Conclusions

The examples discussed in this article illustrate how the current theoretical and experimental research on surfaces has led to a better understanding of the microscopic origins and energetics of surface cohesion. It has been shown that electrostatic forces induced by the creation of a surface alter the atomic arrangements at the surface. In some cases, especially directionally bonded solids such as semiconductors, the surface is reconstructed into a crystallographic group that is different from the bulk. However, all surfaces, even those with the same two-dimensional symmetry as the bulk, are altered from the hypothetical truncated bulk. The induced forces are strong enough to create a multilayer relaxation of the outermost atomic planes.

Research on surface crystallography has been extended to surfaces of binary metal alloys. The atomic displacements induced by the surface forces are complex, but, as demonstrated by the successful analysis of the reconstruction of the NiAl(110) surface, many problems are tractable and will provide important additional information concerning the atomic interactions in nonuniform environments.

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Electron- and Photon-Stimulated Desorption: Probes of Structure and Bonding at Surfaces

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Techniques for analyzing the structure and composition of solid surfaces with electron and photon beams often cause radiation damage in samples. Damage-producing processes compete with information-producing events during measurements, and beam damage can be a serious perturbation in quantitative surface analysis. There are, however, substantial benefits of electron- and photon-stimulated damage processes for studying molecules adsorbed on surfaces. Direct information about the geometric structure of surface molecules can be obtained from measurements of the angular distributions of ions released by electron- or photon-stimulated desorption. The directions of ion emission are determined by the orientation of the surface bonds that are ruptured by beam irradiation. Moreover, photon-stimulated desorption studies that make use of synchrotron radiation reveal the fundamental electronic excitations that lead to bond-breaking processes at surfaces. These measurements provide new insights into radiation-damage processes in areas as diverse as x-ray optics and semiconductor electronics.

ELECTRONS AND PHOTONS ARE WIDELY USED AS PROBES for surface chemical and structural analysis in a number of surface measurements, including Auger electron spectroscopy, x-ray photoelectron spectroscopy, and scanning electron microscopy. The assumption in most of these studies is that the bombarding electrons and photons are relatively unperturbing probes that do little damage to the structure or composition of the surface being characterized. In fact, electron and photon bombardment can induce various bond-breaking processes at surfaces that are analogous to gas-phase electron- and photon-induced dissociation. In most surface analyses, this radiation-induced rupture of surface bonds is a nuisance to be avoided or minimized; in the cases described here, analysis of the surface dissociation (desorption) products can be beneficial by providing insights into the structure and bonding of surface species. This information comes from electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD) studies of surfaces, which are the subject of much experimental and theoretical interest (*1*–*5*).

In ESD and PSD, beams of energetic electrons or photons (typically about 10 to more than 1000 eV) incident on surfaces

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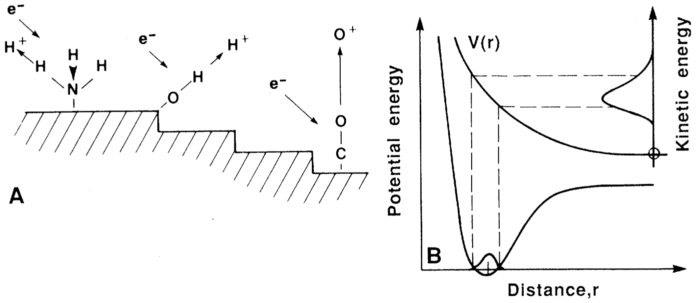

Fig. 1. (A) Schematic bonding configurations for adsorbed molecules on a stepped surface, showing the relation between surface bond angle and ion desorption angle in ESDIAD. The step heights have atomic dimensions. (B) Schematic potential energy diagram illustrating stimulated desorption of surface species. Electronic excitation from the attractive ground-state potential curve to the repulsive excited-state potential curve can lead to desorption of energetic species. $V(r)$ is the potential energy as a function of the atom-surface separation r.

containing terminal bulk atoms, or adsorbed monolayers of atoms or molecules, cause electronic excitations in the surface species. These excitations can result in desorption of ions, ground-state neutrals, or metastable species from the surface. Similarly, electronic excitation of bulk atoms can cause atom displacements, leading to radiation damage (such is the case in electron microscopy). A major difference that distinguishes ESD and PSD processes at surfaces and bulk radiation-damage events from gas-phase dissociative ionization processes is that the surface and bulk provide pathways for electronic deexcitation that are not available in the gas phase.

During the last few years, there have been substantial advances in understanding the mechanisms and extending the applications of ESD and PSD (*1–5*). Extensive theoretical work has provided new insights into the nature of the electronic excitations and the energy-localization processes that cause bond breaking and desorption (*6*). Angle-resolved ESD and PSD measurements are well-established tools for characterizing the geometry of surface molecules: ion desorption directions are related directly to the orientations of the ruptured bonds (*7, 8*). The use of synchrotron radiation to probe the thresholds and energy dependence of desorption has, in many cases, provided a detailed understanding of the multiple-electron excitations that induce desorption. Criteria have been recognized that govern the stability of surfaces to ionizing radiation (that is, radiation damage); this is a key issue in surface analysis (*9*).

This article examines the following aspects of the electron-surface and photon-surface interactions: (i) the basic physics of electron and photon bond-breaking interactions with surfaces, and how desorption is initiated; (ii) applications of ESD and PSD to surface science, with emphasis on the determination of molecular structure at surfaces by means of ESD ion angular distributions (ESDIAD); and (iii) the perturbing effects of electron and photon beams in surface analysis (*10*).

Basic Physics: Experimental Considerations

As a background for discussing the mechanisms of ESD and PSD, it is useful to summarize the basic experimental observations that characterize ESD and PSD measurements in the electron and photon energy range 10 to 1000 eV (*1–5*).

Desorption products. The observed ESD and PSD desorption products include positive and negative ions as well as ground-state neutrals and vibrationally and electronically excited neutrals (metastables). Because of their relative ease of detection, positive ions have been the focus of most ESD and PSD studies. For adsorbed monolayers of small molecules on surfaces, the most common ions observed are atomic (for example, $H^{\pm}$, $O^{\pm}$, F^{+}, Cl^{+}), but substantial quantities of molecular ions ($OH^{\pm}$ and $CO^{\pm}$) are also seen. Generally, yields of positive ions are 10 to 100 times greater than yields of negative ions. For condensed multilayers, the dominant ions are generally atomic (for example, H^{+} from condensed H_2O or CH_3OH), but complex polyatomic ions are also observed (with lower probability). Neutral desorption products include both atomic and molecular species; metastable atoms (Na* and Li*) and molecules (CO* and NO*) have been observed and characterized (*11–13*). The desorbing molecules are often vibrationally hot. Desorbing ions originate in the top one to two atomic layers of the solid surface.

Cross sections. The maximum cross sections for desorption of ions from surfaces ($\sim 10^{-20}$ to 10^{-23} cm^2) are generally smaller than those for the desorption of neutral species ($\sim 10^{-18}$ to 10^{-20} cm^2); both are smaller than typical cross sections for gas-phase dissociative ionization ($\sim 10^{-16}$ cm^2 for 100-eV electrons). For ESD, maximum ion yields are approximately 10^{-6} ions per incident electron; PSD ion yields are usually smaller, although a high PSD neutral yield of 10^{-2} atoms per photon has been reported for Li* from LiF (*11*). The cross sections for desorption of substrate ions are vanishingly small for metal surfaces but can be large for certain maximal valence oxides (such as TiO_2 and WO_3) (*4, 9*).

Threshold energies for desorption. The threshold energy for desorption of neutral molecules (*14*) can be as low as 5 eV; this correlates with a one-electron valence excitation of the adsorbate. Valence and shallow-core excitations (*15*), which lead to ion desorption, have thresholds of 15 eV or greater. Deep-core excitations [for example, C(1*s*) at 280 eV and O(1*s*) at 530 eV] also correlate with ion desorption thresholds because new desorption channels are opened (*16*). Multiply charged ions are also seen at energies above deep-core hole ionization energies.

Energies of desorption products. The most probable range of kinetic energies for ESD and PSD ions is 1 to 10 eV; energies as high as 15 eV have been reported. There are far fewer measurements of neutral products (*14*); their most probable energies are significantly lower (≤ 1 eV). As indicated above, both vibrationally and electronically excited (metastable) species have been observed and characterized.

Sensitivity to bonding mode. ESD and PSD cross sections are sensitive to the mode of bonding of an atom or molecule to a surface. In general, the cross section for breaking an internal molecular bond in an adsorbed molecule is higher than that for breaking the bond to the substrate (for example, ESD of H^{+} from OH bound through the oxygen atom has a much higher cross section than ESD of H^{+} from adsorbed atomic hydrogen).

Ion angular distributions: relation to structure. The utility of ESD and PSD for determining the structure of surface species derives from the fact that ESD and PSD ions do not generally exhibit isotropic distributions. Instead, they desorb in discrete cones of emission in directions determined by the orientation of the surface molecular bonds that are ruptured by electronic excitations. For example, as indicated schematically in Fig. 1A, ESD of CO bound in a "standing up" configuration on a metal surface will result in desorption of O^{+} in the direction of the surface normal; ESD from "inclined" OH, or of H^{+} from NH_3 adsorbed through the nitrogen atom, will occur in off-normal directions. Thus, measurements of the ESDIAD patterns yield direct information about the geometric structure of molecules in surface layers (*3, 7, 8*). Angle-resolved PSD contains similar information, but because of experimental difficulties it is less widely used. Angle-resolved desorption of neutrals and metastables has also been reported (*12*).

ESD and PSD similarities and differences. ESD and PSD are thought to be initiated by essentially the same elementary electronic excitation of the surface (*4*). The equivalence of ESD and PSD excitations has been demonstrated through similarities in desorption threshold energies, in ion energy distributions, in ion angular distributions, and in the nature of the surface species from which desorption occurs. There are differences, however, in the shapes of the ESD and PSD spectral yield curves (ion yield compared to excitation energy) and in the magnitudes of the excitation cross sections for electron and photon excitation. A PSD ion yield curve generally has a sharp threshold that is followed by a maximum and a relatively abrupt decay of the signal. In contrast, ESD spectra have weak thresholds and rise smoothly above threshold. The origin of these spectral shapes and the relevant excitation physics have been discussed (*4*).

Mechanisms of ESD and PSD

It is clear from the data described above that stimulated desorption is initiated by an electronic excitation of a surface molecular bond: neither thermal effects nor direct momentum transfer (such as that between a bombarding electron and a surface atom) can account for the low threshold energies and the observation of massive ions with high kinetic energies.

Stimulated desorption is usually described in terms of specific models, such as the Menzel-Gomer-Redhead model of desorption from covalent adsorbates (*17*) or the Knotek-Feibelman model of desorption from ionic substrates (*9*). In the former model, the primary process is a Franck-Condon excitation or ionization to a repulsive neutral or ionic state, from which desorption can occur. The latter model is particularly applicable to highly ionic systems and is based on the ionization of a core level as the primary process. The interatomic Auger decay of the core hole creates a positive ion at an initially negative ion site, and the expulsion of the positive ion results from the reversal of the Madelung potential. A more generalized Auger-stimulated desorption model has been described (*18*) that extends the Knotek-Feibelman model to less ionic and covalent systems.

Although these models differ in detail, they have much in common. The essential features of the stimulated desorption excitation process, as embodied in all the models, can be described approximately (*3, 6*) as a sequence of three processes (Fig. 1B), as follows: (i) a fast initial electronic excitation ($\sim 10^{-16}$ second) (typically this is a valence or core excitation); (ii) a fast electronic rearrangement ($\sim 10^{-15}$ second) to a repulsive electronic state having a lifetime of about 10^{-14} second (repulsive electronic energy is converted to nuclear motion); and (iii) a modification of the desorbing species (its energy, charge state, or trajectory) as it leaves the surface.

As illustrated in Fig. 1B, the surface bond is excited by electron or photon excitation through a valence or core hole ionization process (on a time scale of about 10^{-16} second). For valence excitations involving one-electron processes, excitation can be direct to a long-lived (10^{-15} to 10^{-14} second) antibonding repulsive state, from which desorption can occur. This can be a major route to desorption of ground-state and excited neutral species. It is widely believed (*3–6*) that ESD and PSD of ions from both covalently bonded and ionically bonded surface species proceed through multielectron excitations that produce two-hole (2h) or two-hole, one-electron (2h1e) excited states. These excited states can be highly repulsive, with hole localization lifetimes on the order of 10^{-14} second, so that the repulsive electronic energy can be converted to nuclear motion. For example, an 8-eV O^+ ion will travel about 1 Å in 10^{-14} second, so that the surface bond is effectively broken. This process is an important route to ionic ESD and PSD products.

The repulsive interaction in the excited electronic state (Fig. 1B) can be described as coulombic in origin and is directed primarily along the direction of the bond that is ruptured by the excitation. Hence, the initial ion desorption angle in ESDIAD is determined by the ground-state surface bond angle. There are, however, final-state effects [process (iii) above] that can influence ion desorption trajectories and yields; these include the surface image force and reneutralization effects (*19*). The image force invariably causes an increase in the polar desorption angle of an ion leaving a planar surface (that is, the trajectory is bent toward the surface). Reneutralization effects (electron hopping to the desorbing species by resonant tunneling or Auger neutralization) also influence the measured ion angular distributions and yields. Recent calculations indicate that, in addition, dynamical distortions of the substrate lattice after the initial excitation can influence the desorption processes (*20*).

Instrumentation

The ideal apparatus for stimulated desorption measurements is complex, having capabilities for independent control of a wide range of parameters in an ultrahigh vacuum (UHV) environment. Such an ideal apparatus (Fig. 2a) would permit measurement of the mass, desorption angle, kinetic energy, and internal energy (electronic, vibrational, and rotational) of ions and neutral species (*4*). All these properties would be studied as a function of the energy, angle of incidence, and polarization of the incident electron or photon beam, and the surface temperature would be controlled to influence surface chemistry; all this would take place at pressures of 10^{-10} torr or less. In addition, probes for characterizing the composition and structure of the surface, such as Auger electron spectroscopy and low-energy electron diffraction (LEED), would be available.

Figure 2b illustrates a UHV system constructed at the National Bureau of Standards for ESD of ions; this system permits mass and energy analysis of desorbing ions (by means of a mass spectrometer and retarding grids, respectively) as well as measurements of the ESDIAD patterns (*8*). A focused electron beam bombards a single crystal sample. The ESD ion beams pass through hemispherical grids and strike the front surface of a double microchannel plate assembly. The output signal from the assembly is accelerated to a fluorescent screen, where it is displayed visually (the ESDIAD pattern). By changing potentials, the elastic LEED pattern from the sample can be generated and observed. The ESDIAD and LEED patterns can be photographed (as has been done in most ESDIAD studies), or they can be recorded with a high-sensitivity video camera and a computer-controlled digital imaging processing system (*21*). The system at the National Bureau of Standards allows acquisition of real-time images or digitization of photographic negatives. Other features include creation of histograms and contour plots of ion intensity as a function of position on the detector and manipulation of the digital image (background subtraction, smoothing, and the like). Other digital imaging ESDIAD systems based on scanning collectors or resistive anode detectors are in use at Jülich (*22*), Sandia (Livermore) (*23*), and the University of Pittsburgh (*24*).

Applications of ESD/PSD to Surface Science

In surface science applications, ESD and PSD are among the few techniques that are sensitive to the presence of hydrogen at surfaces: the yields of H^+ from hydrogen-containing molecular fragments are generally high. Measurements of the energy thresholds for desorption provide bond-specific information; for example, one can distinguish among H^+ originating from adsorbed OH, CH, NH, or adsorbed hydrogen. PSD ion yields have been used as SEXAFS (surface extended x-ray absorption fine structure) probes in synchrotron radiation experiments (*25*) to determine surface structure (nearest-neighbor bond lengths).

Moreover, studies of radiation-induced bond-breaking processes at surfaces provide a detailed view of radiation damage mechanisms. Measurements of the yields and energy states of ions, ground-state neutrals, and metastable species that desorb from surfaces can give information about the initial excitations that can occur deep in bulk solids, although the bulk excitation may subsequently be quenched by efficient energy transfer processes. These studies provide a fundamental basis for understanding such phenomena as radiation damage in electron microscopy and the activation of photoresists or electron beam resists (*26*). Even ion bombardment of solids, in which the dominant damage mechanism is through momentum transfer, can cause damage by electronic excitations (*27*).

ESDIAD. By now, there is a wealth of experimental and theoretical evidence that the direction of ion emission is related directly to the orientation of the surface bond that is ruptured by the excitation. Although there are effects (image force and reneutralization) that can alter the desorbing ion trajectories (*19*), there is a great deal of qualitative and quantitative structural information (in particular, information about bond angles) available in ESDIAD measurements. The structures of atoms and molecules adsorbed on metals (*8*) and of clean oxide substrates have been reported (*15*).

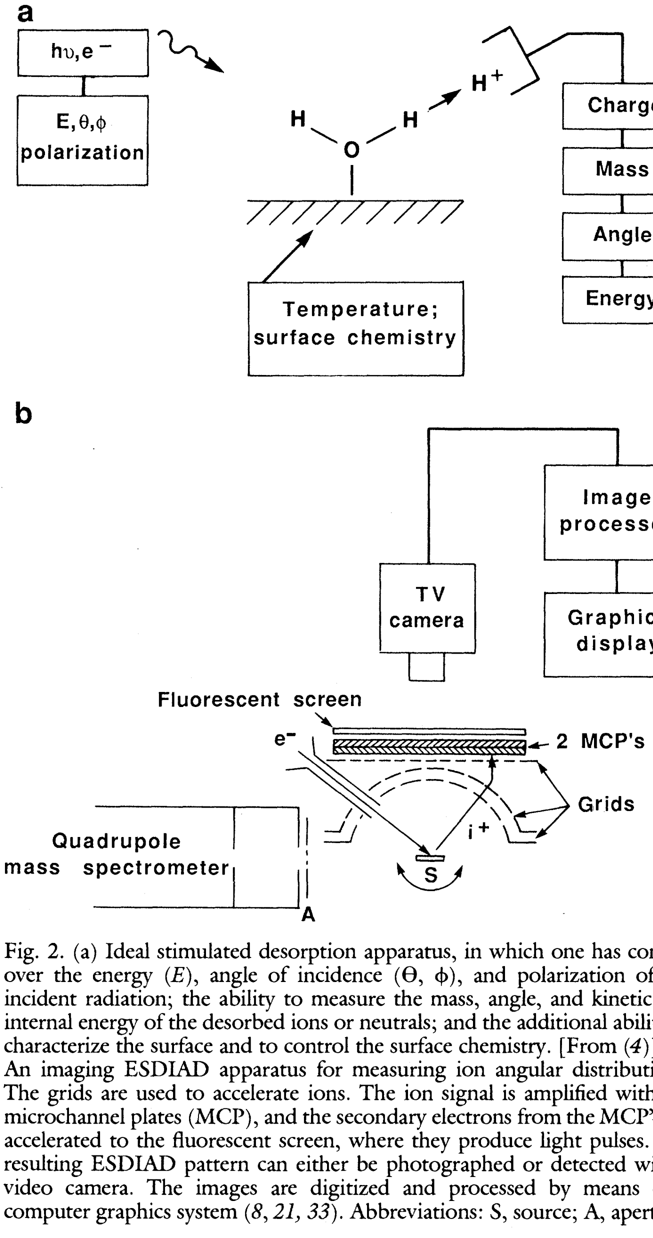

Fig. 2. (a) Ideal stimulated desorption apparatus, in which one has control over the energy (E), angle of incidence (Θ, ϕ), and polarization of the incident radiation; the ability to measure the mass, angle, and kinetic and internal energy of the desorbed ions or neutrals; and the additional ability to characterize the surface and to control the surface chemistry. [From (*4*)] (b) An imaging ESDIAD apparatus for measuring ion angular distributions. The grids are used to accelerate ions. The ion signal is amplified with the microchannel plates (MCP), and the secondary electrons from the MCP's are accelerated to the fluorescent screen, where they produce light pulses. The resulting ESDIAD pattern can either be photographed or detected with a video camera. The images are digitized and processed by means of a computer graphics system (*8, 21, 33*). Abbreviations: S, source; A, aperture.

There are many ESDIAD results (*8*) that confirm molecular structural assignments (for example, for CO, NO, NH_3, H_2O, and C_6H_{12} adsorbed on metal surfaces) made by means of other surface-sensitive techniques. The observations that molecular CO "stands up" on Ni(111) and Ru(001) surfaces (bound through the carbon atom with the molecular axis perpendicular to the surface plane), that it "lies down" on Cr(110) (with the molecular axis parallel to the surface), and that it is "inclined" on surfaces such as Pd(210) illustrate the complexities of bonding for one molecule in different environments. In a recent example (*28*), CO on Ni(110) was found to bond in a "standing up" configuration for CO coverages below about 0.75 monolayer. At higher coverages, up to one monolayer, lateral repulsive interactions between neighboring molecules force the CO into "tilted" configurations, with the molecular axes inclined 19° from the surface normal. Polar molecules such as NH_3 and H_2O are found to bond to many surfaces through the lone pair orbitals on the nitrogen or oxygen atoms, with the hydrogen atoms pointing away from the surface: the binding structures have been determined directly in many ESDIAD experiments (*8*).

Azimuthal ordering in adsorbed overlayers. There is one area in which ESDIAD has provided a detailed new view of structure and bonding on surfaces: the interaction of small molecules (NH_3, H_2O, CO) with adsorbed impurity atoms (O, Br, Na, K) on metal surfaces (*8, 29*). As a result of interaction with the adsorbed additive atom, the surface molecule is often reoriented into a bonding structure different from its local structure in the absence of the additive. For example, a fractional monolayer of preadsorbed oxygen on a Ni(111) surface can induce a high degree of local azimuthal ordering in adsorbed NH_3 and H_2O, even though these molecules have random azimuthal orientations on the clean nickel surface (*29*). In most cases, it appears that the molecule-additive interaction is a short-range, local interaction occurring at nearest-neighbor distances; hydrogen bonding and other electrostatic effects have been postulated.

An example of the influence of electronegative surface additives (Br, O) on the structure and chemistry of H_2O adsorbed on Ag(110) is illustrated in Fig. 3. The objective of the work from which this example derives was to provide a synthetic version of the electrochemical "double layer" that exists at the interface between electrode and electrolyte in an electrochemical cell. The interface simulation was accomplished by adsorbing, in UHV, controlled amounts of bromine and oxygen atoms as well as solvent H_2O molecules onto an initially clean Ag(110) surface (*30*).

Figure 3A shows perspective and contour plots of the H^+ ESDIAD pattern for fractional monolayers of H_2O adsorbed on Ag(110) at 80 K. For adsorbed H_2O, the dominant ESD ion is H^+ from rupture of OH bonds. The random emission centered about the surface normal (center of the pattern) indicates that the adsorbed H_2O is disordered locally; there is no long-range order at any coverage, as determined by LEED. These and other measurements indicate that H_2O is adsorbed in poorly ordered hydrogen-bonded clusters on Ag(110) at 90 K.

In contrast to this situation, the interaction of H_2O with a preadsorbed fractional monolayer of bromine or oxygen atoms on Ag(110) causes the clusters to break up: new surface structures are formed. On bromine-dosed Ag(110), a surface hydration shell containing two H_2O molecules is believed to form around each adsorbed bromine atom. Evidence for a pronounced orientational

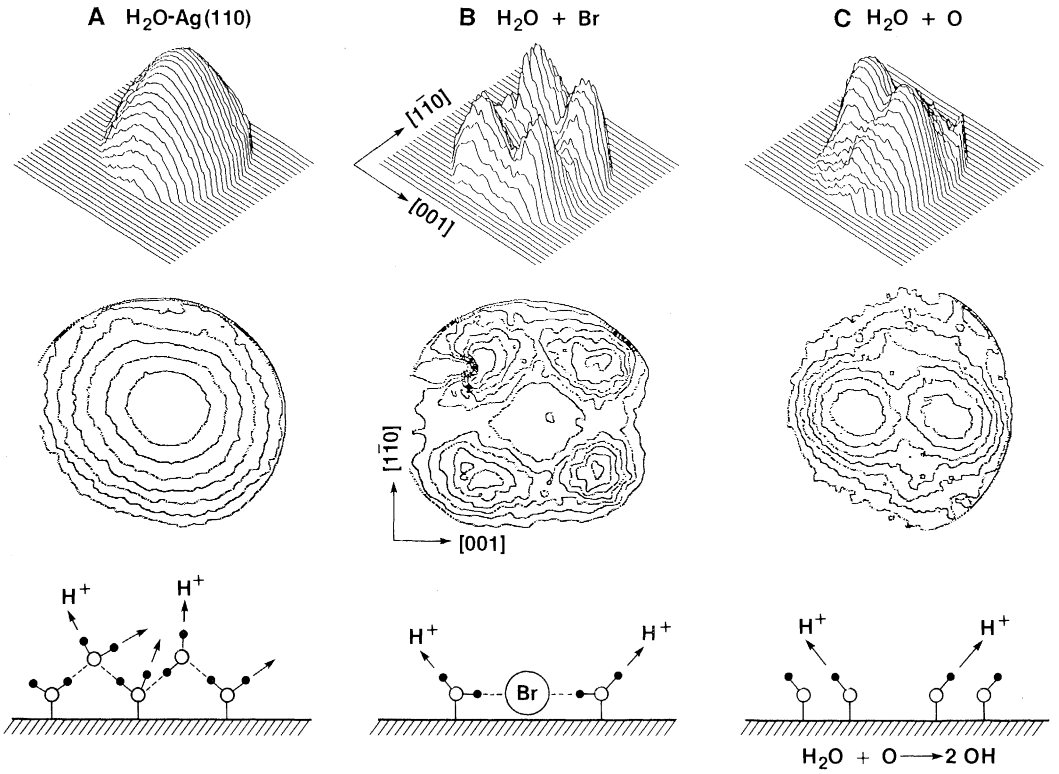

Fig. 3. H^+ ESDIAD patterns and schematic models illustrating the influence of bromine and oxygen on the local structure of H_2O on the Ag(110) surface (*30, 31*). The top row contains perspective plots of the ion intensity displayed on the fluorescent screen of Fig. 2b. The second row contains contour plots of ion intensity for the same measurements as the top row. The third row contains schematic molecular models. (A) H^+ ESDIAD and models for H_2O on clean Ag(110). (B) H^+ ESDIAD and models for H_2O + Br on Ag(110). (C) H^+ ESDIAD and models characteristic of H_2O + O on Ag(110).

ordering of the H_2O molecules adjacent to the bromine is seen in Fig. 3B, where a distinct four-beam H^+ ESDIAD pattern is displayed. A model in which the adsorbed H_2O is stabilized by a hydrogen-bonding interaction with adsorbed bromine has been proposed (*30*); a simplified schematic picture is given at the bottom of Fig. 3.

As shown in Fig. 3C, a very different orientational ordering is found for H_2O adsorbed on oxygen-dosed Ag(110). In this case, the dominant H^+ beams are oriented along [001] azimuths, with weaker beams along [1$\bar{1}$0] azimuths (*31*). H_2O is known to dissociate on oxygen-dosed Ag(110) to form adsorbed OH species [H_2O + O (adsorbed) → 2 OH (adsorbed)], even at cryogenic temperatures. As shown in the lower part of Fig. 3C, the OH species are tilted along [001] azimuths, giving rise to the intense ESDIAD beams in the top part. The weaker beams along [1$\bar{1}$0] azimuths are due to OH-stabilized H_2O.

The dramatic influence of both bromine and oxygen on the structure and chemistry of H_2O on Ag(110) is not an isolated case. There are many examples in which additive atoms exhibit strong effects on adsorbed molecular structures (*8, 29*). This phenomenon—additive-induced changes in bonding geometry—may be related to the mechanisms by which catalyst promoters and poisons influence catalytic reaction pathways.

ESDIAD of H_2O on Si(100): influence of surface vibrational dynamics. Although extensive ESDIAD measurements have been made for adsorbates on metal surfaces, there have been few ESDIAD data reported to date for adsorbates on semiconductors (*15*). One important problem addressed at the National Bureau of Standards concerns the interaction of H_2O with silicon surfaces; the technological importance of this interaction with respect to the wet oxidation process is motivation for understanding the details of the H_2O-Si surface chemistry (*32*).

Although there has been some controversy concerning the state of adsorbed H_2O on silicon at 300 K (is it molecular, or does it dissociate into H + OH?), the strongest evidence is in favor of dissociative adsorption (*32*). The Si(100) surface is believed to undergo a reconstruction involving the formation of surface dimers, and it has been proposed that H_2O dissociates to OH and H bonded to opposite ends of the surface dimer (Fig. 4).

Figure 4 illustrates ESDIAD perspective and contour plots for H_2O adsorbed on a planar Si(100) surface at 300 and 140 K (*33*). It was found in separate experiments that the only ionic desorption product was H^+ and that the H^+ yield from adsorbed OH was substantially higher than that from adsorbed hydrogen. Several facts are evident from Fig. 4. First, there is an emission minimum in the center of the pattern in the direction of the surface normal, so that the OH are tilted with respect to the normal. Second, the pattern at 140 K contains four clearly resolved maxima along [011] azimuths, whereas the pattern at 300 K is less well resolved and has a doughnutlike appearance. The four-lobed pattern arises from two domains of Si(100) dimers, rotated by 90° from one another. The temperature dependence is completely reversible as the sample is heated or cooled between 140 and 300 K.

The reversible temperature dependence of the ESDIAD patterns indicates that the inclined OH species are not rigidly fixed on Si(100) in a few distinct orientations but that they undergo considerable surface motion—in particular, large-amplitude, low-frequency hindered rotations and bending and wagging modes. The ESDIAD pattern represents a "snapshot," at a particular temperature, of the distribution of OH bond orientations measured with respect to the surface normal (*8, 34*). From the temperature dependence, the frequency of the bending and wagging modes is less than 100 cm^{-1}, which is comparable to measurements made on ligands in gaseous molecular complexes.

Summary of information from ESDIAD. Some of the uses of ESDIAD in surface science can be summarized as follows. (i) ESDIAD provides direct information regarding surface molecular structures: ion desorption angles are related to surface bond angles. ESDIAD is not a diffraction technique; real-space images of bond directions are observed. (ii) ESDIAD is sensitive to bond orientation, that is, to the local bonding geometry. Long-range order in the surface adlayer is not necessary to produce an ordered ESDIAD pattern. (iii) ESDIAD is especially sensitive to the orientation of hydrogen atoms in surface molecular complexes. In contrast, LEED is relatively insensitive to the positions of hydrogen atoms in adsorbed molecules. (iv) Finally, ESDIAD is particularly helpful when used in conjunction with other surface-sensitive techniques. Whereas bond directions are determined with ESDIAD, quantitative measurement of the bond length requires a technique such as SEXAFS. Whereas ESDIAD is sensitive to the local order, LEED is sensitive to the long-range order in the surface layer. Vibrational spectroscopy, such as high-resolution electron energy loss spectroscopy, is extremely important for identifying the stoichiometry of surface molecular complexes whose structures are studied by ESDIAD.

ESD and PSD as Perturbations in Surface Analysis: Beam Damage

Care must be taken to minimize or control damage effects when characterizing surface composition, structure, or topography by techniques that involve electron beams (*10, 35, 36*). There are several causes of beam-induced damage in surface analysis (*10, 36*). The first and most important arises from the bond-breaking electronic excitations discussed earlier. Deep-core and valence electronic excitations induced by both the primary electron beam and the secondary electrons released from the sample can cause desorption of surface species, leading to rapid changes in chemical composition and even structure of the surface and near-surface regions. In general, an electron or photon beam incident on oxides and practical surfaces in UHV is a reducing agent. A related effect is electron-stimulated adsorption, in which gaseous molecules adsorbed on the surface are "cracked" by the electron beam, resulting in accumulation of a surface residue. A frequently observed example of this process is the carburization or carbon buildup that occurs on samples in electron microscopes operated in background pressures of 10^{-6} to 10^{-7} torr of hydrocarbon vapors (not UHV). If the background gas contains substantial quantities of H_2O, samples can also be oxidized during electron bombardment.

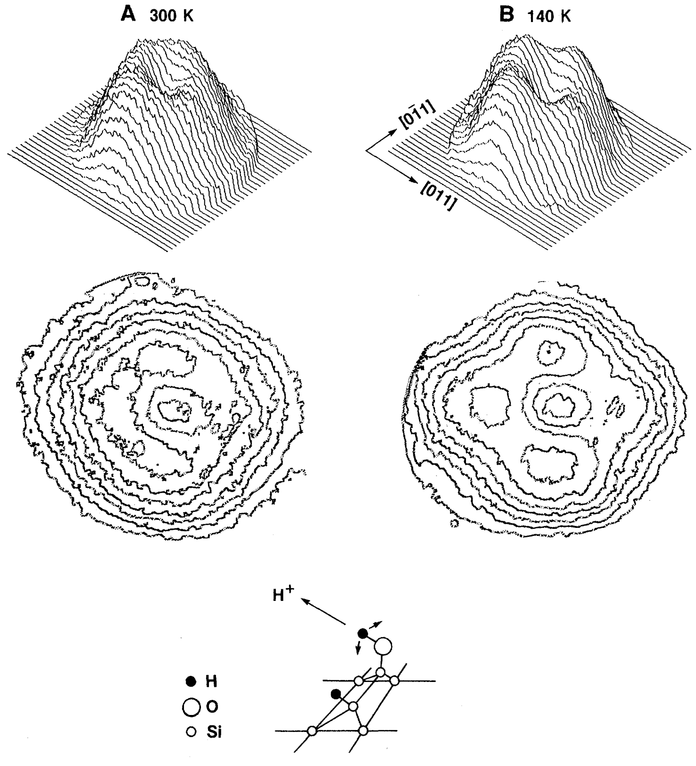

Fig. 4. H^+ ESDIAD and schematic models illustrating the bonding of OH to a Si(100) surface (*33*). (A) H^+ ESDIAD (perspective and contour plots) at 300 K; (B) H^+ ESDIAD at 140 K. A schematic bonding model in which H and OH are bound to both ends of a Si(100) dimer (*32*) is shown at the bottom. The four H^+ beams in (B) are due to ESD from degenerate dimer configurations. The decrease in resolution of ESDIAD at 300 K is due to increased vibrational motion of the OH species.

A second effect is the local heating that can be induced by the primary electron beam (typically 1 to 100 μA and 2 to 5 keV for Auger spectroscopy). The beam is usually highly focused, and the power density can be high (tens of watts per square centimeter for typical Auger spectroscopy). Beam heating is a particular problem when studying insulators, especially powders: it is common to see small particles glowing incandescent during Auger analysis. Undesirable surface chemical reactions, volatilization, surface diffusion, or segregation can be a consequence. In general, the heating becomes more severe as spatial resolution is increased (because of the more highly focused beam). Another beam-induced problem is the surface charging of insulating samples during beam irradiation. Depending on the value of the secondary electron yield, the resultant surface potential can be either positive or negative. In addition to perturbing the measured spectra, the surface charge can cause the electric field–induced diffusion of mobile ions in insulators (an example is electron beam–induced diffusion of Na^+ through soda-lime-silicate glass).

Beam damage effects are usually much worse when using electrons (Auger spectroscopy, LEED, and scanning electron microscopy) than when using photons (x-ray photoelectron spectroscopy). For useful signal-to-noise in all these measurements, the electron flux used in the electron spectroscopies is normally much higher than the photon flux used in the photoelectron spectroscopy. In addition, the damage probability per incident electron is greater than per incident photon.

Which materials are most susceptible to beam damage? Organic materials, biological samples, condensed molecular films, and adsorbed polyatomic molecules are most fragile under electron or photon irradiation. Saturated hydrocarbons are more fragile than molecules with unsaturated bonds. In many of these cases, the beam-induced dissociation probability is similar to that for the isolated gaseous molecule, and it is difficult or impossible to make a measurement without causing damage. There are, however, materials for which increasing the damage caused by electron and photon bombardment is desired: these are the electron- and photon-beam resists used in modern lithography in microelectronic device fabrication (*25*).

Inorganic materials such as oxides and alkali halides are also subject to damage. Knotek and Feibelman (*9*) provided criteria for the stability of ionically bonded solids bombarded by ionizing radiation. The materials most likely to decompose under electron bombardment are maximal valency compounds, in which the cation and anion have large Pauling electronegativity differences. Such materials include TiO_2, V_2O_5, WO_3, MoO_3, SiO_2, and Al_2O_3. The desorption mechanism is initiated by a core hole on the cation with a subsequent interatomic Auger process and the desorption of O^+. Loss of oxygen leads to a reduction of the surface oxide. Nonmaximal valency oxides (NiO, FeO) are much more stable (*19*). Alkali halides are strongly affected by electron bombardment: at ambient temperatures, loss of halogen is the dominant damage process.

Metallic samples are not, in general, subject to significant beam damage: electronic excitations of surface and substrate atoms are rapidly screened by conduction electrons. As mentioned above, however, clean metals can quickly become covered by impurities as a result of electron-stimulated adsorption.

There are several "tricks" that can minimize beam damage in surface analysis. By using a defocused beam or by rastering (scanning) the probed beam rapidly over a large area, the total beam dose can be reduced. In addition, a homogeneous sample can be moved during analysis to expose fresh regions to the beam. Thus important compromises must be made in practical surface analysis between the precision and sensitivity of the analysis and the spatial resolution. Other techniques for reducing damage during analysis have been described (*36*).

Surface analysis is not the only area of science and technology where radiation-induced surface processes are a problem. Photon-stimulated desorption of gases from vacuum walls is a limiting factor in attaining UHV in high-energy synchrotron radiation sources; both ESD and PSD can cause injection of impurities into the plasma discharge from the walls of fusion reactors; stimulated desorption processes have been identified as potential damage mechanisms in ultraviolet laser optical components (*37*); and the photon-induced damage of substrates and thin film coatings is a vexing problem.

Conclusion

This article has had a limited objective, namely, to introduce scientists to some of the benefits and liabilities of ESD and PSD. The emphasis has been on physical concepts and applications of these techniques rather than on a quantitative discussion of mechanisms.

There are many challenges and much excitement in ESD and PSD. The use of high-flux, polarized synchrotron radiation at high photon energies (⩾500 eV) is stimulating studies of surfaces and adsorbates in the energy range of deep cores. Although most ESD and PSD studies have focused on ions, measurements of the internal energy and angular distributions of neutrals (and metastables) are appearing. The expanding interest in ESD and PSD mechanisms and fundamental excitations should have increasing impact on technology in areas as diverse as x-ray optics, electron beam lithography, and electron microscopy.

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