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Chemically-Induced Surface Structural Rearrangements Studied by Shadow-Cone-Enhanced SIMS

N. WINOGRAD,* J. BURNHAM, AND C. XU

Department of Chemistry, Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

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Major efforts are underway to unravel the special role that surfaces play in influencing chemical reactivity. A particularly important aim is to elucidate the relationship between surface chemistry and structure. Information of this sort, which involves a complete crystallographic determination of the location of atoms in the first few layers of a solid, is essential to the formulation of generalized theories of the surface chemical bond. With this end in mind, a number of surface spectroscopies with structure determination capabilities are being vigorously pursued throughout the world, including low-energy electron diffraction (LEED),[1] scanning tunneling microscopy (STM),[2] surface EXAFS,[3] electron stimulated desorption,[4] and photoelectron holography.[5] Despite rapid progress with all of these methods, many are inherently limited to specific types of materials, and there are still only a few systems whose atomic bond lengths and angles have been reproduced by at least two separate techniques.

Ion scattering methods show considerable promise for the direct study of surface structure. With these methods, an energetic particle is scattered from a target. From the resulting collisions, the location of atoms can often be deduced from rather straightforward measurements. Experiments have been performed over a kinetic energy range from several electronvolts to greater than 10^6 eV. Although the incident particle can damage the surface, it is often possible to carry out the experiment using sufficiently low doses that damage effects are not observed. The analysis usually involves direct triangulation and does not require inversion from reciprocal lattice space, which is required for diffraction techniques.

An important reason behind the success of ion scattering methods is attributed to special shadowing and focusing mechanisms[6] associated with energetic two-body collisions. It is easy to illustrate this principle. For collisions above 1 keV, atomic radii are generally small compared to atomic spacings. The collisions occur without the influence of neighboring atoms. Moreover, there is a region of space behind the target atom where no incident particle can penetrate. A diagram of this effect is shown in Figure 1. The resulting feature was first discussed nearly 30 years ago and is generally referred to as a shadow cone.[7] At the edge of the shadow cone, the incident flux is enhanced by at least a factor of 5, and the thickness of the enhanced region is on the order of 0.02 Å.[8]

Nicholas Winograd was born in New London, CT, in 1945. He received his Ph.D. in chemistry from Case Western Reserve University in 1970 and immediately joined the faculty of Purdue University. He moved to Penn State University in 1979, where he is now Evan Pugh Professor of Chemistry. Winograd has had a longstanding interest in the fundamentals of ion/solid interactions and has pursued the development of new experiments and theoretical models to unravel their complexities.

Jay Burnham received a B.A. degree in chemistry from Potsdam College in 1987. He is currently completing his Ph.D. Thesis at Penn State University on secondary ion desorption from metal and semiconductor interfaces.

Chen Xu received a B.S. degree in physics in 1982 from Nanjing University and his Ph.D. degree in 1990 from the University of Newcastle. His doctoral research focused on metal surface structure analysis with medium-energy ion scattering. He is currently a postdoctoral research associate at Penn State University and is working with N. Winograd in the study of the kiloelectronvolt bombardment of metal and semiconductor surfaces.

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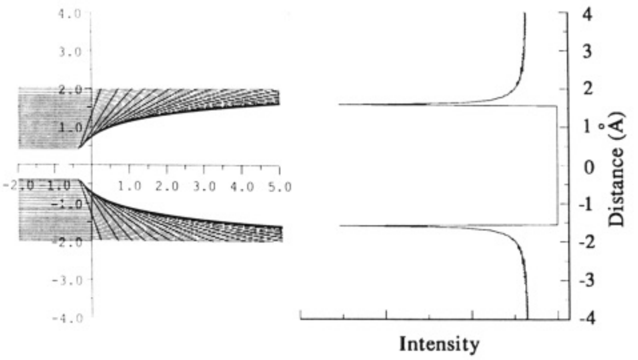

Figure 1. Two-dimensional representation of the formation of a shadow cone. The left panel shows the trajectory of 3-keV Ar^+ ions as they pass a Ni atom at various impact points. The right panel shows the intensity of the ion beam at various lateral displacements 5 Å behind the Ni atom.

Shadow cones can provide a direct path to surface structure studies. At megaelectronvolt energies, the shadow-cone radius is very small (~0.1 Å), and its presence can be detected by measurement of the intensity of the reflected beam as a function of scattering angle. This configuration, associated with Rutherford backscattering spectrometry (RBS), has provided some of the best data related to the structural changes that occur at the surfaces of single-crystal metals.[9] For example, these measurements have shown that the first layer of many metals is relaxed inward by a significant fraction of the interlayer distance, presumably due to a rearrangement of electrons at the cleaved surface. The experimental generality of RBS is somewhat restricted to systems with specific mass ratios where the backscattering cross sections are very small. Moreover, the equipment is large and exists only in a few laboratories worldwide.

Shadow cones have proven useful in the kiloelectronvolt range as well. An important development occurred about 12 years ago when Aono and co-workers[10] proposed that the shadow-cone edge could be utilized for structural analysis by placing the detector near the primary ion source. As we shall see, it is possible to accurately determine the shape of the shadow cone at these energies, so measurement of the critical angle yields a direct measure of the surface bond length. The experimental configuration is shown schematically in Figure 2b. These experiments have been employed by several workers[11] to examine the changes that occur in the near surface region of a solid during chemisorption. The methodology is referred to as impact collision ion scattering spectroscopy (ICISS).

Shadow-Cone-Enhanced SIMS

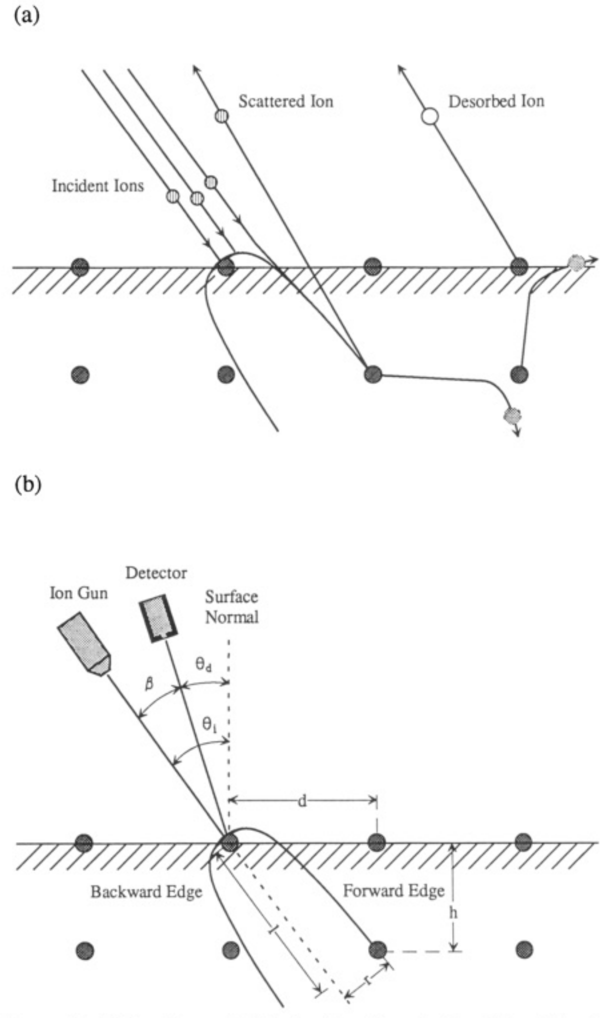

Figure 2. (a) A schematic illustrating the relationship of shadow cones with scattered and desorbed particles. (b) Parameter definitions for the shadow-cone-enhanced desorption experiment. The ion beam is incident at θ_i; the desorbed secondary ions are detected at θ_d and $\beta = \theta_i - \theta_d$. The shadow cone is described by a radius r at a distance l behind the target atom. The d and h values describe the bond length in the plane of the surface and between the first and second layers, respectively.

Concomitant with these various experiments, much progress has been made over the last few years in elucidating the dynamics of ion/solid collisions. For example, when a solid is struck by a heavy particle with kiloelectronvolt energies, the momentum which is imparted to the crystal initiates a cascade of atomic motion. This collision-induced process has been successfully modeled using molecular dynamics computer simulations.[12] Here, the forces between the atoms are calculated from an appropriate interaction potential function. There have been enormous advances in obtaining many-body potential functions for a range of solids which can yield accurate dynamics modeling. For example, it is now possible to calculate energy and angular distributions of atoms which desorb from bombarded single crystals which agree well with experimental data.[13] Similar calculations are proving useful in yielding mechanistic details about the events which lead to ionization of desorbed particles.[14] These results, in turn, are leading to a better understanding of secondary ion mass spectrometry (SIMS) and fast atom bombardment (FAB), two methods which are prevalent in the mass spectrometry community.

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It is interesting to speculate about the interrelationship between the formation of shadow cones as described earlier and the nature of the events that lead to particle desorption. Figure 2a illustrates the relationship of shadow cones with scattered and desorbed particles. Particle desorption is initiated when there is a high degree of motion created near the target surface. The degree of motion depends in large measure on the impact parameter of the primary particle. That is, specific impact points on the surface exhibit very high yields while other points are rather inactive for sputtering. This observation has led to the concept of atoms sputtered per incident ion or ASI distributions.[15] For example, for 1-keV Ar^+ ions on Cu, the Cu yield is calculated to vary from 0 to over 15, depending upon the nature of the impact point. It would be interesting to be able to find these high-action points in the laboratory, a dim prospect considering the aiming accuracy required.

However, by combining what we know about shadow cones and information gained from studying ASI distributions, there is a way to find these high-action points. Recall that the shadow-cone edge is less than 0.02 Å in width. Moreover, the flux of particles within this edge is at least 5 times higher than the flux of particles away from the edge. By changing the angle of incidence of the primary beam, in effect, we can "aim" this beam to specific high-action points in the target. The points should correspond to intersection of the shadow-cone edge with nearby atoms as shown in Figure 2a and should be easily detectable in the laboratory. With knowledge of the shadow-cone shape, it is then feasible to determine atomic positions using simple triangulation in a manner similar to that developed for ICISS.

The geometry of the shadow-cone-enhanced desorption experiment is illustrated in Figure 2b. In principle, the detector should be configured to collect all desorbing ions, regardless of their angle or kinetic energy. Most experiments to date, however, have been performed with a fixed angle β and with a detector set to collect only the high-kinetic-energy particles. With this configuration, the shadow-cone-enhanced desorption concepts may be more carefully evaluated.[16] Moreover, it has been shown that, for θ_d between ±45°, ion neutralization effects are not of sufficient magnitude to shift the angles of the intensity maxima, although the relative intensity of the peaks may be altered somewhat.[17] This is a convenient geometry, then, for indirectly examining the behavior of neutral atom ejection.

To see how this idea works, let us first consider the results from a simple, well-characterized surface that has been examined by several approaches. The Ag{110} system is a particularly good test case since the spacing between the first and second layers has been found, by both RBS and LEED, to be about 10% shorter than the bulk spacing.[18–20] There are two major features in these distributions which correspond to intersection of the shadow cone with a first-layer atom ($\theta_{ic} \sim 70°$) and with a second-layer atom ($\theta_{ic} \sim 35°$). In this case, the angle associated with an enhanced intensity feature is designated as θ_{ic}. The maxima along each azimuth occur at slightly different angles since the neighbor distances obviously depend on crystal orientation. There is a minimum near $\theta_i = 50°$ because there is a channel that allows the primary particles to penetrate deep into the solid without causing very much desorption.

From the position of the peaks it is possible to calculate d (see Figure 2b) if the shadow-cone shape can be determined. There are a number of ways to find this shape. First, however, it is important to note that the interactions which create the shadow cone involve energies which are much larger than the cohesive energy of atoms in the solid or the chemical bond energy of surface molecules. The scattering angles will be essentially the same regardless of chemical environment. Second, it has been found empirically over the years that a form of the Thomas–Fermi potential referred to as the Molière potential quite accurately describes the scattering between two gas-phase particles. This potential has the form[21]

$$V_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} \sum_{n=1}^{3} \alpha_n \exp(-\beta_n r_{ij}/a)$$

where $Z_i e$ and $Z_j e$ are the nuclear charges of the projectile and target atoms, r_{ij} is the distance between the two particles, α_n and β_n are the empirical constants, and a is a constant determined from gas-phase scattering experiments.[22]

From this potential energy function, the shadow-cone shape may be approximated either by an analytical expression or by computer calculation. The latter method is very easy to carry out using a small personal computer. Using an established procedure, l is determined as a function of r so either d or h can be found by simple triangulation (see Figure 2b).

For the Ag{110} case, the value of d is known to be identical to the bulk spacing since the LEED data show that the ordering in the surface layer is the same as in the bulk.[20] Hence, a mechanism whereby the forward edge of the shadow cone intersects an adjacent surface atom can be used to check the numbers. The agreement between theory and experiment is on the order of ±0.5°, a value which translates into an uncertainty in the bond length of ~±0.05 Å.

From this point, other mechanisms may be investigated which do not have known bond distances. To find an unknown spacing, the distances are adjusted until θ_{ic} from the experiment matches the calculated value. An example from the Ag{110} case is shown in Table 1, where values of h are determined by this procedure.

There are two points associated with this data that need further elaboration. First, the large error found along the ⟨110⟩ azimuth is disturbing. From a detailed analysis of two-dimensional computer simulations,

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Table 1. Experimental and Calculated Values of θ_{ic} and Measured Values of h for Ag{110}

	h (Å)		θ_{ic} (deg)	
azimuth	bulk	relaxed; measd	exptl	calcd
⟨100⟩	2.889	2.77	36.5	36.5
⟨110⟩	2.889	2.77	29.5[a]	23.2[a]
⟨211⟩	1.445	1.33	31.5	31.5

[a] See text for analysis of discrepancy.

however, the source of this error can be clearly associated with distortions of the shadow-cone shape by nearby atoms.[17] Along densely packed crystallographic directions, the shadow-cone edge extends beyond more than one atom. This effect can be corrected by using a more detailed model or perhaps by increasing the kinetic energy of the primary particle to decrease the shadow-cone radius. The most expedient approach is to be alert for the possibility of distortions and avoid using data from these mechanisms.

The second point is related to the values of the bond distances themselves. From inspection of the crystal surface, it can be seen that the distance calculated along ⟨211⟩ is the distance between the first and second layers of Ag{110}, h_{12}, while the distance calculated along ⟨100⟩ is the distance between the first and third layers, h_{13}. Hence, $h_{23} = h_{13} - h_{12} = 2.77$ Å $- 1.33$ Å $= 1.44$ Å. This result shows that there is a relaxation of the first layer inward by nearly 10% of the bulk spacing, and that the perturbation to the spacing below the second layer is much smaller. This inward contraction has been generally observed on metal surfaces.[23] It is ascribed to rearrangements of the electron density due to the discontinuity created at the interface. The magnitude of the effect is found to be roughly proportional to the openness of the particular crystallographic orientation (i.e., {110} relaxes more than {111}, etc.).[23]

Chemisorption of Chlorine on Ag{110}

How do surfaces respond after reacting with adsorbed molecules? This is a fundamental question for surface chemists, and the answer may hold the key for postulating generalized theories of surface reactivity.[24] To illustrate some of the issues, here we consider the simple but important example of Cl chemisorption on Ag{110}. The behavior of this system has been widely studied since Cl and Ag are important parts of the ethylene oxidation catalyst.[25] Many of the basic chemical properties are established. For example, Cl_2 reacts with Ag at room temperature to form chemisorbed Cl atoms. These atoms can arrange in ordered overlayers [p(2×1) and c(2×4), which is the LEED notation that corresponds to 50% and 75% of a monolayer, respectively]. The bond lengths associated with these layers have been reported for Ag{110} to be (2.56 ± 0.04) Å as measured by SEXAFS.[26] This value is shorter than the value found in bulk AgCl of 2.77 Å, but it is longer than that found for gas-phase AgCl dimer, which is 2.28 Å.

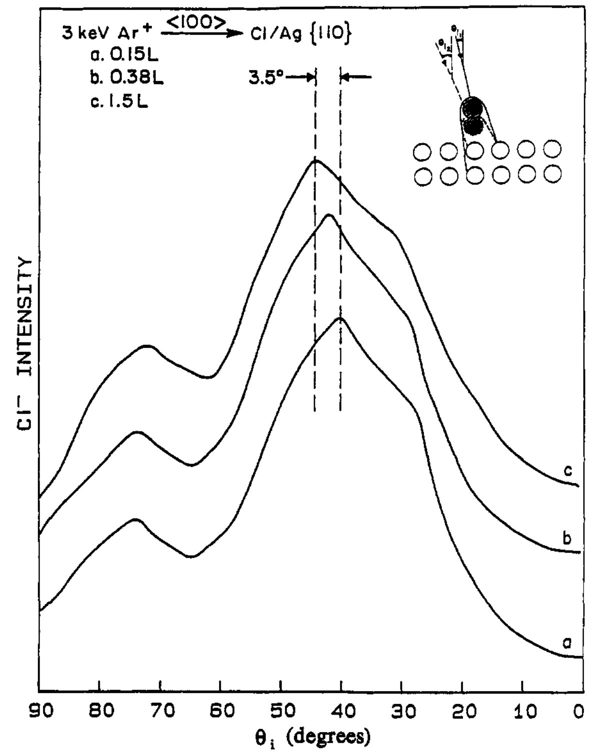

Figure 3. The sputtered Cl^- ion intensity as a function of the angle of incidence of Ar^+ ions, θ_i, from a Ag{110} surface exposed to Cl_2 gas. The spectra shown here are obtained with $\beta = 30°$. Insert: Model of the angular shift of the shadow cone for an effective interaction with the near-surface atom (open circle) as the height of the adsorbate (shaded circle) is changed.

The shadow-cone-enhanced SIMS technique offers a unique view of this system because the method is sensitive to low coverages of Cl atoms, ordered overlayers are not required, and the data needed for bond length measurements can be recorded quickly.[27] The angular distributions of Cl^- ions ejected from Ag{110} reacted with various amounts of Cl_2 are shown in Figure 3. The main feature near $\theta_{ic} = 40°$ is assigned to the interaction of the edge of a Cl shadow cone with an adjacent Ag atom. Note that this feature shifts by 3.5° to higher angles as the exposure to Cl is increased. This result suggests that the Ag–Cl bond length is contracting as a function of surface coverage. The summary of results is shown in Figure 4, where the data show that the bond distance is 2.91 Å in the lowest coverage and falls to 2.50 Å, in good agreement with the SEXAFS numbers, by the time an ordered structure is observed by LEED.

A change of bond length with coverage is not often found in surface crystallography experiments. In this case, we can postulate a simple explanation for the effect which is based on the idea that isolated Cl atoms form an ionic bond with the substrate. If the Ag–Cl interaction is highly ionic, the bond should have a significant dipole moment. Presumably, dipole–dipole interactions between nearby Cl^- atoms force charge back into the Ag substrate and the bonding becomes more covalent. The metallic surface in this case forms a fascinating template which allows the same bond to exhibit rather schizophrenic behavior. Notice that the biggest effect is observed *before* the LEED pattern is visible. This makes intuitive sense since the very

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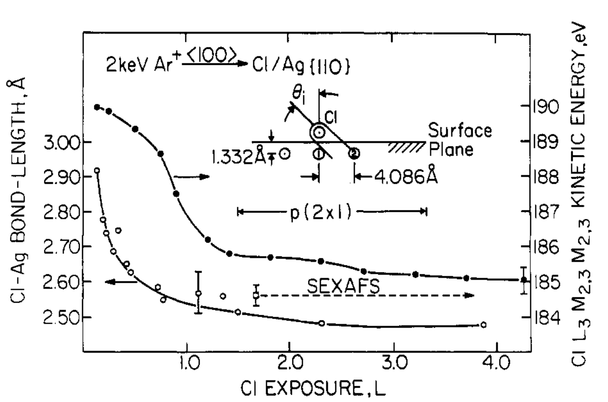

Figure 4. Ag–Cl bond-length change (○) and Auger Cl L_3-$M_{2,3}M_{2,3}$ kinetic energy (●) as a function of Cl_2 exposure at 300 K. The reported value refers to the distance between the center of silver atom 1 and the Cl atom. The p(2×1) LEED pattern was observed in the exposure region as shown. The bond lengths from the SEXAFS experiments are associated with the LEED pattern; the same value was also obtained at a coverage beyond 4 L and associated with the c(4×2) LEED pattern. Insert: The shadow-cone-induced desorption mechanism used to calculate the bond length is shown. The interplanar spacing refers to the relaxed clean-surface Ag{110} value. The shadow-cone shape was calculated using a Thomas–Fermi–Molière potential with a scaling factor of 0.86.

formation of an ordered overlayer implies that there are interactions between the adsorbed atoms. Hence, we believe that the study of isolated adsorbates will be a key future area for surface structure studies.

Surface Buckling during the Oxidation of Ni{001}

Another important type of chemisorption-induced surface rearrangement involves the buckling of second-layer metal atoms in response to the formation of the adsorbate bond. This phenomenon is particularly important to be able to characterize since a highly localized atomic displacement suggests that the chemisorption bond itself is not delocalized through the band states of the metal substrate. The effect has been observed for a limited number of systems, and so far the results are confusing, with some adsorbates pulling second-layer atoms up and some pushing them down and away from their second-layer positions.[1,28]

The shadow-cone measurements are uniquely suited to observing this effect. For Ni{001}, for example, there is a shadow-cone-induced yield maximum from the clean surface that corresponds to the bond distance between a first-layer atom and an adjacent second-layer atom.[29] When this surface is allowed to react with enough oxygen to form a $^1/_4$-monolayer overlayer [p(2×2) in the LEED notation], a second yield maximum is observed to occur at a critical angle which is 3.5° lower than the clean surface. These results are shown in Figure 5. By following the procedure for converting these maxima to bond lengths we find that this corresponds to a bond length difference of (0.26 ± 0.12) Å. One set of Ni atoms in the second layer is pushed away from the surface while the other set remains virtually unaffected.

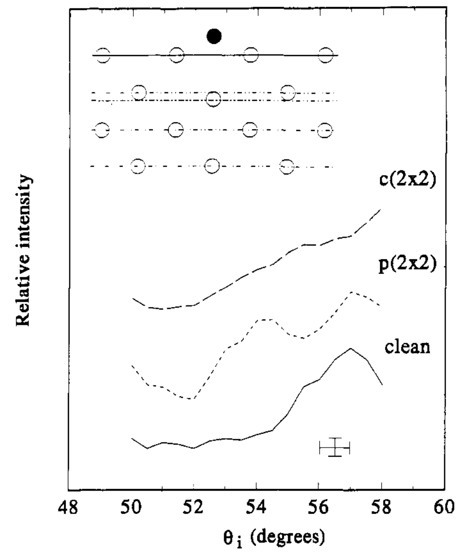

Figure 5. The relative intensity of 13-eV Ni^+ ions desorbed from clean Ni{001}, p(2×2)O/Ni{001}, and c(2×2)O/Ni{001} plotted as a function of the ion beam incidence angle. The ion beam is parallel to the ⟨100⟩ crystal direction. Included in the lower right hand corner are the error bars for the measurement. The insert is the cross section of a generic adatom/substrate system to illustrate the buckling of the second-layer atoms: (○) substrate atom; (●) adatom.

As the coverage is increased further to 0.5 monolayer of oxygen, the c(2×2) surface, these features are unfortunately smeared out. However, using other known distances and the approximation that the O–Ni bond length is the same as for the p(2×2) surface, we find that the buckling still persists for this coverage but is reduced slightly in magnitude to (0.20 ± 0.12) Å. These results are in general agreement with recent LEED measurements[30] but provide a rather direct indication that there are at least two bond distances induced by oxygen chemisorption.

Development of a general theory of buckling has so far proven elusive. There are a number of contradicting observations. For example, ethylidyne ($\equiv CCH_3$) adsorbed onto Pt{111} pushes the second-layer atom directly below it away by 0.08 Å,[28] but ethylidyne adsorbed on Rh{111} pulls this second-layer atom closer by 0.1 Å.[1] The presence of adsorption-induced rearrangements of this sort, however, are fundamentally important to obtaining a clearer picture of the surface chemical bond. Novel theoretical contributions are urgently needed.

Rearrangements on GaAs{001} Surfaces

The last example we consider here involves the characterization of semiconductor surfaces. These materials, such as Si and GaAs, are especially interesting to surface scientists not only because of their obvious technical relevance but also because they display a rich diversity of surface structures[31] which need to be characterized. The reason for this unique diversity is that crystal cleavage creates surface atoms with dangling bonds that retain unpaired electrons. To achieve a minimum energy configuration, certain sets of surface

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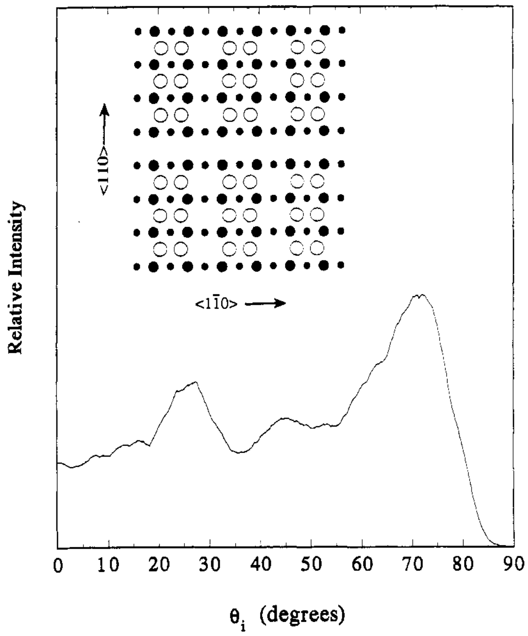

Figure 6. The relative intensity of 20-eV Ga^+ ions desorbed from the GaAs{001}-(2×4) surface by 3-keV Ar^+ ion bombardment, plotted as a function of the ion beam incidence angle, relative to the surface normal. The ion beam is parallel to the $\langle 1\bar{1}0 \rangle$ crystal direction. The insert is a schematic of the GaAs{001}-(2×4) model surface: (◯) first-layer As atom; (●) second-layer Ga atom; (•) = third-layer As atom.

atoms may pair up to alleviate this coordinative unsaturation. Many of these reconstructions are inherently very complex, but can play an important part in influencing surface electronic properties. Moreover, since these surfaces act as templates for epitaxial thin film growth, their structure can influence the quality of artificially created superlattices.

An important system is the GaAs{001} surface, which is employed in the fabrication of a variety of high-speed optoelectronic devices. A proposed arrangement of an As-terminated surface for a particularly important structure is shown in Figure 6.[32] This surface can only be prepared using molecular beam epitaxy so there are technical challenges associated with combining surface characterization objectives with the synthetic objectives. In any case, this surface is quite fascinating since it crystallizes in the zinc blende structure and the layers alternate between As and Ga compositions. Due to coordinative unsaturation, the As atoms pair up in rows, doubling the lattice periodicity. Presumably due to the excess negative charge that builds up on the surface, some of the dimers are missing, although the precise number is controversial.[33]

We have measured the intensity of second-layer Ga atoms ejected from the surface as a function of the ion beam incidence angle. The results of this experiment are shown in Figure 6.[34] The crystal direction, $\langle 1\bar{1}0 \rangle$, corresponds to shooting the incident beam directly along the As_2 bond, in an azimuthal direction parallel to the missing row of As atoms. The spectrum consists of four major peaks at polar angles of θ_{ic} = 70.1°, 63.0°, 44.5°, and 25.8°. There are many other distinguishable features in the spectrum which have been confirmed to be real structure, but their interpretation awaits future generations of research students. The main peaks have been assigned on the basis of parallel molecular dynamics calculations.[34] From these calculations the As_2 distance is determined from the small shoulder at $\theta_{ic} = 63°$ to be (2.73 ± 0.10) Å. This value is within experimental error of a recent estimate using maxima in the current observed from scanning tunneling microscopy of 2.8 Å.[2] These numbers suggest that the dimer bond distance is much closer to the bulk As bond distance with 3-fold coordination than to a tetrahedral covalent As bond involving sp^3 hybridization.[35]

Conclusions and Prospects

The development of new and more versatile surface structure techniques is a continuing research goal of surface scientists. The use of shadow cones to probe the location of atoms in the first few layers of a solid has become a particularly useful tool in this regard. It is especially interesting that the method requires no fancy equipment by surface science standards: an ion gun, mass spectrometer, and sample manipulator with two rotational degrees of freedom. The data are quite sensitive to low coverages and yield numbers which have a useful degree of accuracy, albeit not as good as other, more sophisticated approaches.

It will be interesting to compare the results obtained from the various techniques. For some shadow-cone experiments involving ion scattering, systematic differences have been observed when the results are compared with those of diffraction techniques.[23] To date, results from shadow-cone-enhanced SIMS have matched, within experimental error, structural parameters obtained by other techniques.[27,29] These error limits are still quite large, however, and improved precision is clearly desirable. Early results suggest that sample cooling to minimize vibrations may provide such improvement.

Here we have given several examples of how structural studies can give direct information about the rearrangement of surface atoms. Moreover, examination of the behavior of adsorbates on surfaces makes it possible to see how these atoms interact, redistribute their charges, and localize electrons with specific bonds. All of this information is critical input for the development of more sophisticated models of surface bonding.

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