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Partial-density of occupied valence states by x-ray standing waves and high-resolution photoelectron spectroscopy

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We describe an experimental method by which site-specific valence-electronic *structure* may be obtained. It utilizes the spatial dependence of the electric-field intensity that results from the superposition of the incident and reflected x-ray beams within the vicinity of a crystal x-ray Bragg reflection. Resolution of the anion and cation contributions to the GaAs valence-band density of states is demonstrated.
Keywords:

1. Introduction

One of the most powerful experimental tools for examining the electronic structure of a solid or film is photoelectron spectroscopy. Due to the conservation of energy between the incident photon and the ejected photoelectron, much direct and important electronic information pertaining to the occupied valence-band density of states has been obtained for many materials. This information has been used to establish the validity of complicated band-structure calculations for metals, semiconductors, insulators, and alloys[1].

Typical photoemission measurements are performed with excitation sources that are assumed to be monochromatic plane waves. As the intensity of a plane wave is constant over the dimensions of the crystalline-unit cell, standard photoemission measurements are therefore unable to produce *direct,* site-specific valence electronic structure. As many of the recent density of states calculations that have been performed for compound materials are atomic specific, such information is necessary for the detailed comparisons between theory and experiment that are required to further enhance our understanding of solid-state bonding.

This limitation of the photoemission process has been partially mitigated by experiments that have exploited either the photon-energy dependence or Cooper minimum [2] of the atomic cross sections of the atoms within the unit cell [3,4,5], or the photon- energy dependence of the Fano [6] resonant behavior of these atoms near a core-ionization threshold [7]. Additionally, x-ray photoelectron diffraction, utilizing the differences between the phases and scattering amplitudes of the atoms within the unit cell, has also been used to obtain site-specific information [8].

Here we describe a new experimental method for obtaining site-specific valence-electronic structure. Unlike the methods described above that rely on the detailed atomic properties of the atoms within the unit cell, it utilizes only the spatial variation of the electric-field intensity that occurs within the vicinity of a crystal x-ray Bragg reflection.

The intensity of this field is given by the superposition of the incident $\mathbf{E}_0$, and reflected $\mathbf{E}_h$ x-ray beams that travel with wave vectors k, and kh, polarization vectors $\mathbf{e}_0$, and $\mathbf{e}_h$, and frequency ω:

$$\mathbf{E}(\mathbf{r},t) = [\ \mathbf{e}_0 E_0 e^{i\mathbf{k_0 \cdot r}} + \mathbf{e}_h E_h e^{i\mathbf{kh \cdot r}}] \ e^{-i\omega t} \qquad (1)$$

$\mathbf{k}_0$ and $\mathbf{k}_h$ are connected by the Bragg condition $\mathbf{h} = \mathbf{k}_h - \mathbf{k}_0$ where $\mathbf{h}$ is a reciprocal lattice vector of the crystal. For a symmetric reflection, this field squares to give the electric-field intensity at a point r in space:

$$I(\mathbf{r}) = |\mathbf{E}_0|^2 \ [1 + R + 2\sqrt{R} \cos(\nu + \mathbf{h \cdot r})] \qquad (2)$$

Here ν is the phase of the complex reflectivity function R, and it is determined by the ratio of the complex-field amplitudes: $E_h/E_0 = \sqrt{R}e^{i\nu}$. Germane to the method is the unique ability to position the maxima (or minima) of the electric-field intensity at any location within the crystalline-unit cell by experimentally varying the phase of the complex reflectivity function between $0 < \nu < \pi$. This is achieved by slightly varying either the sample angle or the photon energy within the natural width of the crystal x-ray Bragg reflection [9].

Because the probability of emission of an electron from an atom in an external electric field is proportional to the electric-field intensity at the location of its atomic core (dipole approximation [10]), by selectively positioning the electric-field intensity within the unit cell and recording high-resolution valence-photoelectron spectra, spatially resolved components to the photoemission valence-band density of states may be easily obtained.

To illustrate the principle of the,technique, figure 1 shows a theoretical calculation of the electric-field intensities and their spatial dependence relative to the GaAs atomic planes at the GaAs(lll) and GaAs(-l-l-l) Bragg back-reflection conditions for photon energy $h\omega = 1900.05$ eV. The use of the two reflections at this particular photon energy was chosen to maximize the contrast between the emission from the Ga and As atoms, as determined by our previous scanned x-ray standing-wave measurements [11].
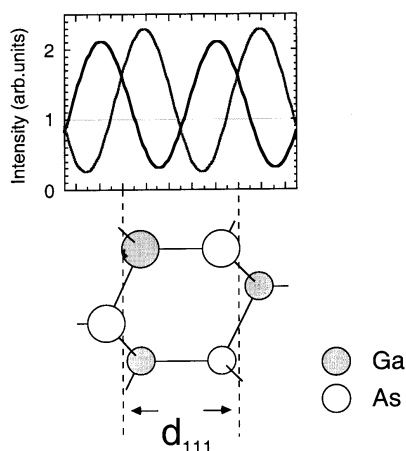
Figure 1. Theoretical calculations of the normalized electric-field intensity for the GaAs(111)(shaded line) and GaAs(-l-l-l) (bold line) Bragg back-reflections conditions at photon energy $h\omega$ = 1900.05 eV. This photon energy maximizes the electric-field intensity on the Ga atomic planes for the (Ill)reflection and on the As atomic planes for the (-1-1-I)reflection. The spatial positions of the field intensities within the crystalline-unit cell are shown relative to the Ga and As atomic planes. The dotted line represents the electric-field intensity away from the Bragg condition which is constant and equal to 1.

The fields have been normalized to the electric-field intensity away from the Bragg condition where R = 0. At photon energy $h\omega$ = 1900.05 eV, the phase difference v between the incident and reflected fields is such that the maximum of the electric-field intensity is close to the Ga atomic planes for the GaAs(lll) reflection, and close to the As atomic planes for the GaAs(-l-l-l) reflection. Significant contrast then between the Ga and As contributions to both the core and valence electron-emission spectra can be obtained for this heteropolar zinc-blende crystal.

2. Experimental details

The experiment was performed at the Stanford Synchrotron Radiation Laboratory using the "Jumbo" double-crystal monochromator and a standard, ultra-high-vacuum chamber. Figure 2 shows the Ga and As core and valence electron-emission spectra in the vicinities of the GaAs(lll) and GaAs(-l-l-l) Bragg back-reflection conditions. The spectra were recorded with a double-pass cylindrical mirror analyzer (CMA) operating with x-ray photoelectron slits at a pass energy of 50 eV to give an electron-energy resolution of - 1 eV. The monochromator was operated with a pair of InSb(lll) crystals to give a photon-energy width of - 0.7 eV. The photon energy used to record each spectrum was chosen to place the maximize of the electric-field intensity on either the Ga or As atomic planes for the GaAs(lll) and the GaAs(-l-l-l) reflections, respectively, as described above.

3. Results and discussion

The data exhibit the well known x-ray standing wave effect [12] for both the Ga 3d and the As 3d core
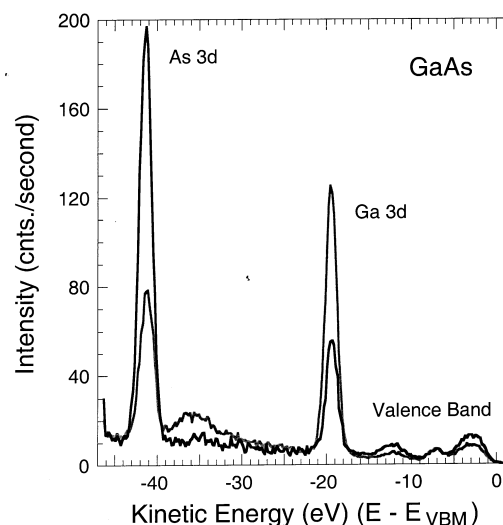

Figure 2. Comparison of the photoemission spectra, referenced to the valence-band maximum, for the GaAs(lll) (shaded lines) and GaAs(-l-l-l) (bold lines) reflections over the kinetic-energy range of the Ga 3d, As 3d, and valence-electron emission. For the GaAs(lll) reflection, the maximum of the electric-field intensity was placed on the Ga atomic planes. For the GaAs(-l-l-l) reflection, the maximum of the electric-field intensity was placed on the As atomic planes. Note the enhancement of the emission from the on-atom atomic planes and the suppression of the emission from the off-atom atomic planes in each case.

levels, as well as for the crystal valence band. What is important to see is that the emission from either of the preferentially excited Ga or As atomic planes is enhanced by over a factor of 2 relative to its emission from the condition where it is suppressed. In a standard x-ray standing-wave experiment, the maximum of the electric-field intensity is scanned through the crystalline-unit cell by experimentally varying the phase of the complex reflectivity function, while the intensity of a core, Auger, or fluorescence line is monitored to locate the position of a particular atom within the unit cell [12]. Our experiment is a departure from the standard x-ray standing-wave technique in that we use the energy dependence of the complex reflectivity function to selectively position the maximum of the electric-field intensity within the unit cell. Concomitantly recorded, high-resolution valence-photoemission spectra then directly produce spatially resolved valence electronic structure.

Figure 3 compares the valence band regions of the two spectra from figure 2. Note the large differences between the spectra dependent on which of the atomic planes; i.e., either the anion or cation atomic planes, were preferentially excited. The features at the lowest and highest kinetic energies are enhanced when the maximum of the electric-field intensity is placed on the As electronic cores, whereas the feature at intermediate kinetic energy is enhanced when the maximum of the electric-field intensity is placed on the Ga electronic cores.

Under conditions of constant electric-field intensity, the valence photocurrent can be approximated as the sum of the different partial-density of states ρpi arising
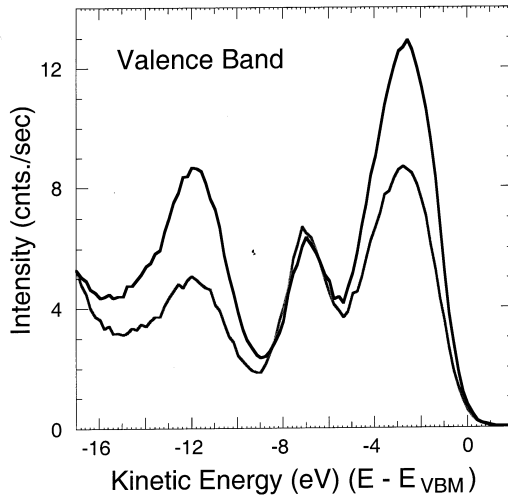
Figure 3. Comparison of the Ga (shaded line) and As (bold line) GaAs valence photoemission spectra from figure 2. Note the sensitivity of the spectra to the location of the electric-field intensity within the crystalline-unit cell. The features at the lowest and highest binding energies are enhanced when the maximum of the electric-field intensity is placed on the As atomic cores, whereas the feature at intermediate kinetic energy is enhanced when the maximum of the electric-field intensity is placed on the Ga atomic

from the different i atoms of the crystalline-unit cell multiplied by the energy dependent, relative cross section σ_i of each of the energy states [5]:

$$I(E,h\omega) \propto \Sigma_i \, \rho_i(E)\cdot\sigma_i(E,h\omega) \qquad (3)$$

For the case of a spatially modulated x-ray field, it is easily shown that in the dipole approximation this expression is generalized to include the electric-field intensities at each of the different atomic positions [13]:

$$I(E,h\omega) \propto \Sigma_i \, \rho_i(E)\cdot\sigma_i(E,h\omega) \, [1 + R + 2\sqrt{R}\cos(\nu + \mathbf{h}\cdot\mathbf{r}_i)] \quad (4)$$

For the case where R = 0; i.e., away from the Bragg condition, the above expression reduces to equation 3. Note that equation 4 contains the individual contributions to the valence-electron spectra $\rho_i\sigma_i$, but multiplied by the electric-field intensities at the positions of the cores. Consequently, for a two atom unit cell such as GaAs, all that is necessary to uniquely resolve the individual chemical components of the GaAs valence band is to obtain valence spectra at two different electric-field conditions and then solve a simple set of two linear equations. In these equations, the coefficients of the individual partial-density of states are the relative electric-field intensities at the Ga and As sites. They may either be calculated theoretically as in figure 1, or they may be determined experimentally from the core-level data shown in figure 2. Figure 4 shows the resulting chemically resolved components of the GaAs valence band obtained by taking the appropriate linear combinations of the spectra from figure 3. Note the even larger differences between the two electronic structures.
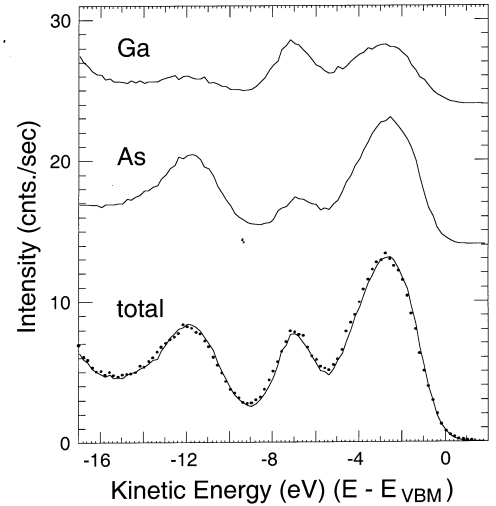
Figure 4. Chemically resolved Ga and As contributions to the GaAs valence band. The top curve shows the cation emission, and the lower spectra shows the anion emission. The bottom curves compare a valence spectrum recorded off the Bragg condition (dots) with the sum of the individual anion and cation components (solid line). The spectra have been offset for clarity.

From the theoretical calculations of Cohen and Chelikowski [14], it is well established that the three lobes observed in the valence band of GaAs, which are typical of all the covalent semiconductors [15], are directly correlated with the crystalline band structure; they arise from the hybridization of the Ga and As 4s and 4p orbitals. The first lobe corresponds to the most tightly bound-electron band; electronic states within this lobe are strongly localized on the As-anion sites and originate from the As atomic 4s level. The second lobe is more complex, and the character of the electronic states changes from Ga-cation 4s to As-anion 4p with increasing kinetic energy going from the band edge to the band maximum. The third lobe includes the top two valence bands; it extends to the valence band maximum and is mostly of As-anion 4p character. Clearly, our data support these theoretical conclusions.

In order to further demonstrate the validity of our approach, the bottom panel of figure 4 compares a valence spectrum recorded off the Bragg condition (dots) with the sum of the individual Ga and As components (solid line). Away from the Bragg condition the electric-field intensity is constant over the dimensions of the unit cell, so the valence spectrum should appear as the simple sum of the anion and cation contributions (equation 3). Note that the two spectra are indistinguishable within the experimental uncertainties, thereby experimentally justifying the approximations used in our derivation of equation 4.

Conclusions

We have demonstrated that valence-photoelectron spectra recorded in the vicinity of a crystal x-ray Bragg reflection can reveal site-specific valence information. It is our hope that this method will provide useful information pertaining to the detailed electronic structure of more complex

crystalline materials that are currently of interest to the scientific community.

Acknowledgements

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