X-ray induced persistent photoconductivity in Si-doped Al\textsubscript{0.35}Ga\textsubscript{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\textsubscript{0.35}Ga\textsubscript{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.

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. Examples of deep-level traps are Si dopants in Al\textsubscript{x}Ga\textsubscript{1-x}As, which act as DX centers when \(x > 0.22\). DX centers can be optically excited to a shallow donor state. At low temperatures, this state is metastable because of the resulting structural rearrangement (Fig. 1A). In the ground state, substitutional Si dopants in Ga sites are displaced from the tetrahedral site resulting in a large bond-rupturing displacement. In the excitation process, the Si atom moves to the tetrahedral site, and two electrons are injected into the conduction band, increasing the conductivity. At temperatures below \(\sim 80\) K the induced photoconductivity is persistent. Excitation of DX centers using visible light has been studied extensively in various semiconductor compounds over the last few decades. Here, we demonstrate that irradiation by X-rays can also induce persistent photoconductivity in Si-doped Al\textsubscript{0.35}Ga\textsubscript{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, 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). 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. 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. On the other hand, XAFS studies on CdTe:In claimed that X-rays do not induce photoc excitation based on the observation that consecutive XAFS scans were reproducible. 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 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 non-locality of the photoexcitation process.

The sample consisted of a Si-doped Al\textsubscript{0.35}Ga\textsubscript{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\textsubscript{0.35}Ga\textsubscript{0.65}As spacer, a 1 µm thick Al\textsubscript{0.35}Ga\textsubscript{0.65}As:Si layer, and a 10 nm thick GaAs cap layer. The doping concentration is estimated to be \(5 \times 10^{19}\) cm\(^{-3}\), which was extracted from temperature dependent Hall measurements.

Figure 2 shows the conductance measured as the sample was cooled in the dark. From 300 K down to 115 K, the conductance plotted on a logarithmic scale as a function of inverse temperature shows a linear behavior. The steep decrease of the conductance is due to the carriers liberated after X-ray photoexcitation, are compensated by X-ray induced changes in their configuration. The steep decrease of the conductance is due to the carriers liberated after X-ray photoexcitation, are compensated by X-ray induced changes in their configuration.

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 \(\sim 6\) mm to illuminate the region between...
the two ohmic contacts. The vertical width of the beam was less than 1 mm. At 300 K, no photoconductivity was detected. The photoconductivity became noticeable around 210 K, where the effect was about 1%. Fig. 2 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. 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. 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. 1 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 follows closely 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: $8.7 \times 10^{-7}$ S for the Ga K-edge with an incident flux of $4.15 \times 10^{10}$ photons/s, and $8 \times 10^{-7}$ S for the As K-edge with $4.23 \times 10^{10}$ 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 absorbe to the Si dopant is not required since the Si dopants are believed to be directly bonded to As, not Ga.

As displayed in Fig. 1, persistent photoconductivity was induced at 24 K by illuminating the sample with a defocused Ga K-edge beam. After a few minutes’ X-ray irradiation, the conductance rose sharply by more than seven orders of magnitude. The saturated value of the conductance was $8.04 \times 10^{-4}$ S, higher than the room temperature conductance of $2.66 \times 10^{-3}$ S. At this value, the sample may be considered metallic. The photoconductance persisted even after the beam was turned off and remained constant during the monitored time, which was 17.5 hrs. The thermal decay of the persistent photoconductance, monitored during the warm up process in the dark (Fig. 3), shows an annealing temperature $\sim 100$ K.

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

$$\frac{dG/dt \times N_{\text{sat}}}{2G_{\text{sat}}I_0}.$$  

Here $dG/dt$ is the initial slope of the conductance, $N_{\text{sat}}$ is the total number of photogenerated electrons at saturation, $G_{\text{sat}}$ 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 $n_{\text{sat}} \sim 4 \times 10^{18}$ cm$^{-3}$. From the measured values for $\frac{dG}{dt} = 1.33 \times 10^{-5}$ S/s, $N_{\text{sat}} \sim 3 \times 10^{13}$, $G_{\text{sat}}$, and $I_0 = 2.8 \times 10^{10}$ photons/s, we obtain $Q \sim 10$. 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 non-local. The starting point is to note that at the Ga K-edge, the penetration depth of the incident photons is $\sim 15$ 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 of the order of $10^{-3}$) times the number of nearest (for As K-edge) or next-nearest (for Ga K-edge) neighbors, multiplied by the probability that a photon is absorbed in the active layer ($\sim 1/15$). This would give $Q \sim 10^{-3}$. Our result of $Q \gg 1$, it is evident that the excitation is highly non-local 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 ($2 \times 10^{-15}$ cm$^2$) with the cross-section for core-hole excitation ($3 \times 10^{-20}$ 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. 2). Eventually, these secondary electrons and holes thermalize to the band edges. The extent of non-locality 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 differ by more than three 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 in the visible light case.

To summarize, we have investigated the excitation of DX centers using X-rays in Si-doped Al0.35Ga0.65As. Our key results are that X-rays are very efficient in inducing photoconductivity and that the predominant excitation mechanism is indirect and non-local. 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 non-locality is governed by the diffusion of the secondary photons and charge carriers.

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FIG. 1. A 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 $E_b$ for the DX center to decay to the ground state, the binding energy $E_b$, and the barrier to excite the DX center $E_a$ are shown in the diagram. B (a) Initial core-hole excitation, followed by either (b) photon emission, or (c) Auger process, which eventually leads to (d) the collection of secondary carriers thermalized at the band edges.

FIG. 2. Conductance as a function of temperature measured in the dark during cool down process plotted together with the conductance during warm up after persistent photoconductance was induced at 24 K.

FIG. 3. Effect of X-ray irradiation on the photoconductance as a function of time. 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.

FIG. 4. Energy-dependent photoconductance measured simultaneously with the fluorescence yield 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, respectively. The fluorescence 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.

FIG. 5. Persistent photoconductance induced at 24 K using a defocused beam with energy at the Ga K-edge. The conductance rose sharply upon X-ray irradiation, and saturated at 8.0 $\times$ 10$^{-4}$ S. The conductance remained persistent after the beam was turned off for more than 17 h, with no signs of decaying.
Soh *et al.* Fig. 1
Soh et al. Fig. 2

The figure shows the activation energy distribution for a material. The activation energy is given by the parameter $G(S)$. The plot represents the system's behavior under two conditions: cooling in the dark (blue circles) and warming up after X-ray excitation (red diamonds). The x-axis represents the inverse temperature $1/T (K^{-1})$, while the y-axis shows the activation energy $G(S)$. The data points highlight the change in activation energy with temperature.
Soh et al. Fig. 3
Soh et al. Fig. 5