

Photoconduction extended x-ray-absorption fine structure of GaAs

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Photoconduction spectra of GaAs samples at photon energies around the Ga and As *K* edges were measured. Extended x-ray-absorption fine-structure oscillation was observed in these spectra. It is found that the spectrum shape of the photocurrent depends on the sample thickness. A microscopic theory is presented to determine the photoconduction response to x-ray absorption. The theory is in good agreement with experiment.

Extended x-ray-absorption fine structure (EXAFS) was first observed in transmission measurements of the x-ray-absorption coefficients.¹ Later, it was found that the phenomenon of EXAFS oscillation exists also in a wide class of processes that involve the relaxation of excited electrons after the absorption of x-ray photons in solids. These are the EXAFS of fluorescence,² total electron yield,³ x-ray-excited optical luminescence (XEOL),⁴ elastic Auger yield,⁵ and photoacoustics,⁶ etc. They have attracted much attention and are widely used currently.⁷

EXAFS oscillation in photoconduction signals in a liquid was observed by Sham and Holroyd,⁸ who showed that the spectrum shape was dependent on the sample thickness, just as in the case of XEOL, and was quite different from the transmission spectrum. In this work, we have measured the photoconduction spectra of GaAs samples of different thickness at photon energies around the *K* edges of Ga and As, and developed a microscopic theory to account for the experimental results.

To decrease the dark current we used the Cr-doped semi-insulator GaAs as our sample, with a resistivity ρ larger than $10^7 \Omega \text{ cm}$ at room temperature. Two samples *A* and *B* were prepared. The electrodes of sample *A* (Fig. 1) were made of indium pellets on the sample surface, *d* (the electrode depth into the sample) was about $3 \mu\text{m}$, and *L* (the gap between the electrodes) was 2 mm. Sample *B* was a GaAs crystal cut into a strip of 1 mm in width, 15 mm in length, and 2 mm in thickness (Fig. 2). The electrical contact of the two $15 \times 2 \text{ mm}^2$ indium elec-

trodes on both flanks of sample *B* was secured by indium alloy. In this case, *L* and *d* were thus 1 and 2 mm, respectively.

The experimental setup was simple. The second ion chamber in transmission measurements was replaced by the sample, which was used as a detector to measure the photocurrent.

The spot of x-ray photons from beamline 4W1B at the Beijing Synchrotron Radiation Facility was defined by a slit of size $0.5 (H) \times 12 (V) \text{ mm}^2$ and monochromatized by a Si(111) double-crystal monochromator. Higher harmonics were rejected by detuning the Bragg angle of the second crystal of the monochromator. The electron energy and current of the storage ring were 2.2 GeV and 30 mA, respectively, during the experiment. After going through the first ion chamber (intensity monitor), the monochromatized x-ray beam shone on the sample which was submerged in liquid nitrogen at 77 K to reduce the thermal excitation of carriers. A dc voltage of 300 V was applied to the electrodes and the photoconduction current was measured by a Keithley 427 current amplifier. Fluorescence EXAFS was also measured. The incident x-ray beam and the fluorescence detector were in a plane perpendicular to the sample surface, and made the same angle of 45° from both sides with the surface normal. For comparison, a conventional transmission EXAFS measurement of GaAs powder was conducted at 77 K.

The photoconduction spectra of samples *A* and *B* were

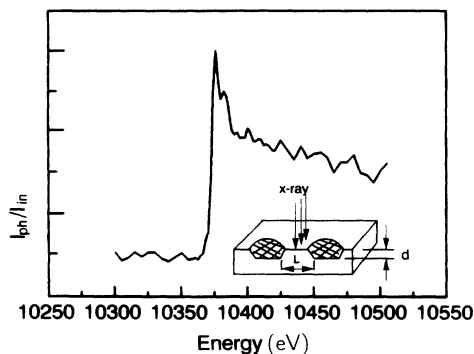


FIG. 1. Photoconduction spectra of sample *A*.

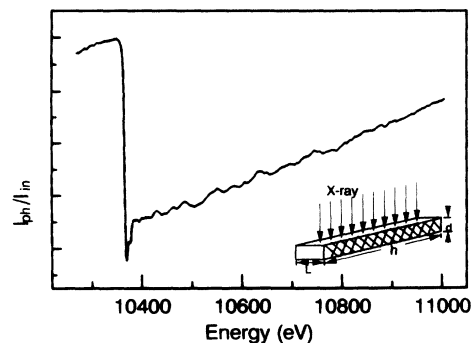


FIG. 2. Photoconduction spectra of sample *B*.

measured around the K edges of Ga and As. The results around the Ga K edge are plotted in Figs. 1 and 2, where the ordinate represents the photoconduction current I_{ph} normalized to the current of the incident photon monitor I_{in} , and the abscissa represents the incident photon energy.

It is seen EXAFS-type oscillation exists in the photoconduction spectra from both samples. The spectrum shape for sample A is identical to the ordinary transmission EXAFS spectrum, while for sample B the spectrum is inverted, dropping abruptly at the K edge of Ga, and rising with energies both before and after the K edge. This shape was observed also in XEOL spectra.⁹ The spectra around the As K edge are similar to the corresponding ones around the Ga K edge.

For analysis, the photoconduction spectrum of sample B is inverted to compare with the transmission EXAFS spectrum of GaAs, as they are drawn together in Fig. 3(a), where the background has been removed from both spectra by linear fitting and both are normalized. It is clear that the amplitude of the EXAFS oscillation in the photoconduction spectrum is smaller than that in the transmission case.

A comparison between the Fourier transforms of the photoconduction measurements, fluorescence measurement, and transmission absorption measurement for sample B around the Ga K edge is shown in Fig. 3(b) within the range of $k = 2.6 - 13 \text{ \AA}^{-1}$ and with linear weight in k adopted (no phase correction was made). It is seen that the positions of the coordination peaks coincide while the

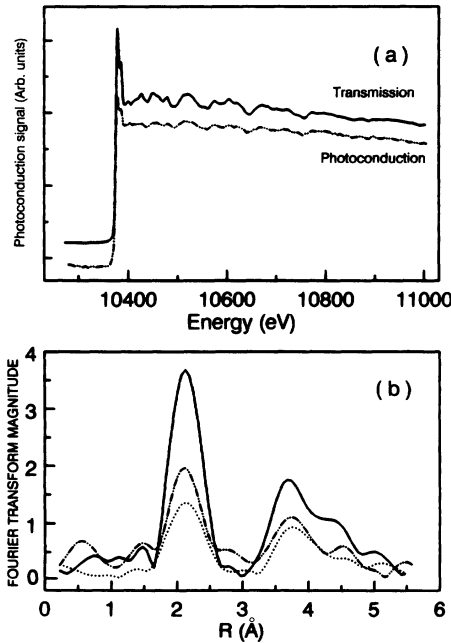


FIG. 3. (a) Comparison of the photoconduction of sample B in Fig. 2 with transmission spectrum. Background has been removed by linear fitting and the spectra normalized. The photoconduction spectra has been inverted. (b) Fourier transform of the transmission (solid line), photoconduction (dash-dotted line), and fluorescence (dotted line) EXAFS. No phase-shift correction has been considered. k weight was adopted.

heights are different. The intensity of the peaks in the photoconduction and fluorescence spectra is weaker than that in the transmission spectrum. Taking the transmission spectrum as the "known" standard, the distance and coordination number of the first shell of the Ga atoms can be determined from the photoconduction spectrum. The distance thus determined deviates only by $\pm 0.008 \text{ \AA}$ from the standard one, i.e., it is exact within the accuracy of EXAFS experiments. The coordination number determined in this way deviates from the standard one by 60%. This is very similar to the analysis in fluorescence EXAFS measurements of high-concentration samples, where self-absorption correction must be considered.

We now establish a microscopic theory for the analysis of the EXAFS phenomenon in photoconduction spectra. The absorption of x rays in a semiconductor produces a number of secondary electrons and holes in the sample through a series of complicated processes. The yield of these electron-hole pairs is¹⁰

$$Y(E) = \frac{E}{\epsilon}, \quad (1)$$

where E is the energy of the incident x-ray photons and ϵ is the radiation ionization energy, i.e., the average energy required to produce an electron-hole pair. For GaAs at 77 K, $\epsilon = 4.9 \text{ eV}$.

Extra carriers are produced by x rays. If we denote the number of extra electrons and holes per unit volume by Δn and Δp , respectively, then the photoconduction caused by extra carriers has the form¹¹

$$\begin{aligned} \Delta\sigma(E) &= q(\Delta n\mu_n + \Delta p\mu_p) \\ &= \frac{q(\mu_n\tau_n + \mu_p\tau_p)SI_{AB}(E)Y}{L^2} = AI_{AB}(E)E, \end{aligned} \quad (2)$$

$$A = \frac{q(\mu_n\tau_n + \mu_p\tau_p)S}{L^2\epsilon},$$

where I_{AB} is the flux density of absorbed photons (photon/cm²s); S is the area illuminated by the x rays; μ_n and μ_p are the electron and hole mobility, respectively; τ_n and τ_p are the lifetimes of extra electrons and holes, respectively; and L is the distance between the electrodes. From Eq. (2), the photocurrent induced by x-ray absorption is

$$\Delta I(E) = \Delta\sigma(E)V = AI_0(E)VE, \quad (3)$$

where V is the voltage applied on the electrodes of the sample.

Since for a specific sample and a given voltage V , A is a constant, from Eq. (3) the photoconduction current will be proportional to the energy of the incident x-rays photons. We tested this linear relation within an energy range of 1.5 keV just below the Ga K edge; the result was in the affirmative. This linear relation exists also in XEOL spectra.¹²

In passing through a sample, x-ray photons are absorbed by the photoelectric effect and undergo elastic and Compton scattering on electrons. Some photons escape

the sample by scattering. As the energy of the incident x rays becomes close to the K edge, absorption increases drastically and the photoconduction increases consequently. On the other hand, the escape of fluorescence photons as well as photoelectrons and Auger electrons tends to decrease the photoconduction. With these processes taken into consideration, the photocurrent can be written as

$$\Delta I(E) = AVI_0(E) \left\{ \left[1 - \exp[-\mu_t(E)d] \right] E - \sum_{i,j} I_{fi,j}(E) E_{fi,j} - \sum_{i,j} I_{ai,j}(E) E_{ai,j} - \sum_{i,j} I_{si,j}(E) E_{si,j} \right\}, \quad (4)$$

where $I_{fi,j}$, $I_{ai,j}$, and $I_{si,j}$ represent the intensity of the fluorescence, Auger, and scattering processes, respectively; $E_{fi,j}$, $E_{ai,j}$, and $E_{si,j}$ the energy of the fluorescence photons, the Auger electrons, and the scattering photons, respectively; μ_t is the total absorption coefficient; and I_0 is the flux density (photons/cm²s) of the incident x rays.

In our experiment, the effect of scattering is negligible, since the cross sections are small at low energies.¹³ The mean free paths of Auger electrons and photoelectrons are much shorter than the sample thickness in this experiment, and their effect on the photocurrent is negligible in comparison with fluorescence, which is by far the dominant process in photoconduction. In what follows we will concentrate on the contribution of this process to photoconduction.

We denote the fluorescence intensity escaping from the forward and the backward sample surfaces by I_{ff} and

I_{fb} , respectively. They can be calculated by the expressions

$$I_{ff}(E) = \frac{\Omega}{4\pi} \sum_{i,j} \frac{I_0(E) \omega_i f_{i,j} \mu_i(E)}{\mu_t(E) + \mu_t(E_{fi,j}) \cos \theta_i / \cos \theta_f} \times \left[1 - \exp \left[-\frac{\mu_t(E)}{\cos \theta_i} + \frac{\mu_t(E_{fi,j})}{\cos \theta_f} \right] d \right], \quad (5)$$

$$I_{fb}(E) = \frac{\Omega}{4\pi} \sum_{i,j} \frac{I_0(E) \omega_i f_{i,j} \mu_i(E)}{\mu_t(E_{fi,j}) \cos \theta_i / \cos \theta_b - \mu_t(E)} \times \left[\exp \left[-\frac{\mu_t(E)d}{\cos \theta_i} \right] - \exp \left[-\frac{\mu_t(E_{fi,j})d}{\cos \theta_b} \right] \right], \quad (6)$$

where θ_i represents the incident angle of the x rays to the normal of the sample surface; θ_f and θ_b represent the angles between the fluorescence radiation and the normal of the forward and the backward surfaces, respectively; ω_i represents the fluorescent yield from the K shell of element i ($i = \text{Ga}$ or As); $f_{i,j}$ the transition probability in the K series (e.g., $K\alpha$, $K\beta$, etc.); μ_i the absorption coefficient of element i ; $\mu_t(E_{fi,j})$ the total absorption coefficient at fluorescence energy $E_{fi,j}$; and Ω the solid angle.

It is necessary to integrate over the solid angle in order to calculate the contribution of all the fluorescence photons escaped from the sample. From Eqs. (4)–(6), the photocurrent has the form

$$\Delta I(E) = AVI_0(E) \left\{ \left[1 - \exp[-\mu_t(E)d] \right] E - \sum_{i,j} \frac{\omega_i f_{i,j} \mu_i(E) E_{fi,j}}{2} \times \int_0^{\pi/2} \left[\frac{1 - \exp\{-[\mu_t(E)/\cos \theta_i + \mu_t(E_{fi,j})/\cos \theta]d\}}{\mu_t(E) + \mu_t(E_{fi,j}) \cos \theta_i / \cos \theta} + \frac{\exp[-\mu_t(E)d/\cos \theta_i] - \exp[-\mu_t(E_{fi,j})d/\cos \theta]}{\mu_t(E_{fi,j}) \cos \theta_i / \cos \theta - \mu_t(E)} \right] \sin \theta d\theta \right\}. \quad (7)$$

For very thin samples, we have

$$\Delta I(E) = AVI_0(E)d \left[\mu_t(E)E - \sum_{i,j} \frac{\omega_i f_{i,j} \mu_i(E)}{\cos \theta_i} E_{fi,j} \right] \quad (8)$$

and for thick samples, we have

$$\Delta I(E) = AVI_0(E) \left\{ E - \sum_{i,j} \frac{\omega_i f_{ij} \mu_i(E)}{2\mu_t^2(E)} \left[\mu_t(E_{fi,j}) \cos \theta_i \ln \left[\frac{\mu_t(E_{fi,j}) \cos \theta_i}{\mu_t(E) + \mu_t(E_{fi,j}) \cos \theta_i} \right] + \mu_t(E) \right] E_{fi,j} \right\}. \quad (9)$$

In our experiment, $\theta_i = 0$, and the photocurrent spectra calculated with the help of Eq. (7) with respect to different values of d are shown in Fig. 4. The absorption coefficients used for the calculation are quoted from Ref.

13. It is seen that the spectrum shape changes with d , the thickness of the sample. For thin samples the spectrum shape is like that in the transmission case; there is a jump at both the Ga and As K edges, and for energies above

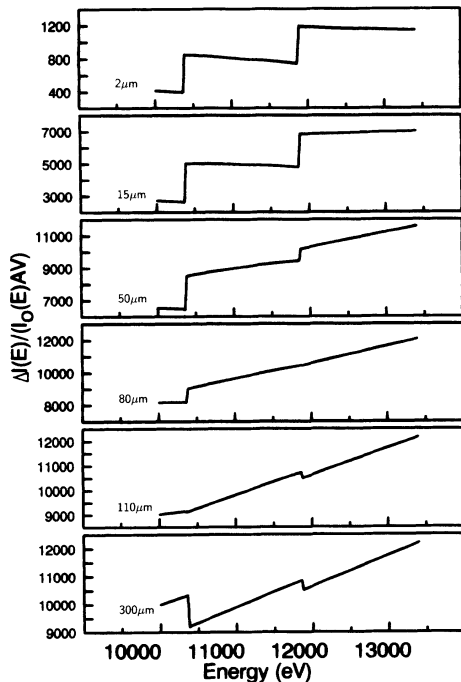


FIG. 4. Calculated results according to Eq. (7) for different sample thickness d .

and below these edges the photocurrent is a decreasing function of the photon energy. For samples of thickness about $15 \mu\text{m}$, the photocurrent at energies above the As K edge starts to increase with photon energy. The reason is that absorption starts to dominate over other factors in the energy dependence in Eq. (7). For samples of thickness about $50 \mu\text{m}$, the photocurrent becomes an increasing function at energies above both the Ga and As K edges; the jump height decreases with increasing thickness d . For samples of thickness about $75 \mu\text{m}$, the spectrum shape at the As K edge is converted. For samples of thickness about $110 \mu\text{m}$, the spectrum shape is also converted at the Ga K edge. For samples thicker than $300 \mu\text{m}$, x rays are in fact totally absorbed in the samples, and the photocurrent spectrum will not change with thickness. It is remarkable that at some particular thickness the photocurrent spectrum loses its near-edge resonance feature. This phenomenon has been observed in liquid photoconduction measurements.⁸

With the fact that the scattering photons and Auger electrons have a probability of escaping from the sample taken into consideration, the change of the photocurrent spectrum shape will occur at smaller thicknesses. Furthermore, if the secondary fluorescence is also taken into consideration, the inversion of the spectrum at the As K edge will occur at even smaller thicknesses.

We have calculated the photoconduction and fluorescence XAFS spectra at the Ga K edge by Eqs. (9) and (5), respectively. In the calculation the data from the transmission spectrum measured on sample B at energies around the Ga K edge are taken for the total absorption coefficient $\mu_t(E)$, and the values for μ_{As} are from Ref. 13. The calculated photoconduction spectrum is put together with the measured one in Fig. 5(a), from which it is seen that the agreement between theory and experiment is

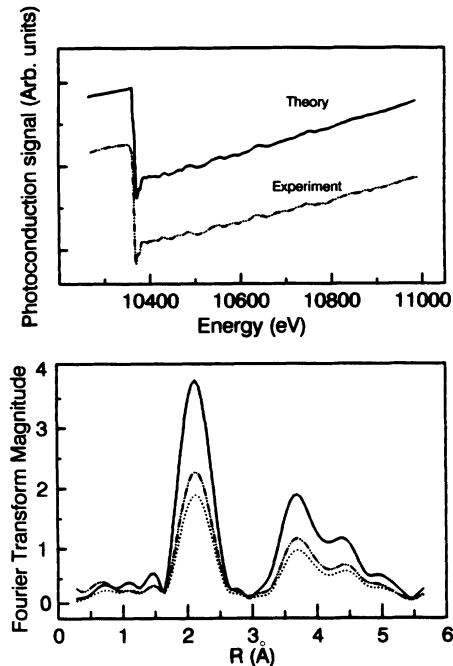


FIG. 5. (a) Photoconduction spectra calculated according to Eq. (5) and experimental of sample B . (b) Fourier transforms of the transmission spectrum (solid line) and theoretical spectra of photoconduction (dash-dotted line) and fluorescence (dotted line).

quite good. The Fourier transforms of the calculated photoconduction spectrum, the calculated fluorescence spectrum, and the measured absorption spectrum from sample B are put together in Fig. 5(b). Comparing Fig. 5(b) with Fig. 3(b), we see that the theory and experiment are in good agreement.

In conclusion, we have observed EXAFS oscillation in photoconduction spectra from GaAs samples, which contains the same EXAFS information on the neighboring structure of the absorbing atoms as in the transmission absorption measurements. However, care must be taken in getting the coordination number from the photocurrent EXAFS spectrum, and due correction must be made. An immediate application of this observation is that the sample under study can be used directly as the detector for measuring the x-ray absorption, instead of resorting to an extra detector like the second ion chamber in the transmission measurement case or the semiconductor detector in fluorescence measurements. This might turn out to be useful in some particular cases, such as the study of particular layers in some semiconductor devices.

We have presented a theory for the calculation of the photoconduction response to x-ray absorption in a semiconductor sample, which accounts for the measured spectrum shape, in particular, the dependence of the spectrum shape on the sample thickness, quite well. The theory applies also to XEOL experiments.

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