J. Synchrotron Rad. (1999). **6**, 341–343

Direct measurement of valence charge asymmetry in GaAs using X-ray standing waves

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Through detection of valence photoelectrons, the technique of x-ray standing waves directly measured the charge asymmetry of the GaAs valence band. Using the back-reflection geometry for the (111) and $(\bar{1}\bar{1}\bar{1})$ diffraction planes, we determine from the coherent distances of the standing waves, that a majority of the valence electrons reside on the As atoms of this heteropolar crystal. These measurements agree well with the GaAs bond polarity calculated from the values of the Hartree-Fock terms. In contrast, the valence standing waves for germanium determine the valence charge to be symmetric. The coherent fractions of the standing waves of Ge and GaAs are reduced compared to those of core-level standing waves, indicating the delocalization of valence charge. This technique using low energy x-rays together with valence photoelectron detection can be more generally applied to the study of chemical bonding.

Keywords: : X-ray standing waves; valence band photoemission spectroscopy; bond polarity

1. Introduction

The traditional use of the X-ray standing wave (XSW) technique has been to determine the atomic positions of foreign surface or impurity atoms relative to the diffracting planes of a host crystal (Woodruff, 1998, and Zegenhagen, 1993). The atomic distribution determined from the characteristic absorption yield curves corresponds to the core-level electrons excited by the standing wave field, and since core states are highly localized, it is assumed that the core-level electron positions are at the atomic centers. In this study, we characterize the bulk valence electron distribution of Ge and GaAs using valence band photoemission yield XSW. We demonstrate that large bond polarity effects are observable in raw valence band XSW data, and the coherent distance of this valence band data is a direct determination of the bond polarity.

2. Experiment and Description of Technique

All XSW experiments were performed on Beam Line 3-3 (JUMBO) at Stanford Synchrotron Radiation Laboratory (SSRL) with a double-crystal InSb(111) monochrometer and a Pt-coated quartz focusing mirror upstream of the monochrometer. Samples were single-crystal cleavable bars. The front surfaces were Ge(111) and the nonpolar GaAs(110) surfaces, while the samples were oriented so the $(1\bar{1}0)$ direction was vertical. Samples were cleaved in vacuum, and the pressure throughout the experiment was less than 5×10^{-11} torr.

The experiments were performed in the backreflection configuration, with the incident beam normal to and reflecting off of the (111) plane of Ge and the (111) or $(\bar{1}\bar{1}\bar{1})$ planes of GaAs. The photon energy required for backreflection is approximately 1900 eV for all reflections. Near the Bragg condition, the incident and reflected X-rays superpose to form a standing wave with the spatial periodicity of the diffracting planes (~3.27 Å). The phase of the standing wave intensity changes by π as the photon energy is scanned through the Bragg condition. The intensity maxima of the standing wave move from halfway in between the diffracting planes to on the diffracting planes as the photon energy is increased from the low energy side to the high energy side of the reflectivity. By monitoring absorption through photoemission yield from a particular core level as the standing wave intensity profile moves with photon energy, we can determine the distribution of distances of the absorbing atoms from the diffracting planes in the direction perpendicular to the plane, e.g. the (111) direction. Similarly, by monitoring the variation of the valence band photoemission peak height, we can probe the position distribution of valence charge along the (111) direction.

In the dipole approximation, the x-ray standing wave absorption yield can be fit to the equation

$$Y(E) = 1 + R(E) + 2 f_c \sqrt{R(E)} \cos(\nu(E) - 2\pi D_c) \quad (1)$$

where the reflectivity R(E) and phase ν(E) of the standing wave are functions of the photon energy E. The fit finds the values of D_C and f_C, which are the coherent distance and fraction, respectively, and are the phase and magnitude of F_H, the Fourier component of the electron density in the direction perpendicular to the diffracting planes. The coherent distance D_C (in units normalized to the plane spacing) is the phase-averaged distance of the charge distribution from the diffraction plane. The coherent fraction f_C reflects the spread in position of the charge distribution, with increased spatial extent resulting in a decreased coherent fraction. As seen from the equation, the coherent distance D_C affects the phase and overall shape of the standing wave yield, while the amplitude of the feature is proportional to the coherent fraction f_C.

The photoelectron yield was measured using a cylindrical mirror analyzer, the axis of which was along the polarization vector of the synchrotron radiation. The constant initial state (CIS) mode was used, where the electron kinetic energy is changed with the photon energy to track the photopeak. For both Ge and GaAs we monitored the valence band and the shallow 3d core-levels so the kinetic energy of core and valence electrons are similar. The kinetic energy is 1860-1895 eV, making the measurement bulk-sensitive.

3. Ge Results: (111) Reflection

Figure 1 presents the standing wave data for the core-level Ge 3d and valence band (Ge VB) photoelectron yields, as well as a diagram of the Ge crystal atomic arrangement. The lineshapes of the Ge 3d and valence band yields are similar, indicating an identical coherent distance $D_C = 1$, which is on the (111) atomic plane. The coherent fraction of the Ge VB standing wave is 0.661±0.046, which is reduced only 5% from the Ge 3d coherent faction of 0.693±0.038, as is evident from the raw data. Because the coherent fraction reflects the spread in position of the monitored charge distribution, we anticipated a larger reduction in coherent fraction than measured due to the delocalization of the valence band initial state. One possible explanation for why the reduction is small may be due to a final state localization effect of the photoemission process at these high kinetic energies (Solterbeck *et al.*, 1997).

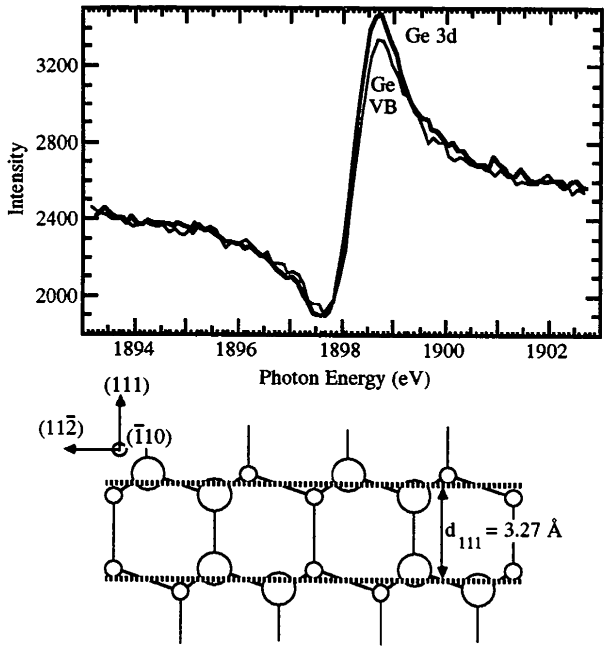

Figure 1
Top: X-ray standing wave data for Ge monitoring Ge 3d and Ge valence band (Ge VB) photoemission near the Ge(111) Bragg condition. Bottom: Atomic arrangement in bulk Ge with (111) diffraction planes indicated.

4. GaAs Results: (111) and $(\bar{1}\bar{1}\bar{1})$ Reflections

Contrary to the homopolar Ge case, the valence band standing wave data for the heteropolar GaAs crystal along the polar (111) and $(\bar{1}\bar{1}\bar{1})$ reflections clearly reflect the polarity of the GaAs bonds, as seen in Figures 2 and 3. For the (111) reflection, the As or Ga atoms are 1/8 of a plane spacing above or below the (111) diffraction plane, respectively. The core-level As 3d and Ga 3d standing wave data have lineshapes and coherent distances corresponding to these atomic positions (see Figure 2). The valence band standing wave lineshape is at a distance between the As 3d and Ga 3d lineshapes, since the photoelectrons in this case come from both As and Ga atoms; however, the lineshape is closer to that of the As core than to that of the Ga core, indicating the valence charge distribution of the GaAs bond is weighted towards the As atom. The measured shift of the valence band coherent distance from the bilayer midplane is +0.057±0.015 plane spacings.

Flipping the sample around allows us to look at the $(\bar{1}\bar{1}\bar{1})$ reflection, for which the As and Ga atomic positions are reversed with respect to the diffraction plane (bilayer midplane) when compared to the (111) reflection. By comparing Figures 2 and 3 one can see the lineshapes of the core-level As 3d and Ga 3d standing wave data have reversed. In the $(\bar{1}\bar{1}\bar{1})$ case (Figure 3) the valence band standing wave data again has a lineshape between the two core-level lineshapes, being more similar to that of the As core, once again reflecting the polarity of the GaAs bond. The measured shift of the valence band coherent distance from the bilayer midplane is −0.057±0.012 plane spacings, which is equal and opposite to the shift for the (111) reflection.

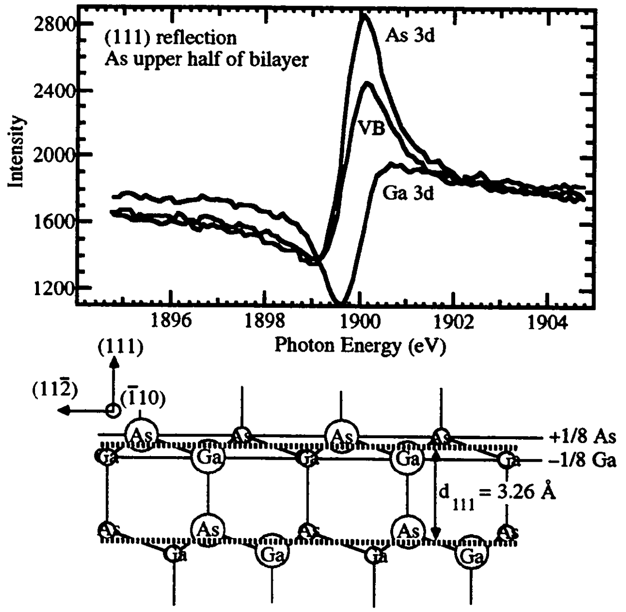

Figure 2
Top: X-ray standing wave data for GaAs monitoring As 3d, Ga 3d and GaAs valence band (GaAs VB) photoemission near the GaAs(111) Bragg condition for the (111) reflection. Bottom: Atomic arrangement in bulk GaAs for the (111) reflection with (111) diffraction planes indicated.

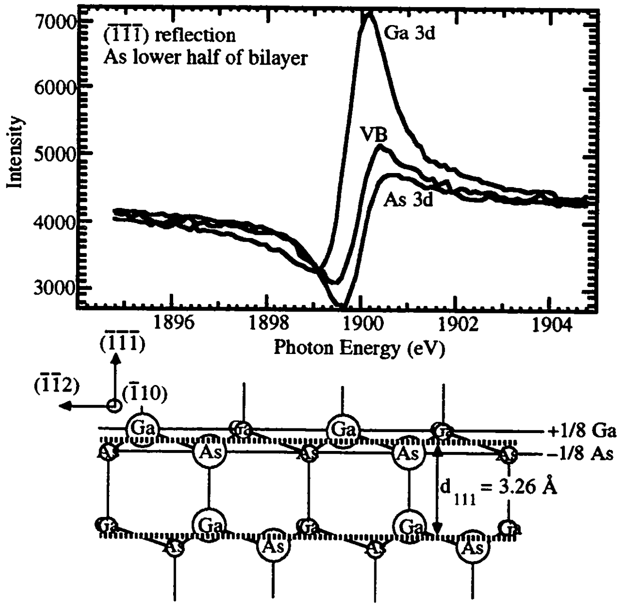

Figure 3
Top: X-ray standing wave data for GaAs monitoring As 3d, Ga 3d and GaAs valence band (GaAs VB) photoemission near the GaAs(111) Bragg condition for the $(\bar{1}\bar{1}\bar{1})$ reflection. Bottom: Atomic arrangement in bulk GaAs for the $(\bar{1}\bar{1}\bar{1})$ reflection with $(\bar{1}\bar{1}\bar{1})$ diffraction planes indicated.

5. Estimate of GaAs Bond Polarity

Using the measured coherent distances and a simple model of the charge distribution, we can obtain a quantitative measure of the polarity of the valence charge distribution. If we assume a distribution

$$\mathrm{f(D)} = \frac{1+\alpha_p}{2}\,\delta\,(\mathrm{D} - \mathrm{D_{As}}) + \frac{1-\alpha_p}{2}\,\delta\,(\mathrm{D} - \mathrm{D_{Ga}}) \quad (2)$$

where D is the distance of the charge from the diffracting plane. This distribution places the valence charge at the positions of the As and Ga atomic cores and weights the fraction of charge on As or Ga with the polarity parameter α_p. Note that this model ignores the different cross sections for the Ga and As 4s and 4p orbitals and assumes that the electron emission is negligible between the atoms. (We have experimentally verified that the coherent fraction of the valence band is reduced only by 5%.) It is easily shown that

$$\alpha_p = \pm \tan(2\pi\,(\mathrm{D_{c,VB}} - \bar{\mathrm{D}})) \quad (3)$$

where $\mathrm{D_{c,VB}} \pm \bar{\mathrm{D}}$ is the experimentally observed shift of the valence band coherent distance from the bilayer midplane.

Averaging the results of the two reflections to reduce the error bar gives a measured polarity of $\alpha_p = 0.37 \pm 0.07$. This value agrees well with the value of $\alpha_p = 0.32$ calculated by Harrison (1989) for GaAs using sp^3 hybrids and Hartree-Fock term values. Inclusion of cross section effects would weight the As term preferentially by a small amount, bringing our results into even closer agreement with theory. Such calculations are currently being performed.

6. Conclusion

The valence band standing wave technique has been demonstrated to provide an accurate quantitative method for measuring bond polarity. Striking polarity effects are visible in the raw data which we have explained using a simple, intuitive model, and suggests that more complicated experiments are possible. By comparing localized core level yields to valence band photoemission yields from homopolar Ge and heteropolar GaAs crystals, we verify that valence band standing wave measurements reflect the symmetry of Ge bonds and the polarity of GaAs bonds as well as a small delocalization of the valence charge.

7. Future Work

This study confirmed the ability of valence band standing wave measurements to determine the bond polarity in bulk semiconductors. In the study, the electron analyzer accepted a large portion of the valence band so our results reflect the entire valence charge distribution. With improved energy resolution, it should be possible to investigate the position distribution of different valence states, and use of an angle-resolved spectrometer offers the unique possibility of measuring both the momentum and position of valence states and Fermi edges. In addition, by working at shallower take off angles, investigation of surface bonding may be possible.

8. Acknowledgements

The experiments were performed at Beam Line 3-3 at Stanford Synchrotron Radiation Laboratory, which is supported by DOE, Office of Basic Energy Sciences. Additional support was provided by the National Institute of Standards and Technology.

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(Received 10 August 1998; accepted 3 December 1998)