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Brief Reports

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Conversion-electron extended x-ray-absorption fine-structure measurements of ion-damaged GaAs

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Extended x-ray-absorption fine-structure (EXAFS) measurements of ion-implanted GaAs have been made using conversion-electron detection. This total-electron-yield detection technique (termed CEEXAFS) allows near-surface sensitivity with a sampling depth of 700—1000 Å. Measurements of the Ga absorption edge show that implantation of 10^{16} cm^{-2} of Zn ions at 180 keV into GaAs produces heavy lattice damage (amorphization) to a depth of about 700—900 Å. After rapid thermal annealing, the amorphous layer is found to be recrystallized and structurally indistinguishable from unimplanted material. The sampling depth of CEEXAFS has been measured for the first time, using standards with known depth-dependent structure. The CEEXAFS technique greatly reduces Bragg-peak contamination of the EXAFS signal from single-crystal materials, and allows measurement of a variety of samples which cannot be fabricated as thin layers for conventional transmission or fluorescence EXAFS measurements. The method permits examination of the local environment of host atoms (in this case Ga) in the near-surface region without interference from the underlying bulk and without the distortions found in fluorescence EXAFS measurements of concentrated samples.

Ion implantation is now involved in the fabrication of almost all semiconductor devices. Ions are implanted to alter the electrical properties of the surface layer of a semiconductor by introducing a controlled amount of an electrically active impurity. These implantations heavily damage the lattice, since every host atom in the implanted region undergoes repeated ion collision with sufficient energy to displace the host atom in the lattice. To produce doping, the damage must be annealed out and the implanted ions moved into substitutional sites. Implantation is also used, without annealing, to produce insulating amorphous regions which provide electrical isolation in semiconductor circuits. This technological usage gives a strong impetus to studies of the processes of damage and annealing in ion-implanted semiconductors.

Since extended x-ray-absorption fine structure (EXAFS) has proven to be a useful tool for investigating the structural relaxation and crystallization of evaporated or sputtered amorphous semiconductors,[1,2] it is natural to try to extend its use to ion-damaged layers. To do this when measuring host-atom absorption edges requires the use of some method which will make EXAFS near-surface sensitive on a depth which is comparable to the implant depths. In this report, we describe the use of a simple electron detection scheme which provides the needed surface sensitivity.

Surface sensitivity on a scale of 100—1000 Å, or about 1—3 % of the typical x-ray penetration depth, is needed to study implanted layers by EXAFS. Possible detection methods include the use of electron total-[3] or partial-[4] yield, and Auger[5] or photoyield[6] detection in ultrahigh vacuum (UHV). It is also possible to combine fluorescence detection with a grazing-incidence or total-external-reflection[7,8] geometry to study submonolayer systems and shallow interfaces without the use of high-vacuum systems.

Each of these methods has disadvantages which makes it unwieldy for the study of implanted layers. The experimental complexity of UHV electron detection methods is unnecessary since we are not measuring the properties of a clean surface. X-ray total reflection combined with fluorescence detection (FREXAFS) is better suited to studying thin films since the x rays typically penetrate only 50 Å. Fluorescence detection with a grazing-incidence geometry provides greater penetration, but the signal is distorted due to the fact that the host atoms are not dilute.[9,10] Fluorescence detection used with single-crystal substrates also suffers from contamination of the signal with Bragg peaks.[11]

To avoid the difficulties discussed above, we chose to

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use conversion-electron EXAFS (CEEXAFS), which is closely analogous to conversion-electron Mossbauer spectroscopy (CEMS).[12] It has been shown[13–17] that placing the sample in a thin, He-filled ion chamber permits EXAFS measurements of a near-surface region estimated to be 100–1000 Å in thickness. The ion chamber is almost completely transparent to both the high-energy incident and fluorescent x rays. Electrons, however, produced by the decay of K-shell holes from photoabsorption events near the surface of a sample placed inside the chamber, are able to escape the sample surface and create ionization events in the He gas. The current measured by the ion chamber is thus proportional to the number of absorption events and therefore to the EXAFS signal.

Many different processes contribute to the signal in CEEXAFS, each with its own sampling depth. The electrons which are emitted into the ion chamber include photoelectrons, primary and secondary Auger electrons, secondaries produced by inelastic scattering, and Auger electrons and photoelectrons that have undergone inelastic collisions. CEMS results suggest that the electrons which escape from the sample arise from depths that are no greater than 3000 Å when the initial electron energy is about 7.3 keV, near the Ga K edge of interest in this work.

In CEEXAFS, there are several additional effects which tend to further reduce the sampling depth. Electron production in the ionization detector requires roughly 30 eV per electron-ion pair, so that the total electron yield is weighted by the energy of the electrons leaving the sample. This tends to make the measurement more surface sensitive, since the lower-energy secondary electrons escaping from deeper in the sample are given little weight. EXAFS measurements done by diode or vacuum photocurrent methods[9] have been found to sample substantially deeper ($\sim$20 000 Å) than CEEXAFS, since such measurements detect the total electron current without weighting the electron distribution by energy.

The L-shell hole left by both primary fluorescence and $L-K$-shell Auger decay also produces Auger electrons. These secondary Auger electrons, as well as photoelectrons, escape only from shallower depths, enhancing the surface sensitivity of CEEXAFS. The secondary Auger decay processes help explain the magnitude of the CEEXAFS signal, which is larger than might be expected at high x-ray energies. The fraction of core-hole excitations in the 7–11 keV (K-shell) energy range which decay by Auger processes (the Auger yield) is only about 0.1–0.2. The decay of the L-shell hole has an Auger yield of about 0.6–0.8, however, so that this process contributes substantially to the observed total electron yield. The energy deposited in the detector by the decay of L-shell holes is lower by a factor of about 6–8 per event, than that from the decay of K-shell holes, but the Auger yield is 4–8 times as large. The two Auger processes therefore contribute about equally to the observed signal, and the low primary Auger yield at 7–11 keV is not as serious a problem as it first appears.

Aside from the electron detection system, the experimental arrangement is typical for room-temperature EXAFS. Measurements were made on wiggler line IV-3 at Stanford Synchrotron Radiation Laboratory (SSRL) with a Si(220) monochromator which was detuned to 50% of peak intensity to avoid harmonics. The beam monitor (I_0) chamber was filled with N_2 and the electron detection chamber with He. The current in the ring was typically 10–40 mA at an energy of 3.0 GeV. Under these running conditions, measured electron signals were 5–30 V with a gain of 10^{10}. Signal-to-background ratios were approximately 2:1.

The signal collected in CEEXAFS is similar to that of fluorescence:[10]

$$I_e = \varepsilon(\Omega/4\pi) I_0 \mu_x d \csc\theta (1 - \tfrac{1}{2}\mu_t d \csc\theta + \cdots) , \quad (1)$$

where I_0 is the incident x-ray intensity, ε is an effective total electron yield per photoabsorption event, Ω is the solid angle subtended by the detector, μ_x is the absorption coefficient of the edge being measured, μ_t is the total absorption coefficient of the sample. The angle of incidence of the x rays with respect to the sample surface is θ. The effective average escape depth d of electrons from the sample is a function of the electron energy. Here we take d to be the maximum depth from which any significant number of electrons escape. At normal incidence, the CEEXAFS of any concentrated sample is in the "thin-concentrated" limit where the electron yield is directly proportional to the x-ray absorption.[10] This is in contrast to x-ray fluorescence, where the amplitude of the EXAFS of concentrated samples is seriously distorted due to nonlinearities in the measured fluorescence signal.[9]

Since the processes which contribute to the CEEXAFS signal are complex, we have measured several materials to establish empirically, for the first time, the sampling depth of CEEXAFS. The samples which were used to set bounds on the electron sample depth are as follows. (1) Two samples of GaAs implanted at room temperature with 180-keV Zn atoms at a dose of 10^{16} cm^{-2}. One of these was left as implanted; the other was annealed at 900 F under inert gas by exposure to intense quartz-halogen light in a commercial rapid annealing system. (2) Samples of evaporated Fe on glass substrates with an Al overlayer to prevent oxidation. The Fe samples had thicknesses of 100 and 1000 Å; Fe foil was also measured to provide an Fe sample which can be regarded as infinitely thick. The GaAs and Fe samples have known structural changes with depth which can be used to determine bounds on the sampling depth of CEEXAFS. The CEEXAFS data from the GaAs samples are shown in Fig. 1, and the Fourier transforms of those data are shown in Fig. 2.

The CEEXAFS of the as-implanted GaAs signal shows reduction in the first coordination shell, and within the noise, essentially no second- or third-shell peaks in the Fourier transform. Given the heavy implant dose, we expect that this sample is amorphous to a depth of at least 700 Å, the projected range of the implanted Zn. Since second- and third-shell peaks would not be observed in an amorphous layer,[2,3] we conclude that CEEXAFS is sampling a depth which is comparable to the damaged layer. If the signal magnitude in the second-shell region is attributed to underlying bulk crystal, we estimate that the fraction of crystalline material within the sampling depth

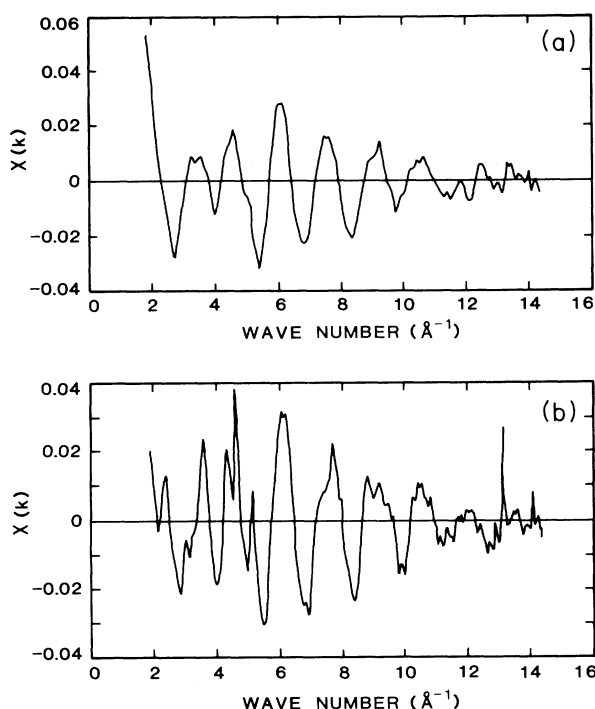

FIG. 1. The Ga edge EXAFS data of (a) GaAs implanted with 10^{16} cm^{-2} Zn atoms at 180 keV. (b) The same implantation after annealing to 900 °C using intense quartz-halogen light.

is less than 15%. Assuming that the GaAs is amorphous to one standard deviation beyond the Zn-ion projected range indicates that the CEEXAFS samples a depth of at most 1000 Å in GaAs.

The results shown in Fig. 2 indicate that the GaAs is amorphized by the implant and that the damage processes disorder the second and third shells much more strongly than the first shell. This is the same result found in deposited amorphous semiconductors, since the second coordination shell can be disordered by bond-angle changes, and the third by dihedral-angle distortions, while the first shell cannot be disordered except through bond stretching.

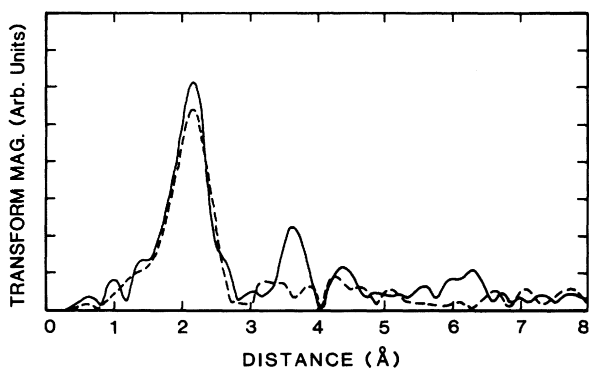

FIG. 2. Fourier transforms of (a) As-implanted GaAs and (b) annealed GaAs.

The relative ease with which bond-angle and dihedral-angle disorder occurs causes the higher shells to disorder more quickly. After rapid thermal annealing the implanted layer is indistinguishable from unimplanted GaAs, showing that, at least on the short range sensed by EXAFS, all of the lattice damage is removed.

In the Fe films, the magnitude of the CEEXAFS signal was simply measured as a function of the film thickness. The signal for the infinitely thick Fe samples was no larger than that for the 1000-Å film, indicating that the CEEXAFS sampling depth is less than 1000 Å. The ratio of the signals of the 1000-Å film to that of the 100-Å film is about 7, giving a sampling depth of 700 Å. Both the implanted GaAs sample and the Fe films indicate that the sampling depth for CEEXAFS of K shells in the 7–10 keV energy range is between 700 and 1000 Å.

The GaAs samples are single-crystal wafers prior to implantation, and even after implantation the region below the implanted layer remains crystalline. Previous EXAFS measurements of ion-implanted semiconductors using fluorescence have suffered from contamination of the signal by Bragg diffraction from the substrate.[11] This is largely eliminated using CEEXAFS because of the transparency of the detector to the diffracted x rays. There are sometimes small remnants of the Bragg peaks in our data [at 13.5 Å^{-1} in Fig. 1(b), for example], which can be eliminated by rotating the sample and repeating the scan. When Bragg peaks do appear, they are typically 2 orders of magnitude less intense than in fluorescence detection. The diffracted x rays can contribute to the CEEXAFS signal only by being absorbed within the electron escape depth of the sample surface and giving rise to increased electron signal. Since the electron escape depth is only 1% of an x-ray absorption length, the Bragg-peak signal is reduced enormously compared to fluorescence detection methods.

The thin-concentrated limit achieved at normal incidence in Eq. (1) is at the expense of about 99% of the incident x-ray intensity, since a typical x-ray penetration depth is 100 times the sampling depth of CEEXAFS. Nevertheless, count rates of 50 MHz were obtained for the GaAs samples. Equation (1) shows that the measured total electron yield is proportional to the x-ray absorption to an accuracy of 0.5%. If the sample is oriented at a small glancing angle θ with respect to the x-ray beam, the vertical penetration of the x rays is reduced by a factor of θ, increasing both the signal and the first correction term to the thin-concentrated limit by a factor of θ^{-1}. The use of low angles of $\theta \approx 0.1$ rad should allow an immediate factor of 10 increase in signal, while retaining the linear response of the thin-concentrated approximation to within 5%. Depending on the signal-to-background ratio, this could extend the use of CEEXAFS to the measurement of near-surface impurities of 1% concentration with signal levels of 1–5 MHz.

We have also used CEEXAFS to study the structural relaxation of ion-amorphized a-Ge.[18] This study allows the utility of EXAFS for studying bulk a-Ge to be extended to thin ion-damaged layers. Without the use of CEEXAFS, such studies are impossible, since there is no other way to separate the signal of the implanted layer

from the underlying chemically identical crystal.

The present result shows CEEXAFS to be an excellent tool for studying ion-implanted layers, since the sampling depth is well matched to the depth of the implants. The near-surface sensitivity of this method adds depth discrimination to the usual chemical specificity of EXAFS. As shown by the results on implanted GaAs, we do not need to rely on a surface-segregated chemical type to achieve near-surface sensitivity. Because of this, we are able to observe the damage and recrystallization of implanted layers without interference from the underlying crystal. CEEXAFS also overcomes difficulties associated with fluorescence measurements of concentrated samples and single-crystal materials. The sampling depth of CEEXAFS is found to be about 700—1000 Å for K edges in the energy range 7—11 keV, and shows little variation between Fe and GaAs. It is suggested that the use of shallow angles to more closely match the electron escape depth to the vertical x-ray penetration depth will allow CEEXAFS to be extended to measurements of shallow, dilute impurities. Comparison of CEEXAFS with diode or photocurrent detection methods shows that the former has a smaller sampling depth by roughly a factor of 20. Operating the ion chamber at a variable He pressure may allow the sampling depth to be adjusted between the $\sim$1000 Å found in this work and the $\sim$20 000 Å found when no He is used. Use of a retarding grid or collection of only those electrons emitted at shallow takeoff angles could be used to enhance the surface sensitivity of this method.

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