Observation of a Photoinduced Lattice Relaxation in CdTe:In

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The local atomic structure of CdTe:In at an In concentration of 6 at. % was investigated by x-ray absorption spectroscopy before and after photoexcitation at 80 K. After photoexcitation, In K edge spectra change in both the near-edge and x-ray absorption fine structure (XAFS) regions, showing a change in local structure. Cd and Te structural parameters are consistent with the structure of CdTe and did not change after photoexcitation. For In, only the first shell contribution is present in the XAFS, indicating a disordered environment beyond the first shell of neighbors. The relation of these observations with the proposed model of a DX center for CdTe:In is discussed.

The study of metastable defects in compound semiconductors has received recent attention due to its implications to the problem of intrinsic limits to doping [1,2] and the fact that these defects can lead to many body phenomena such as photoinduced structural changes [3–6]. The observation of persistent photoconductivity (PPC) and persistent electron paramagnetic resonance (PEPR) in some doped semiconductors, along with the observation of a large difference between the photoionization threshold energy and the thermal level position of defects, suggests that large lattice relaxations are relevant in these phenomena [7,8]. Among the theoretical models of metastable defects, which involve large lattice relaxations, are the DX center with a single breaking bond (SBB) [4], which has been predicted for CdTe:In, and other doped semiconductors [4,9]. This model yields to a negative Hubbard energy U with trapping of two carriers which form a pair in the defect, and can explain PPC and PEPR. Also, if the level of the SBB center lies in the conduction band near the conduction band minimum (CBM) as a resonance, then, at some level of doping, some of the carriers become trapped in this relaxed state. This leads to Fermi level pinning and can explain the existence of intrinsic limits to doping [1]. In this and other models, the local atomic structure of the defect is correlated with its charge state. Hence, a change of the charge state of the defect, e.g., by illumination, will lead to a change of atomic structure [4].

There are few experimental techniques that can provide quantitative information about the microscopic structure around defects helping to test the predictions of theoretical models. X-ray absorption fine-structure spectroscopy (XAFS) has proven to be a useful technique to characterize lattice distortions in semiconductors [10–12]. Photoinduced structural changes have been observed in $Ga_{0.78}Al_{0.22}As$:Sn using high resolution x-ray diffraction [13]. These changes are reflected in the expansion of the lattice constant under illumination. It is difficult, however, to relate this expansion to the local atomic structure around the defect. Nevertheless in other systems, such as the semiconducting parents of high-temperature superconductors, local structural changes produced by illumination have been recently reported [14]. These systems also exhibit electronic changes under photoexcitation, e.g., PPC and photoinduced superconductivity [15].

In the specific case of CdTe:In, the maximum doping concentration after which carrier passivation occurs is $\sim 10^{18}$ [3,16]. This value is consistent with the prediction of an energy of ~ 40 meV above the CBM for the formation of an SBB center [4]. However, some experiments in CdTe:In, in the doping range $\leq 10^{18}$, indicate that the formation of donor-Cd vacancy centers (In_{Cd}-V_{Cd}) can play a major role in passivation [17,18]. Nevertheless, for higher In concentrations experiments indicate that carrier passivation is controlled by the appearance of centers with large lattice relaxation [1,12,19]. Also, SBB-like centers in CdTe:In have been inferred from conductivity experiments under hydrostatic pressure and with alloying with Zn [7].

Consequently, we have selected a sample of CdTe:In in a heavily overdoped regime, which presents strong carrier passivation and PPC, to study possible photoinduced structural changes. A CdTe:In with a 6 at. % indium sample was prepared using close-spaced vapor transport combined with free evaporation in the form of a (~ 80 μm) thick film, which was shaved from the substrate to produce a powder sample for the XAFS measurements. Details of the growth procedure have been previously reported [20]. Elemental concentrations were determined by energy dispersive x-ray spectroscopy using a Jeol 35C electron

microscope. X-ray diffraction (XRD) measurements, performed with a Siemens D5000 show that the sample was single phase with a cubic structure. This was confirmed by a transmission XRD experiment performed at the Stanford Synchrotron Radiation Laboratory (SSRL) Beamline 7-2, finding a cubic single phase with a lattice parameter of 6.44 Å, consistent with the amount of In present [12].

The XAFS samples were mounted in an aluminum holder sealed in the front and back with kapton tape. The holder was then attached to the cold finger of a cryostat, whose windows were sealed with aluminized mylar to prevent photoexcitation. The XAFS spectra were measured at the SSRL Beamline 4-1 with a Si(220) monochromator. Harmonic rejection was accomplished by detuning to reduce the flux to 50% of its maximum level. Data was taken in transmission and fluorescence, using a 13-element Ge detector for the fluorescence measurements. The signal from 11 of these elements was averaged to obtain a scan fluorescence spectrum. A first set of measurements was done after filling the evacuated dark cryostat with liquid nitrogen at $T = 80$ K. Two scans of 1 h each were taken for the K-edge XAFS spectra of Cd and Te, and three scans for In. A second set of measurements was done for the same edges after illuminating the sample for 5 min with the white spectra from a halogen lamp filtered by the 3-mm-thick kapton window with an intensity at the surface of ~ 50 mW/cm^2. Dark conditions were restored by sealing the windows of the cryostat with aluminized mylar before data acquisition. This procedure was repeated before the acquisition of each spectra. This illumination had been used to measure PPC in CdTe:In samples from the same batch [21].

Energy calibration was accomplished by defining the first inflection point in the spectrum of Cd (Te) K edges from undoped CdTe as 26 711 (31 814) eV. For In, the first inflection point of the K-edge absorption spectra of an In foil was used as an energy reference (27 940 eV). E_0 was set equal to the calibration energy such that the photoelectron wave vector is $k = \sqrt{(2m/\hbar^2)(E - E_0)}$. Data was normalized by setting the value of a second order polynomial fit over the pre-edge to zero and a third order polynomial over the region above the edge, setting the difference at E_0 to unity. The XAFS were extracted from the spectra as the difference between the normalized spectra and an adjustable spline function over the region above the edge. The parameters of this spline were determined by minimizing the low frequency residuals ($R \leq 1.2$ Å) in the Fourier transform of each absorption spectrum.

After photoexcitation, from the normalized absorption we observe an increase in the amplitude up to 9 eV above the absorption edge concurrent with a loss of spectral weight in the pre-edge region for In (Fig. 1a). A decrease in the intensity of the Cd spectrum is observed from the edge up to 10 eV (Fig. 1b). For Te, no change was detected (Fig. 1c). Changes in the XAFS are best illus-
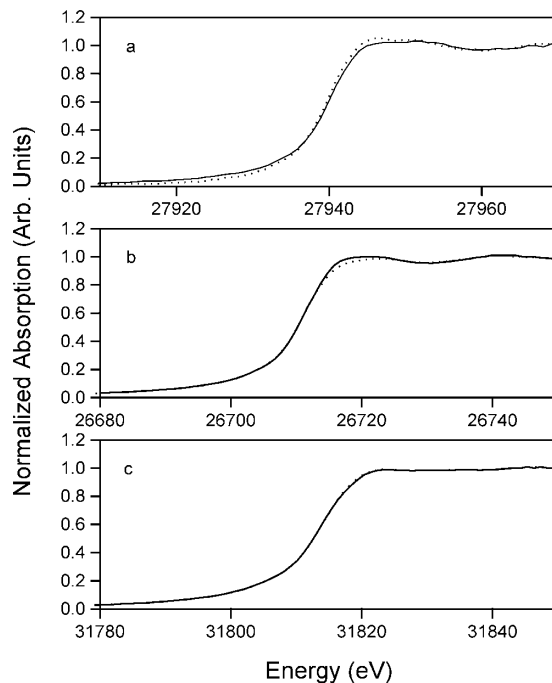

FIG. 1. Absorption edge (K) before illumination (solid line) and after illumination (dotted line) of (a) In, (b) Cd, and (c) Te.

trated in the Fourier transform magnitude (FTM). In the case of In, we observe an increase in the amplitude of the main peak at $R - \Delta = 2.5$ Å (Fig. 2a). This result *directly* shows a change in the structure of the first shell of neighbors around In caused by the photoexcitation. Such a change can be interpreted as either a decrease in the Debye-Waller factor or an increase in the coordination number, if the usual assumption of a Gaussian distribution of neighbors is used. It is also notable that there is no clear indication of further shells from the In FTM. This could originate as a result of having In in different neighbor environments leading to a very broad distribution of farther-out shells. From the Cd FTM, the first peak shows a decrease in amplitude (Fig. 2b); however, the magnitude of this change is smaller than in the case of In and it is within the experimental error. From the Te FTM we do not observe any change in the main peak (Fig. 2c). Changes observed in farther-out peaks are within experimental error. We repeated this experiment after three month periods, at beam lines 4-1 and 4-2 at SSRL after warming and storing the sample at room temperature. Again, the amplitude of the In first neighbor shell increased after photoexcitation, indicating that the photoexcited state is metastable and the ground state could be restored after warming the sample. We note that consecutive scans in the dark, before illumination show no change, indicating that x rays do not produce photoexcitation such as that produced by the optical source.

Quantitative information was obtained fitting the XAFS spectra in k space, over the region $2.6 \leq k \leq 13.4$ Å^{-1}, using the usual XAFS equation [22],
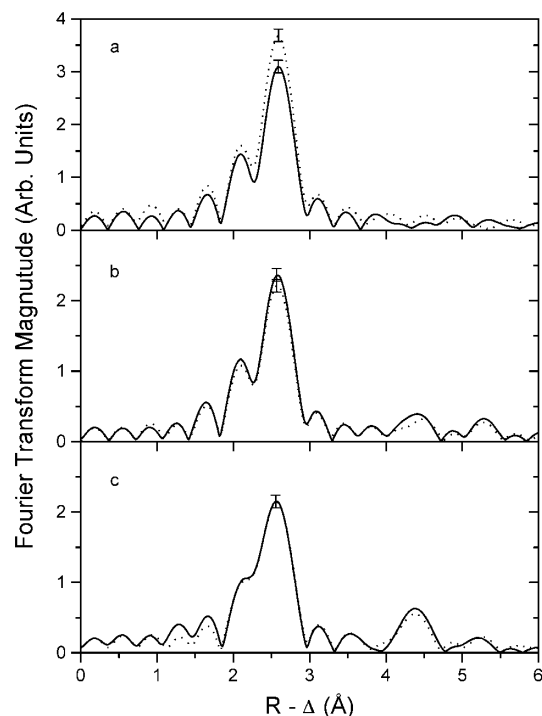
FIG. 2. Fourier transform magnitude of the XAFS before illumination (solid line) and after illumination (dotted line) for (a) In, (b) Cd, and (c) Te.

$\chi(k) = -S_0^2 N \, \text{Im}[e^{2ikR} f_{\text{eff}}(kR)/kR^2]e^{-2\sigma^2 k^2}$, with photoelectron scattering factors, f_{eff}, derived from a standard *ab initio* multiple scattering calculation [23]. For the In XAFS fit, the distance to neighbors (R), the Debye-Waller factor (σ), and the number of neighbors (N) were left as floating parameters. E_0 was set to 6.8 eV above the edge and the multielectron-excitation scale factor was set to, $S_0^2 = 1.2$. Uncertainties in the reported quantities were obtained by comparing fits to the average spectra to fits done on individual scans [24]. The results of the fits are shown in Table I. For In, we obtained a fit that reproduced the spectra using only a single shell of neighbors. Details of the fits to the Cd and Te XAFS will be presented elsewhere. Here, we note only that the distances of the first three shells of neighbors are in agreement with the zinc blende structure of CdTe, and the changes observed in R and σ with illumination are all within experimental error.

Because of the fact that the In XAFS does not exhibit information about farther-out neighbors, we cannot derive a precise model for the defect center. However, the

TABLE I. Results of the fits to the In XAFS before illumination (B.I.) and after illumination (A.I.).

	In (B.I.)	In (A.I.)
R (Å)	2.79(1)	2.80(1)
N	3.8(1)	4.0(1)
σ (Å)	0.056(4)	0.045(4)

observations of (i) a specific change in the nearest neighbor environment and (ii) negligible changes in the Cd and Te XAFS rule out *ab initio* theoretical models which have been proposed in related systems, e.g., double breaking (ZnSe:N) [25] and the triple broken bond center (ZnTe:Cl) [26]. This leaves the SBB centers as the only viable explanation, among the models proposed from *ab initio* calculations, for the observed increase in the coordination number and the reduction of the Debye-Waller factor under photoexcitation [27]. Consequently, we modeled the XAFS and the x-ray absorption near-edge spectra (XANES) produced by SBB centers. In order to model the XAFS we have used an *ab initio* multiple scattering calculation [28]. We have assumed the functional form of the structure for an SBB center proposed in Ref. [9] for CdTe:In. Since in the dark some In atoms will form SBB centers and some will be in their substitutional Cd position, to simulate the XAFS spectrum in the dark we averaged the XAFS produced by the SBB structure with the spectrum obtained, assuming In enters substitutionally for Cd. After illumination the SBB centers will change their structure and In will occupy the normal Cd substitutional site. Hence, we simulated the photoexcited spectrum, assuming all In in the substitutional Cd site. The main result of the simulation is an increase in the amplitude of the first peak after photoexcitation (Fig. 3a). The amplitude of the second and third shells of the simulation is always bigger than that observed experimentally, due to the use of a simplified model for the Debye-Waller factors [23].
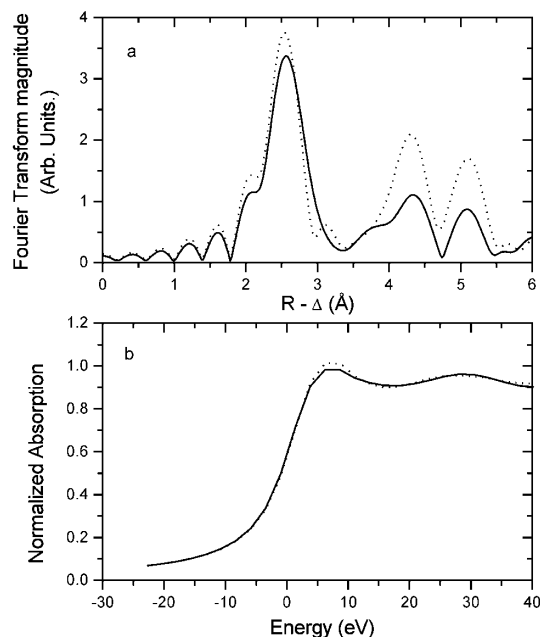

FIG. 3. (a) Fourier transform magnitude of In XAFS simulations. (b) Absorption edge for substitutional In (solid line) and an average of In forming SBB centers and substitutional In [(dotted line) see text].

For the simulation of the XANES we performed a full multiple scattering calculation with spherically symmetric self-consistent scattering potentials, using the program of Ref. [28] in a cluster of 50 atoms centered around an In atom. The comparison of the XANES simulations using In in an SBB center or in a Cd substitutional position shows the same trend as observed in the experiment, namely, an increase in the "white line" and a small loss of spectral weight below the edge (Fig. 3b). To interpret these changes we calculated the projected angular momentum local density of states around In, in the presence of a core hole induced by the x-ray absorption process. The main change in the spectrum is a change in the density of p states of the In, although there are also changes in s and d states not reflected in the K-edge absorption. Simulations of the behavior of XAFS and XANES of Cd and Te edges depend on assumed spatial distributions of these centers. We note that, in spite of the high In concentration (6 at. %), the estimated probability of finding two defect centers adjacent to each other is ~2% (assuming a uniform In distribution through the material). Consequently, our measurements are relevant for the regime in which these centers can be considered as nonoverlapping, as in Ref. [4]. We note that XAFS simulations of In_{Cd}-V_{Cd} complexes yielded FTM's inconsistent with our data, but in consistency with *ab initio* calculations, which do not support the formation of such complexes at these dopant concentrations.

In summary, we have observed a change in the nearest neighbor environment of In, in CdTe:In, after photoexcitation at low temperatures. The photoinduced structural change implies a strong coupling between the charge state and the structure around indium with a barrier that prevents indium from returning to its original position at low temperatures. This observation shows that some indium atoms form centers which change their distribution after illumination, in agreement with the SBB center for CdTe:In. This result shows that strong coupling between the charge state of the dopant of its local atomic structure, originally proposed for III-V semiconductors, is present in II-VI semiconductors and might be a general phenomenon in doped semiconductors.

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