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SURFACE MOLECULAR STRUCTURE FROM ION-NEUTRALIZATION SPECTROSCOPY OF ELECTRONS IN SURFACE ORBITALS

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It is shown that the ion-neutralization spectroscopy determines the orbital energy spectra of surface molecules formed of adsorbed foreign atoms and surface atoms of the substrate. For free molecules such a spectrum yields information concerning molecular symmetry and structure as well as ionicity within the molecule. Using also measured work-function change in adsorption, specific conclusions are drawn concerning O, S, and Se adsorbed in $p(2\times 2)$ and $c(2\times 2)$ arrangements on Ni (100).

In surface physics and chemistry we have not to this point possessed sufficiently powerful experimental methods to determine the local symmetry and molecular structure in which foreign atoms are adsorbed on solids. In its present state of development, low-energy electron diffraction determines only the symmetry of the pattern in which the local structure or surface molecule repeats itself over the surface. Work-function change on adsorption yields an important parameter but its value depends both on ionicity and structure. In this Letter we demonstrate that the ion-neutralization spectroscopy[1] determines the orbital energy spectrum of electrons in surface bonds whose form and energy position, for certain systems at least, enable us to draw specific conclusions about the structure and symmetry of the local molecular arrangement. We present experimental results and conclusions for O, S, and Se adsorbed in $p(2\times 2)$ and $c(2\times 2)$ arrangements on Ni (100).

The orbital energy spectrum is determined by means of the ion-neutralization spectroscopy discussed extensively elsewhere.[1] The method determines a function $U(\zeta)$, called the transition density, which includes both state density and transition probability factors. ζ is the energy measured positively downward into the filled band from zero at the Fermi level. When a foreign atom is adsorbed on a surface, the transition probability of the Auger process is enhanced at the energies of the orbitals of electrons in the surface bonds. The orbital energy states which lie in the energy range of the allowed states of the solid become broadened resonances or virtual states. States lying outside (below) the allowed range in the solid are broadened by the effect of molecular vibration on orbital energy and by lifetime and other effects having to do with the ion-neutralization process. We expect such states to be sharper than the resonances or virtual states.

In Fig. 1 are shown the transition-density functions obtained for clean Ni (100), curve 1, and for this surface with $p(2\times 2)$ and $c(2\times 2)$ surface arrangements involving $X\equiv$ O, S, or Se, curves 2, 2′ to 4, 4′. We note first that the Ni d band, to be seen just below the Fermi level ($\zeta=0$) in curve 1, is drastically reduced in intensity in curves 2, 3, and 4, which correspond to a half-monolayer of the adsorbate X, and somewhat less so in curves 2′, 3′, and 4′ which correspond to a quarter-monolayer of X. This reduction in d-band intensity is direct experimental evidence that the ion-neutralization process is sensitive to wave-function magnitude in the surface layer of the solid primarily. The $U(\zeta)$ functions in Fig. 1 are shown by a dashed line in the energy range $\zeta > 9$ eV because for several good reasons the data are not accurately reproducible here. However, the presence of a peak in this region in curves 3 and 4 and its absence in curves 3′ and 4′ is a reproducible experimental conclusion.

The structure which appears in curves 2, 2′ to 4, 4′ of Fig. 1, not including the residual Ni d-band peak, is taken to be the molecular orbital energy spectrum of the electrons in the bonds of what may be called surface molecules formed of the adsorbate atom and atoms of the first layer

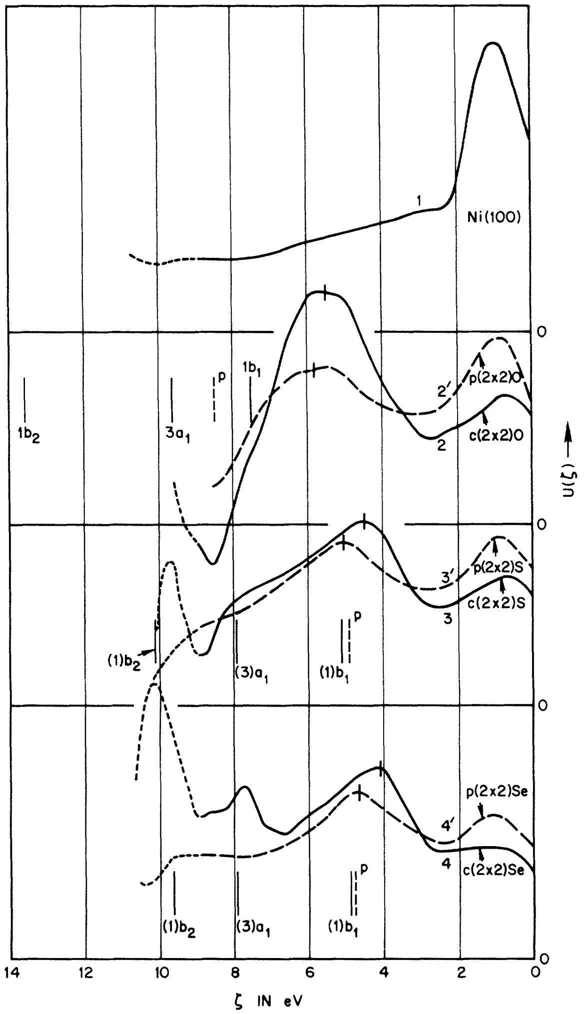

FIG. 1. Transition-density functions $U(\zeta)$ from ion-neutralization spectroscopy for atomically clean Ni (100), curve 1, and for the same surface with $p(2\times2)$ and $c(2\times2)$ structures of O, S, and Se. Energies of atomic and molecular orbitals are also indicated as described in the text.

of the Ni (100) surface. There are three types of such spectra to be distinguished in Fig. 1: (1) Multipeak spectra, curves 3 and 4, in which the highest lying peak at smallest ζ lies near the orbital energy of the p electrons in the free atom X, indicated by the dashed lines labeled p. These lines are plotted at $\zeta = I(X) - \varphi_A$, where $I(X)$ is the free-space ionization energy of the adsorbate atom X and φ_A is the work function of the surface with the specific adsorbate structure present. (2) Single-peak spectra, curves 3′ and 4′, in which the peak lies near the p orbital energy of the free atom; and (3) single-peak spectra, curves 2 and 2′, in which the peak is shifted appreciably (~3 eV) to higher energy (smaller ζ) from the p-orbital energy of the free atom.

It is clear that the orbital energy spectrum tells us much about the character of the electronic orbitals, the local symmetry at the site of the adsorbed atom, and hence about the specific atomic arrangement in the surface molecule. Spectra of type (1) above require a structure which yields several, namely three, inequivalent orbitals in the observed energy range. Spectra of types (2) and (3) indicate structures in which the p electrons reside in equivalent orbitals but which must differ in a significant way so as to produce the difference in energy shift.

The position of a spectrum relative to the orbital energy of the p electrons in the free adsorbate atom is also significant. The orbital energy of an electron in a molecule will lie lower (larger ζ, in our case) than the orbital energy in the free atom if the molecular orbital is bonding, if the orbital involves hybridization with deeper lying atomic orbitals, or if local positive charging occurs in the region of the orbital. The molecular orbital energy will lie higher (smaller ζ) if the atom becomes electronegative in the molecule. We neglect higher lying antibonding orbitals which are usually not filled. An unhybridized lone-pair or nonbonding orbital will be shifted from the orbital energy of the free atom only by the effect of ionicity within the molecule. From these considerations we conclude that the larger energy shifts in curves 2 and 2′ indicate substantial negative charge on the O atom in the $c(2\times2)$ O and $p(2\times2)$ O structures on Ni (100). The relatively much smaller shifts in the S and Se spectra indicate considerably less negative charge on these atoms in their surface configurations.

We have also measured the change in work function $\Delta\varphi_A$ which results when the ordered structures are formed on the atomically clean Ni (100) surface. The results for $\Delta\varphi_A$ are $p(2\times2)$ O, +0.3 eV; $c(2\times2)$ O, +0.37 eV; $c(2\times2)$ S, +0.63 eV; and $c(2\times2)$ Se, +0.25 eV. The method used involves retardation of the incident ion beam at the target surface and will be discussed elsewhere. We have used Gerlach and Rhodin's value[2] of $\varphi = 4.75$ eV for atomically clean Ni (100) in calculating the work functions $\varphi_A = \varphi + \Delta\varphi_A$ for the covered surfaces. We note that despite the evidence in the orbital spectra for relatively large negative charge on O in its surface configurations, $\Delta\varphi_A$ for these structures is less than that for $c(2\times2)$ S.

We turn now to consider specific structures.

Not only must admissible structures each provide the electronic orbitals and atomic charging required by the form and position of the molecular orbital spectra, but they must be consistent with the p-type bonding, and possible hybridizations thereof, characteristic of the p electrons of the X atom. Specific structures recommend themselves for each of the three types of orbital energy spectra. These are, in the same ordinal sequence as above: (1) A bridge-type structure, shown in Figs. 2(a) and 2(b), in which a surface molecule Ni_2X, like the free H_2X molecule and having the same C_{2v} symmetry, is repeated over the surface in a $c(2\times2)$ arrangement. (2) An "unreconstructed" $p(2\times2)$ structure having C_{4v} symmetry in which the X atom lies above the Ni (100) surface without Ni atoms in the same plane. In Figs. 2(c) and 2(d) a particular π-type bonding of p_x and p_y orbitals of X to Ni atomic orbitals is shown. This specific orbital arrangement is possibly less certain than the conclusions that the electrons must be in equivalent orbitals and that the X atom lies above the topmost plane of Ni atoms. (3) A "reconstructed" structure of C_{4v} symmetry, in which the X atoms replace Ni atoms of the topmost metal layer in either $c(2\times2)$ [shown in Figs. 2(e) and 2(f)] or $p(2\times2)$ arrangements providing four equivalent p-type orbitals lying in the surface plane and a possibly somewhat inequivalent orbital perpendicular to the surface plane.

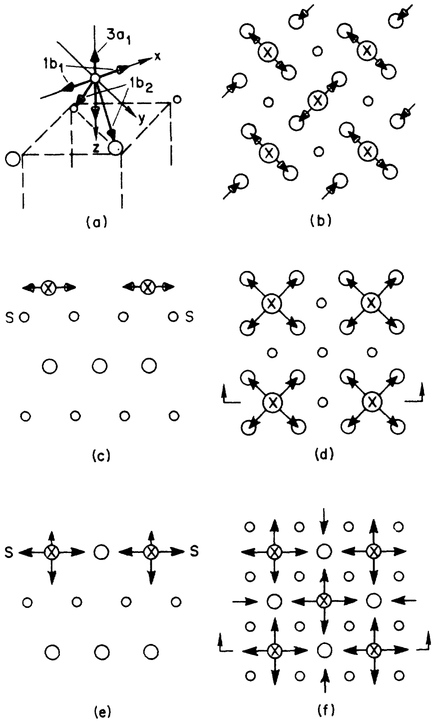

FIG. 2. Specific atomic structures consistent with the p-orbital bonding of the adsorbate atom, the orbital-energy spectra, and work-function changes.

Now we discuss briefly each of these types of surface molecule with respect to the spectra of Fig. 1 and the measured work function changes. The H_2X-like local structure of Figs. 2(a) and 2(b) recommends itself for the $c(2\times2)$ S and $c(2\times2)$ Se surfaces (curves 3 and 4 of Fig. 1) because it alone can provide the inequivalent orbitals required by the spectra. These orbitals, in the accessible energy range, are the lone-pair $(1)b_1$ orbital, and the two bonding orbitals $(3)a_1$ and $(1)b_2$ indicated in Fig. 2(a). Orbital energies and wave functions have been calculated by the Hartree-Fock method for H_2O and H_2S,[3] and orbital energies have also been determined experimentally by molecular photoelectron spectroscopy[4] for all three of the H_2X-type molecules. We have indicated by solid lines the experimental, so-called vertical, energies for the free H_2X molecules in the $X\equiv O$, S, and Se sections of Fig. 1. The corresponding ζ value in each case is obtained by subtracting the work function φ_A from the orbital energy with respect to the ionization limit or vacuum level. The general agreement between the observed orbital resonances in the case of the surface Ni_2X molecules and the orbital energies of the free H_2S and H_2Se molecules is striking even though there is no a priori reason why these orbital energies should necessarily be exactly the same. In the surface case we have a constrained molecule, not completely free as to choice of bond angle, in which Ni atoms replace H atoms.

An important point concerning the Ni_2X surface molecule is that the C_{4v} local symmetry of an X atom placed above four Ni atoms must be reduced to the required C_{2v} symmetry. We believe this is accomplished by the bonding arrangement of Fig. 2(b) in which the "center" Ni_2X molecule is rotated by 90° relative to the "corner" molecules. This results in each surface Ni being involved in only one surface molecule and makes possible the distortion of the Ni atom net from a square to a rhombus by displacements in the surface plane. Such displacements appear reasonable because the bond angles of 101° at S and 94° at Se, which we calculate from single-bond radii for S and Se and bulk position and radius for Ni, are greater than the bond angles of the corresponding free H_2X molecules.

The widths and magnitudes of the peaks in the orbital spectra for this structure are also consistent. The lower lying $(1)b_2$ and $(3)a_1$ orbitals spread less in energy than does the $(1)b_1$ orbital because they either lie below allowed levels in the solid or lie so deep that tunneling between them and the solid is considerably less probable than for the $(1)b_1$ orbital. The magnitude of the peak associated with the $(3)a_1$ orbital is less than the other two because its principal wave-function magnitude lies between the X atom and the solid and between the two lobes of the $(1)b_2$ orbital, thus not being as "visible" to the incoming ion as are the $(1)b_2$ and $(3)a_1$ orbitals.

The molecular structure for the $p(2\times2)$ S and $p(2\times2)$ Se surface arrangements given in Figs. 2(c) and 2(d) appears reasonable in view of both symmetry and charging considerations. When the central molecule of the $c(2\times2)$ arrangement is removed to produce the $p(2\times2)$ arrangement an extension of the symmetry argument given above forces us to conclude that the local symmetry at the "corner" molecules must revert from C_{2v} to C_{4v} symmetry. This eliminates the Ni_2X structure as a possible local structure for the $p(2\times2)$ S and $p(2\times2)$ Se surfaces. Molecular orbital spectra in Fig. 1, curves 3 and 4, are seen to revert to simple one-peak spectra, curves 3′ and 4′, characteristic of equivalent orbitals. We consider this observed change in orbital spectrum, in agreement with the dictates of local symmetry, to be strong evidence in favor of the proposed bonding structures. We believe it reasonable to suggest that the p_x and p_y orbitals of X are placed so as to bond in π fashion with orbitals of the surface Ni as shown in Figs. 2(c) and 2(d) even though we cannot rule out, a priori, the other possibility that the bonds point between the Ni atoms. The third symmetrical possibility which places the X atom directly above a Ni atom seems improbable in view of the p-type bonding of the X atom. The small $\Delta\varphi_A$ and small orbital energy shift indicating small electronegative charging of the X atom are both consistent with the X atom lying above the top Ni plane in an "unreconstructed" arrangement. As we shall see below, a "reconstructed" structure most likely involves large charging and thus large energy shift of the orbital spectrum and is thus clearly to be distinguished from that indicated for the $p(2\times2)$ S and $p(2\times2)$ Se surfaces.

We discuss finally the situation for $p(2\times2)$ O on Ni (100). Here we require structures which provide equivalent orbitals in which the oxygen atom can be strongly electronegative but in which this charging does not result in a large $\Delta\varphi_A$. These restrictions force us to the "reconstructed" surface of Figs. 2(e) and 2(f) in which the O atom replaces Ni atoms in the outermost layer in either a $c(2\times2)$ structure (shown) or a $p(2\times2)$ structure (not shown). No basic change in spectrum is required in going from $c(2\times2)$ to $p(2\times2)$ and enough orbitals are provided so that the O atom can be charged to at least O^-. Because there are nickel atoms in the surface layer which can charge positively, possibly as much as 80% of the negative charge on the oxygen is "dissipated" in components of the dipole moment parallel to the surface leaving a small normal component to cause small $\Delta\varphi_A$. Previous investigators have guessed at this structure based on the small $\Delta\varphi_A$ and the fact that O is electronegative in NiO, for example. However, the large energy shift seen in each ion-neutralization spectroscopy spectrum is the first direct experimental evidence that the O atom is in fact strongly charged in each structure. In the structure of Figs. 2(e) and 2(f) the orbital whose axis is normal to the surface may not be strictly equivalent to those lying in the surface plane and we have attempted to suggest this by the arrow lengths used in the figure.

We consider the present work to provide a new and powerful tool in the study of molecular arrangements at solid surfaces. Surface molecules may be looked upon as a distinguishable "phase" of matter, clearly to be differentiated from free molecules in the gas phase and from the huge molecule which is the bulk solid. Surface molecules differ from free molecules because of the constraints imposed both by the underlying solid and by the neighboring molecules in the surface array. Surface molecules can be formed which have no counterpart among free molecules. All of these characteristics of surface molecules are illustrated in the present work.

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EVIDENCE FOR A SHARP ABSORPTION EDGE IN AMORPHOUS Ge†

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A sharp optical absorption edge has been found at about 0.5 eV for amorphous Ge on a quartz substrate. The edge is comparable in sharpness with the direct edge of crystalline Ge. No evidence for tailing of the band edges into the forbidden band or for a high density of states in the forbidden band is found by these optical measurements. A new density determination gives a value of 4.54± 0.14 g/cm^3.

In an earlier Letter,[1] we described photoemission measurements on amorphous germanium in which the density of states was found to differ from that of crystalline Ge in two important ways. First, the sharp structure in the density of states which characterizes crystalline Ge was completely missing in the amorphous material. Second, the valence band appeared to have narrowed in the amorphous material with a marked increase in the number of states appearing within a volt of the band maximum. In this Letter we extend the earlier work by examining the sharpness of the band edges and density of states in the forbidden gap.

A number of authors[2,3] have discussed the possibility of the loss of any sharply defined band edge in amorphous semiconductors, such as amorphous Ge, and/or suggested that large numbers of states occur in the "forbidden" gap. We looked for evidence of such states in the photoemission energy distribution curves (EDC); however, no evidence was found. In fact, the leading edge of the amorphous EDC was found to be as sharp as that from single Ge crystals.[4] This suggests a relatively sharp edge in the filled density of states and led us to examine the infrared optical absorption for other evidence of a sharp band edge. We report here evidence for such edges. If there were large numbers of empty states lying between the Fermi level and the bottom of the conduction band, this would give rise to significant optical absorption in the infrared; we report here absorption measurements in this spectral range and find no evidence for large numbers of states in the gap. A new determination of the density is also reported.

The density measurements are of importance since theoretical considerations of amorphous Ge often depend on the density. A case in point is the recent calculation by Herman and Van Dyke[5] of the change in density of states of crystalline Ge when the density changes to that determined by Clark[6] for the amorphous material.

While the results of optical studies of amorphous Ge in the infrared and absorption-edge region have been reported by a number of authors,[6-8] in none of these studies has there been any attempt to achieve sensitivity to values of the absorption coefficient of less than 100 cm^{-1}. In order to determine α's in the range of 10 cm^{-1} in the region of the absorption edge, we have used special techniques[9] to deposit films of uniform thickness on extremely smooth (7-Å rms roughness) fused silica blanks as well as on commercially polished KCl substrates. The films were deposited at a rate of 10 Å/sec in a vacuum of 5 $\times 10^{-7}$ to 2×10^{-6} Torr. The vacuum system was let up to an atmosphere of dry argon and the films measured immediately in an atmosphere of dry N_2. Film thickness and uniformity were determined using fringes of equal chromatic order.[10] Average deviations in film thickness measured on random regions of the films have varied from ±4 Å on an 820-Å film to ±28 Å for a 20 654-Å