused and focused Ga *K*-edge beam. After a few minutes of x-ray irradiation with the defocused beam, the conductance rose sharply by more than 7 orders of magnitude. The saturated value of the conductance was 8.0×10^{-4} S, higher than the room temperature conductance of 2.7×10^{-4} S. In contrast, the focused beam caused the conductance to rise at a rate of only 3% of the defocused-beam rate, and it took 1 order of magnitude longer to reach a saturation value of 7.4×10^{-4} S (lower than the saturation value of the defocused beam). At the saturated value of the conductance, the sample may be considered to be metallic. The photoconductance persisted even after the beam was turned off and remained constant during the monitored time (>17.5 h).

The thermal decay of the persistent photoconductance, monitored during the warmup process in the dark (Fig. 2), shows an annealing temperature of about 100 K. The conductance reaches a minimum around 120 K and starts rising as the system is warmed up further. Anomalous behavior is observed around 135 K, where the conductance drops again

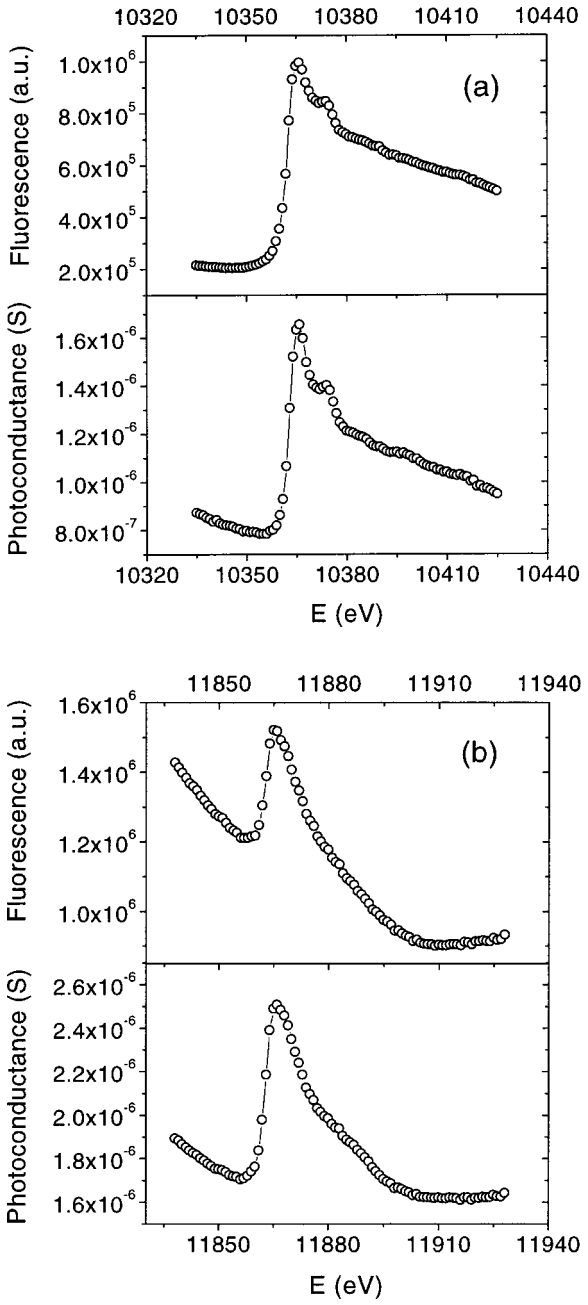

FIG. 4. Energy-dependent photoconductance measured simultaneously with the fluorescence intensity at 180 K. Scan (a) and (b) correspond to the Ga and As *K* edge, respectively. The photoconductance exhibits an edge at the same location as the fluorescence for both Ga and As *K* edges, implying that core–hole excitation is an efficient primary step for the excitation of *DX* centers.

before starting to rise at 150 K. At this temperature, the curve merges with the dark current conductance. We speculate that the small peak at 135 K arises from electron capture by a second kind of *DX* center, with a somewhat higher capture barrier. The ratio of the concentrations of the two types of *DX* centers can be roughly estimated from the ratio of the conductance at saturation to the conductance at the minimum around 120 K. This value is approximately 200, the majority of the *DX* centers having an annealing temperature of about 100 K.

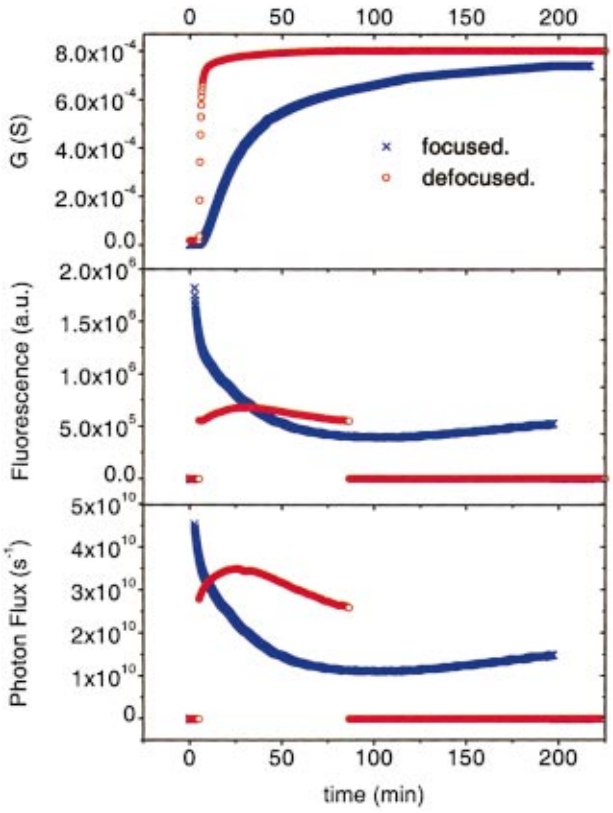

FIG. 5. (Color) Persistent photoconductance induced at 24 K using both a defocused and focused beam with energy at the Ga *K* edge. For the defocused beam case, the conductance rose sharply upon x-ray irradiation, and saturated at 8.0×10^{-4} S. The conductance remained persistent after the beam was turned off for more than 17 h, with no signs of decaying. For the focused beam case, the conductance rose at a rate of only 3% of the defocused-beam rate and it took 1 order of magnitude longer time to reach a saturation value of 7.4×10^{-4} S (lower than the saturation value of the defocused beam).

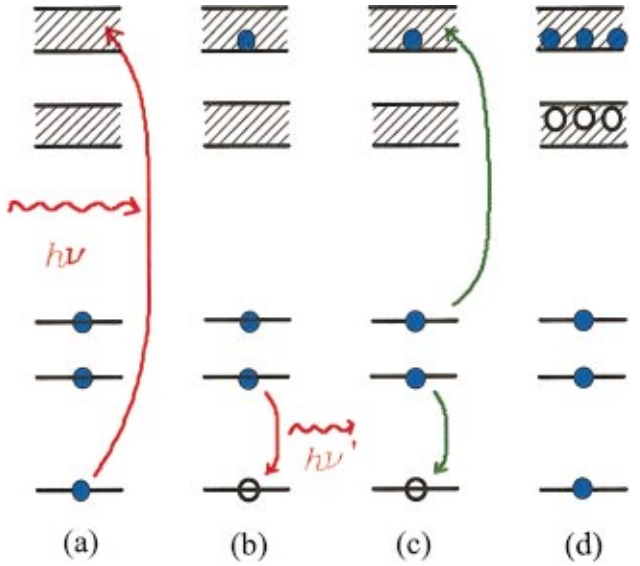

FIG. 6. (Color) (a) Initial core–hole excitation, followed by either (b) photon emission, or (c) an Auger decay, which eventually leads to (d) the collection of secondary carriers thermalized at the band edges.

III. DISCUSSION

The quantum yield Q, defined as the number of *DX* centers converted into shallow donors per incident photon, can be extracted from the photoconductance data at 24 K and is given by

$$\frac{dG/dt\times N_{\mathrm{sat}}}{2G_{\mathrm{sat}}I_0}. \tag{1}$$

Here dG/dt is the initial slope of the conductance, N_{sat} is the total number of photogenerated electrons at saturation, G_{sat} is the saturated value of the conductance, and I_0 is the incident photon flux. Previous measurements using visible light have shown that the saturation density of photogenerated carriers in this sample is $n_{\mathrm{sat}}\sim4\times10^{18}$ cm^{-3}.[16] From the measured values for $dG/dt=1.2\times10^{-5}$ S/s, $N_{\mathrm{sat}}\sim3\times10^{13}$, G_{sat}, and $I_0=2.8\times10^{10}$ photons/s, we obtain $Q\approx8$ for the defocused beam. Analogous calculations for the focused beam case yield a value of $Q\approx0.2$, which is a factor of ~40 smaller. This clearly illustrates the importance of the beam and electrical contact geometries when determining the measured efficiency of the photoexcitation process, which is properly obtained by uniformly illuminating the sample. The fact that for each incident photon a large number of *DX* centers are converted to shallow donors is strong evidence for our model of indirect excitation of *DX* centers. From this value of Q, we can judge the extent to which the excitation process is nonlocal. The starting point is to note that at the Ga *K* edge, the penetration depth of the incident photons is ~15 μm. Thus, the number of incident photons absorbed in the 1 μm thick Si-doped layer is 1/15 of the incident photons. If photon absorption only within the next-nearest neighbor shell of the Si donor were to lead to excitation, the maximum value for Q could be approximated by the donor to host atom density ratio (which is on the order of 10^{-3}) times the number of nearest (for the As *K* edge) or next-nearest (for the Ga *K* edge) neighbors, multiplied by the probability that a photon is absorbed in the active layer ($\sim1/15$). This would give $Q\sim10^{-3}$. From our result of $Q\gg1$, it is evident that the excitation is highly nonlocal and secondary processes need to be invoked to describe the excitation of *DX* centers. A comparison of the cross section for the excitation of *DX* centers (2×10^{-15}cm^2) with the cross section for core–hole excitation (3×10^{-20}cm^2) further illustrates the efficiency of the former process.

After the initial core–hole excitation, Auger processes or secondary photon emission occur, which create a cascade of secondary electrons, holes, and photons (Fig. 6). Eventually, these secondary electrons and holes thermalize to the band edges. The extent of nonlocality of the excitation process is governed by the diffusion length of the secondary photons and holes. It is worthwhile to compare the newly discovered phenomenon — excitation induced by x rays — to the previous experiments using visible light since the energy scale of the incident photons differs by more than 3 orders of magnitude. Interestingly, the excitation process is indirect in both cases. When using visible light, the most efficient way to excite *DX* centers is by first creating electron–hole pairs through band-gap excitation. The electrons and holes diffuse and thermalize to the band edges. A hole recombines with a

DX center, which excites the *DX* center into a shallow donor. As a consequence, an electron is emitted to the conduction band, resulting in the generation of two electrons in the conduction band for each band-gap excitation. Although the x-ray excitation process initially involves a core–hole excitation, the subsequent processes induced by the secondarily generated carriers, which eventually thermalize at the band edges, are the same as for visible light.

IV. SUMMARY

To summarize, we have investigated the excitation of *DX* centers using x rays in Si-doped $Al_{0.35}Ga_{0.65}As$. Our key results are that x rays are very efficient in inducing photoconductivity and that the predominant excitation mechanism is indirect and nonlocal. Secondary electrons, holes, and photons, which are created following the original core–hole excitation, are primarily responsible for the conversion of the *DX* centers into their shallow donor state. Therefore, each absorbed incident photon converts a large number of *DX* centers, resulting in a high quantum yield for the conversion process. The extent of nonlocality is governed by the diffusion of the secondary photons and charge carriers. We propose this photon energy-dependent photoconductance as a novel method to measure XAFS in such systems since the absorption of x rays is directly manifested in the photoconductance. The size of the system where this new XAFS method is applicable is limited only by the ability to attach current/voltage leads.

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