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Surface spectroscopy of Schottky-barrier formation on Si(111) 7×7: Photoemission studies of filled surface states and band bending

G. Margaritondo,* J. E. Rowe, and S. B. Christman
Bell Laboratories, Murray Hill, New Jersey 07974

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The formation of Schottky barriers between Si(111) 7×7 and group-III metals has been studied by ultraviolet photoemission spectroscopy. Modifications of the band bending and of the work function occur for low values of metal coverage (one to four monolayers). The "intrinsic," clean surface states are simultaneously replaced with "extrinsic" metal-related interface states. A two-step empirical model is proposed for the formation of the barrier. The first step is saturation of interface bonds, and the second step, critical in determining the junction properties, corresponds to the formation of a thin region with properties intermediate between that of a metal and of a semiconductor. Our experiments emphasize the need for a detailed theoretical treatment of the interface chemical bonds and underline the inadequacy of "macroscopic" models for metal-semiconductor junctions.

I. INTRODUCTION

The interest in Schottky barriers (SB) has been increasing for a long time due to the wide range of their applications in solid-state devices.[1] However, a fundamental understanding of the physical and chemical properties of metal-semiconductor interfaces is still very primitive. Chemical trends of SB properties are among the most puzzling theoretical problems of the last three decades. It is known that the SB height, ΔV, as measured by C-V or I-V characteristics,[2] is nearly *independent of the metal work function* in covalent semiconductors.[2,3] The contrary is true for ionic semiconductors, and it has been proposed[4] that this is one aspect of a "fundamental" covalent-ionic transition, occurring for many different physical properties. The aim of most theoretical approaches has been to explain the properties of all the Schottky barriers with the same model. Little effort has been devoted toward explaining the specific properties of particular metal-semiconductor interfaces. On the other hand, many theoretical approaches use physical entities such as surface states[5] or resonances,[6] and surface plasmons[7] which are strongly dependent upon particular properties or even the history of the interface.

The concept of SB Fermi-energy pinning by surface states was introduced by Bardeen in 1947[5] and is widely accepted[8,9] as a suitable explanation for the insensitivity of ΔV to the metal for Si, Ge, and GaAs. Later the existence of surface states at the atomic, intimate metal-semiconductor contact was questioned by Heine,[6] who replaced them with electronic resonances associated with the tailing of metal wave functions into the semiconductor. Image-charge potential effects have been subsequently treated by Crowell in a self-consistent way.[10]

Within the framework of a dielectric theory, the nonexistence of long-wavelength surface plasmons with energy smaller than the direct gap has been proposed[7] as a general condition to get the SB height independent of the metal. This condition, which is related to the polarizability of the semiconductor, has been questioned by Inkson,[11] on the basis of a many-body approach.[12] Inkson proposed instead the *complete* "closure" of the gap in covalent semiconductors near the interface as the explanation for the pinning of the Fermi level E_F. In 1974, Phillips[13] pointed out that a complete description of the metal-semiconductor barrier would require a theory of chemical bonds at the interface. Such a theory is still beyond most present computational capabilities, and Phillips suggested the use of the chemical theory of dielectric constants[14] to deduce the polarizability value at which the fundamental ionic-covalent transition[4] takes place.

The most controversial point about Schottky barriers in covalent semiconductors is the existence of and the microscopic nature of surface states at the metal-semiconductor interface. Electrical measurements[1,2] are not able to settle this controversy, since they are not directly related to the microscopic SB physical properties. Even in the case of electrical properties directly related to the existence of surface states (such as the "anomalous" temperature dependence of I-V characteristics),[8] it is impossible to completely overcome the spacial-averaging character of electrical measurements. Without direct experimental proof the surface-state model is essentially tautological,[7] and only a detailed knowledge of the local density of states at the interface can provide a reliable check of its validity.

Surface-sensitive experimental techniques have been applied in recent times to study the formation of Schottky barriers on Si,[15,16] Ge,[15] and III-V compounds.[15,17,18] The local density of empty states in the gap has been determined by partial-yield measurements[17] and by core-level electron-energy-loss spectroscopy.[15] Eastman and Freeouf[17] have reported that the "intrinsic" surface states peculiar to clean (110) GaAs surfaces are still present after Pd or In metal evaporation. They also found that the position of E_F, as given by electrical measurements of ΔV, lies close to the lower edge of the empty, clean-surface-state distribution. This would indicate that the surface-state model is correct for this case, and that intrinsic surface states play an important role for SB on the (110) surface. However, the (110) surface has peculiar structural characteristics that may explain[15] the existence of clean-surface states under the metal overlayer. This is not true for Ge, Si, and GaAs (111) and (100) surfaces, for which core-level electron-energy-loss spectroscopy data[15] show that the metal overlayer replaces the empty intrinsic surface states with new interface states located near the metal atoms.

Ultraviolet photoemission spectroscopy (UPS) has been applied by Spicer *et al.*[18] to study submonolayer cesiation of GaAs(110) and InP(110). The position of E_F is correlated with the density of empty interface states in the gap, but this correlation is not as simple as that reported in Ref. 17, and may involve some of the mechanisms described by the above theoretical models.[6,12] More recently,[16] preliminary results on the Ga-Si interface have indicated that the parallel use of several different electron-spectroscopy techniques can provide a much more complete step-by-step description of the local density of states, the surface crystallography and the collective excitations during SB formation.

A general result of all these new experiments is the emphasis of the "local" character of SB properties. The overall validity of the surface-state model is also confirmed, although the observed differences among the various surfaces suggests that one must be careful in generalizing the detailed microscopic results valid for a particular metal-semiconductor system to all Schottky barriers. It appears difficult to properly describe a given metal-semiconductor interface without dealing with the particular structural and electronic properties of *that specific* interface, and a "general" theoretical model valid for all the metal-semiconductor interfaces appears a more and more difficult goal. The first examples of theoretical efforts describing a *particular* interface have recently appeared.[19,20]

In the present paper we carry out a step-by-step study of SB formation between a covalent semiconductor (silicon) and three different trivalent, simple metals (aluminum, gallium, and indium). The primary experimental tool has been UPS, but other additional techniques have also been employed to characterize the surface. The choice of group-III metals seems particularly favorable, since these atoms have properties close to that of silicon and are common substitutional impurities in the bulk. This is likely to simplify the theoretical treatment of the SB interface. Moreover, a Fermi-level pinning mechanism is required to actually get a barrier between Si and these metals, since the crude comparison of their work functions to the silicon electron affinity would indicate *little or no barrier formation.* The UPS data provide information about the local density of filled states, and give some indication of the electric charge distributions through work-function changes. These points will be extensively discussed in Sec. V, where our conclusions will be compared to available theories and to some of their probable future developments.

II. EXPERIMENTAL TECHNIQUES

Clean (111) silicon surfaces were prepared by argon-ion sputtering in a multiple-technique, ultrahigh-vacuum chamber described elsewhere.[21] Photoemission measurements were performed with a double-pass cylindrical-mirror electron analyzer and windowless resonance lamp. The base pressure was 5×10^{-11} Torr and the working pressure was typically 2×10^{-10} Torr. The silicon samples were In-doped p-type and As-doped n-type,[22] with carrier concentrations n and p ~10^{16} cm^{-3}. After cleaning by Ar-ion sputtering, the samples were annealed at high temperature (~700–850 °C) and slowly cooled, to produce sharp 7×7 low-energy-electron-diffraction (LEED) patterns. The cleanliness of the surface, in particular with regard to possible carbon contamination, was frequently checked by Auger-electron spectroscopy.

The metal overlayer was then deposited by using a molecular-beam-epitaxy technique, where the metal is melted in a cylindrical over, providing a stable well characterized, collimated beam. The rise in pressure during the evaporation and the above annealing was less than a factor of 2. The evaporation rate, monitored *in situ* with a water-cooled quartz thickness monitor, ranged between 1–4 Å/min. The evaporation rate was also checked *a posteriori* for some of the films, with standard interferometric techniques. During the evaporation, the substrate temperature was below 110 °C. The changes in LEED patterns were used as an additional check to determine the equivalent thickness of a metal monolayer. The LEED results roughly correspond to the conventional one-adatom-per-substrate-atom definition of a monolayer, and are 1.5 Å for Al, 1.5 Å for Ga and 2 Å for In.

UPS data were taken for metal coverages ranging between a fraction of a monolayer and 10–20 monolayers; measurements were also carried out on thick metal films (of ~100–300 layers) for comparison. We observe that for the clean Si(111) samples E_F lies near the intrinsic bulk position, and this corresponds to a band-bending length of ~2.7×10^{-5} cm in the depletion approximation. Since the escape depth at the energies we used is of the order of 20 Å,[23] our UPS data reflect the position of E_F at the surface. We shall see that the band bending is modified by the metal, but the width of the space-charge region is always much larger than the escape depth. Almost all the UPS data were taken at one photon energy, viz., the uv argon radiation of a microwave resonance lamp.[24] The uv radiation impinged on the sample at an angle of 70° with respect to the surface normal, which was coaxial to the electron analyzer. On-line data averaging and processing was performed with an 8K PDP-8/L minicomputer.

III. PHOTOEMISSION SPECTRA

Figures 1–3 show the energy distribution curves (EDC's) for photoemitted electrons from the clean Si(111) 7×7 surface (dashed curve), and by Al, Ga, and In metal-covered surfaces (solid lines), respectively. All the data appearing in each figure were taken for increasing thicknesses of the same metal overlayer, keeping the photon flux constant. The position E_F has been determined by linear interpolation of the photoelectric edge of a tantalum sheet in contact to the sample, and it is coincident with the sharp edge of the EDC's in the case of thick overlayer spectra. It is known[25] that the clean-surface peak lying 4.8–5 eV below E_F corresponds to a peak in the bulk-silicon energy distribution of the joint density of states.[26] The distance between this peak and E_F decreases with the metal coverage. This indicates a change in the

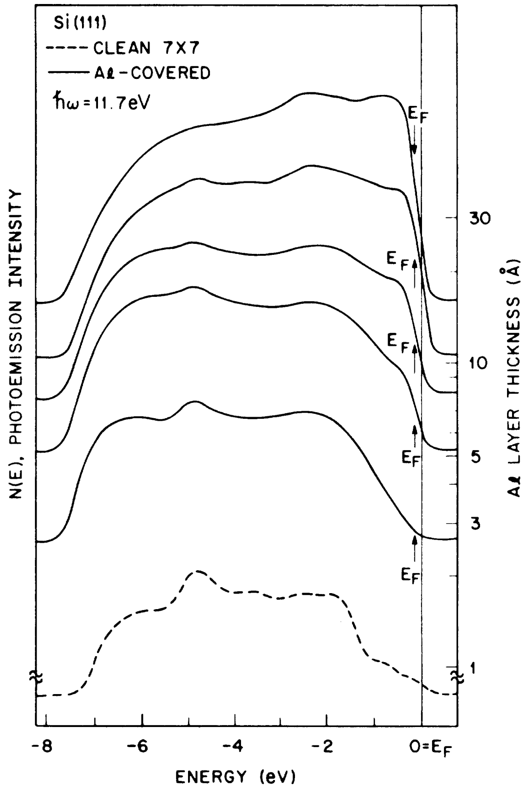

FIG. 1. Photoelectron spectra for a clean Si (111) 7 ×7 surface (dashed line) and for increasing Al coverages (solid lines). The curves have shifted to align the bulk-silicon feature at ~−4.8 eV, and the arrows indicate the position of the Fermi level for the metal-covered surface EDC's.

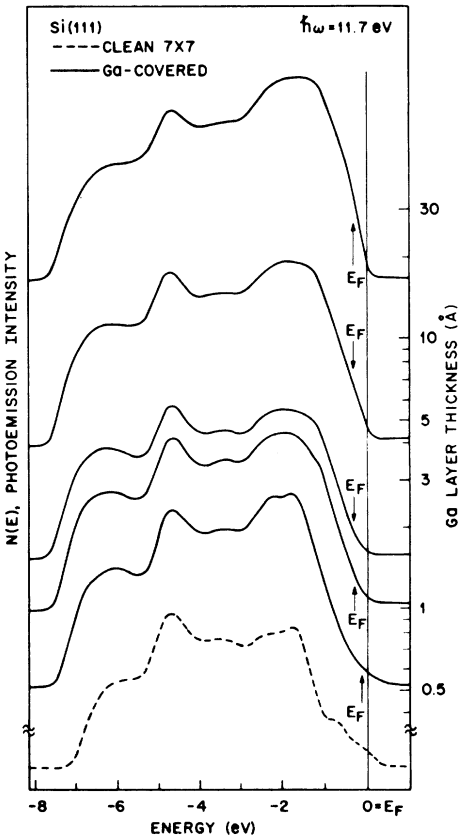

FIG. 2. Photoelectron spectra for several gallium coverages.

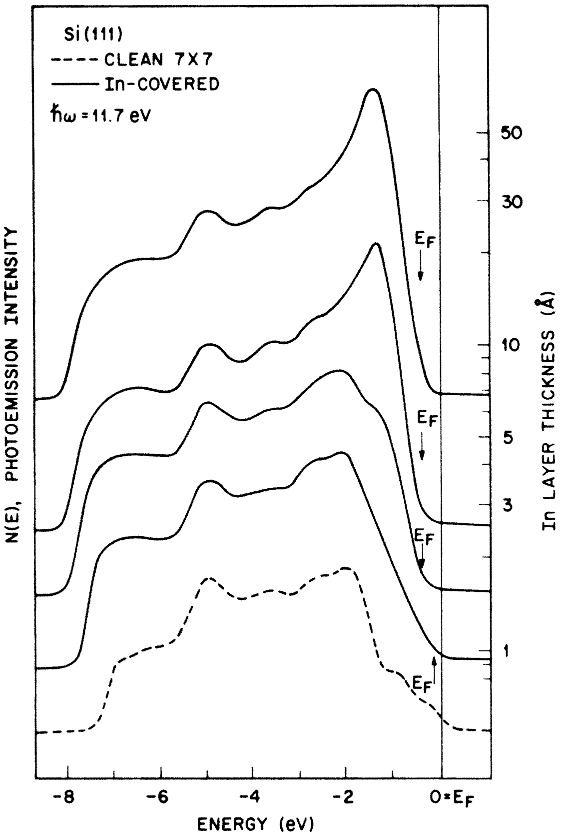

FIG. 3. Photoelectron spectra for several indium coverage values.

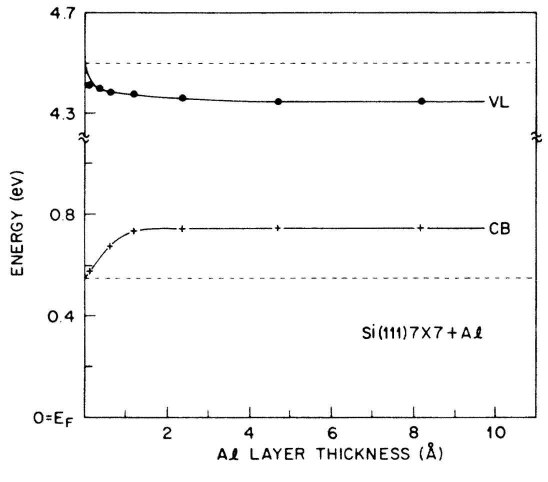

FIG. 4. Position of the conduction-band minimum CB (crosses) and the vacuum level VL (dots) vs Al coverage. The dashed lines correspond to the clean-surface position. The vertical scale is referred to the Fermi level. The position of CB has been evaluated subtracting the clean surface value of $E_F - E_v = 0.55$ eV and the measured shift of E_F from the energy gap, $E_c - E_v = 1.1$ eV. The uncertainties are ~0.1 eV for the energy and ~15% for the thickness.

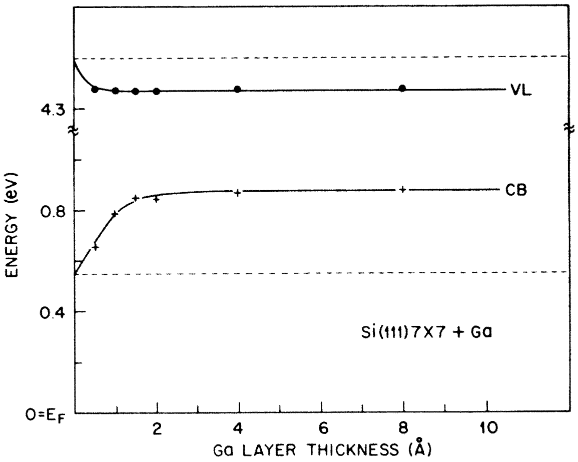

FIG. 5. Conduction-band edge CB and valence-band edge VL vs Ga coverage.

relative position of E_F and the valence band near the interface. The metal overlayer, then, significantly modifies the clean-surface band bending due to dangling bonds. All the curves of Figs. 1–3 have been plotted keeping the bulk-silicon peak position constant. For the metal-covered data curves E_F is then displaced from zero, since the energy scale is referred to the Fermi level of the clean surface. This displacement is emphasized by the lower solid curve in Figs. 4–6 which show the conduction band edge (CB) (referred to E_F) and the vacuum level (VL) as a function of the metal coverage. For thick coverages this quantity should correspond to the barrier height, ΔV_B, given by electrical measurements and it is in good agreement with previous results.[2,3] The behavior monotonically increases with metal coverage and saturates around 1–2 monolayers. For Al the

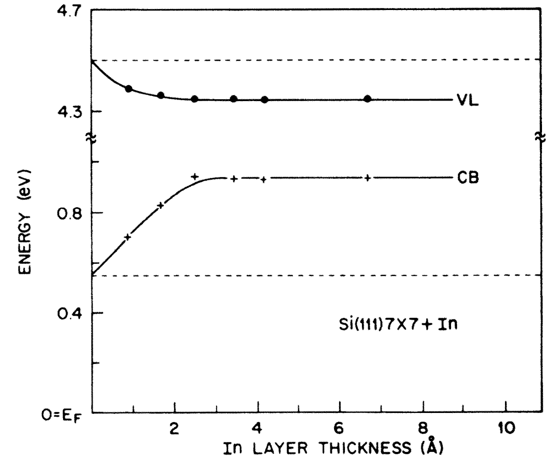

FIG. 6. Conduction-band edge CB and valence-band edge VL vs In coverage.

saturation value is 0.75±0.1 eV, to be compared to experimental values of[3] 0.76 and[2] 0.71 eV for ΔV, both measured on Al-cleaved Si junctions.[27] For Ga and In the saturation values of ΔV_B are 0.85±0.1 and 0.95±0.1 eV; the available experimental data for SB in clean silicon do not include these metals, and range between 0.70–0.82 eV,[2,3] with no clear dependence on the metal. It is interesting to observe that a behavior similar to that of E_F is present for the work function, ϕ. This can be seen by the upper curve of Figs. 4–6 (which show the position of the vacuum level (VL) with respect to E_F). For the clean surface, the value of VL is 4.5±0.1 eV larger than E_F, corresponding to a silicon electron affinity of 3.95±0.1 eV (other experimental values[28] range between 3.75–4.3 eV). The saturation values of ϕ are 4.32±0.1 eV for Al, 4.37±0.1 eV for Ga, and 4.34 ±0.1 eV for In. [For comparison, the reported values of ϕ are 3–4.4 eV for Al (recent determination: 4.21 eV)[2] and ~4 eV for Ga.] An important point is that the metal overlayer causes a *decrease* of ϕ for all the three metals. As above mentioned, a simple comparison of the metal and semiconductor work functions would have predicted no barrier for these junctions. On the other hand, the movement of E_F within the gap is in contrast to a model only based on intrinsic surface states. It is clear that much information has to be obtained from the change of the local density of states at the interface.

IV. LOCAL DENSITY OF STATES

It is an interesting question how the spectra of Figs. 1–3 compare to that of pure Al, Ga, and In samples. A large number of measurements of UPS[30] and x-ray photoemission spectra[31] are available for aluminum. Three main spectral deviations from the free-electron density of states have been found, corresponding to the valence-band L_2', X_4, and K_1 points. The most intense of these peaks is K_1, lying ~1 eV below E_F. Available UPS data for indium[32] and gallium[33] also show a few broad features. To emphasize the effect of metal coverage, it is convenient to take the difference between the solid and dashed curves of Figs. 1–3. These differences are reported in Figs. 7–9. Before taking the difference the spectra were shifted with respect to each other to align the bulk-silicon peak. This removes the "derivative" effects present on difference curves due to changes in band bending.

It is evident from all the curves of Figs. 7–9 that a small metal coverage causes a marked decrease of the density of states near E_F. It has been shown[34] that the states which are removed are strongly localized near the surface, and their origin is related to the silicon dangling bond states and resultant back-bond states. The role played by the back bonds has been pointed out by the azimuthal threefold symmetry of angle-resolved UPS measurements.[35] The disappearance of these states at the beginning of the SB formation indicates that the first layer of metal adatoms tend to saturate the silicon dangling bonds. This also corresponds to the disappearance of empty clean-surface states in the gap at the same stage of the SB formation, which has been reported for the Ga-Si junction in Ref. 15. We already explained[15] why this is not in disagreement with the reported presence of clean-surface states on the metal-covered GaAs(110) surface.[15,17] On the other hand the clean-surface charge density per atomic double layer in our samples is ~2.7×10^{11} cm^{-2} (in the depletion approximation), while the clean-surface-state density in the gap is ~8×10^{14} cm^{-2}. A simple redistribution of the surface charge in

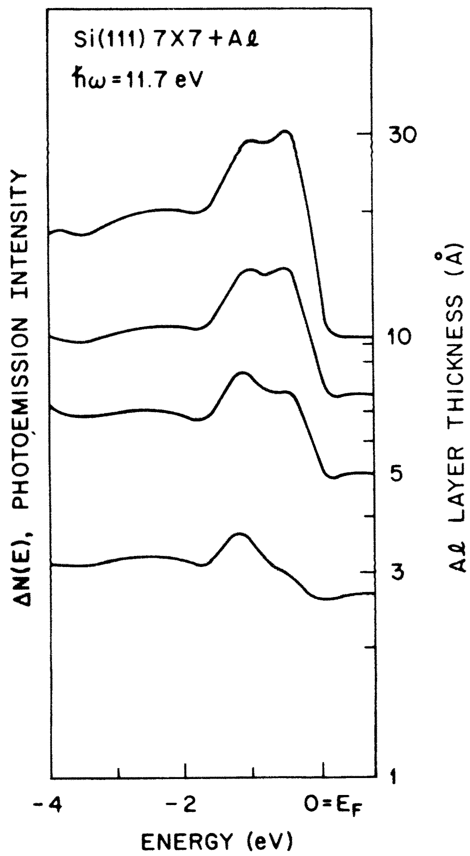

FIG. 7. Photoemission difference curves between the solid lines and the dashed curve of Fig. 1. Notice that the metal-covered surface EDC's have been shifted as in Fig. 1 before taking the difference.

already existing surface states cannot explain a *downward* displacement of E_F by a few tenths of an eV, and its subsequent pinning in a new position. A change of the density of states in the lower part of the gap must then occur.

The difference curves of Figs. 7–9 provide a picture of how the metal overlayer changes the density of *filled* surface states near the valence-band edge. For all three metals we observe that two metal-related features occur in the energy range 0 to −3 eV. Their positions are −1.3 and −2.2 eV for Ga and −1.2 and −2.1 eV for In. For Al the low-energy peak is at −2.5 eV and the high-energy one is a doublet with components at −0.5 and −1.1 eV. The broad peak at lower energies is already present at the submonolayer coverage and does not change much in intensity while the coverage increases. The narrower high-energy peak, on the other hand, increases with metal coverage. Its intensity becomes comparable to that of the lower-energy peak for thickness values at which E_F and ϕ saturate. At higher coverages one can observe that the negative lobe of the difference curve decreases in intensity, and this is due to an increased tailing into the gap of the high-energy peak. These two metal-related features do not correspond to the non-free-electron-density-of-

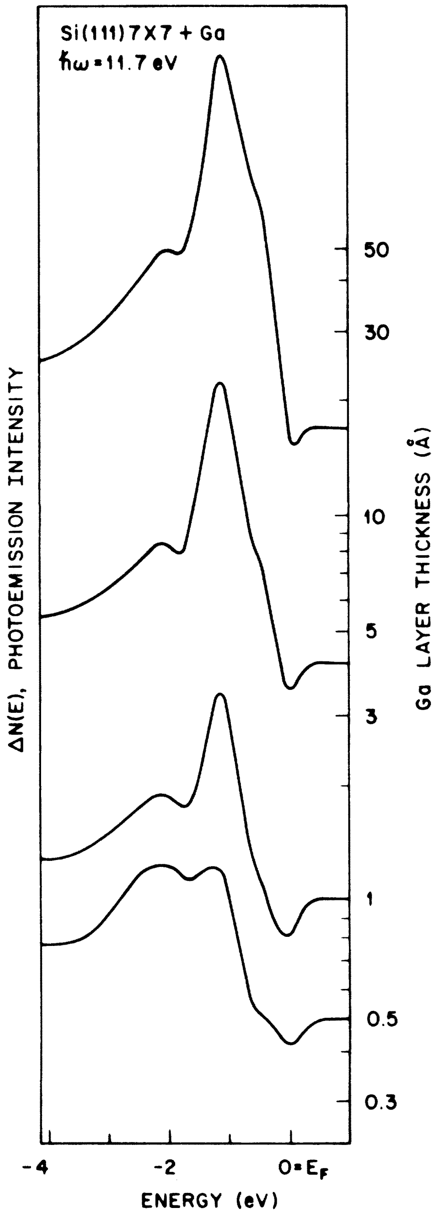

FIG. 8. Photoemission difference curves for Ga on Si (111) 7×7.

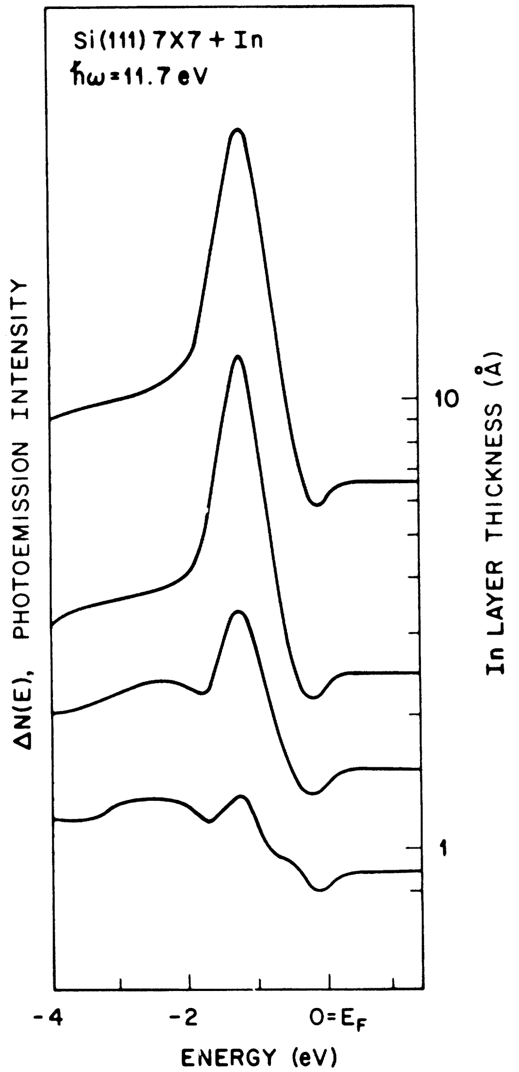

FIG. 9. Photoemission difference curves for In on Si (111) 7×7.

states features shown by photoelectric data on pure Al, Ga, and In.[31-33] The higher-energy peak is closer to E_F than the first bulk-metal feature with a narrow shape completely different from the broad UPS bulk-metal peaks. The lower-energy peak, on the other hand, appears on the spectra *before* the higher-energy one, and thus it cannot be a bulk-metal feature.

We propose that the formation of Schottky barriers on Si(111) 7×7 may be described as a two-step process. The second of these steps, most important in determining the properties of the junction, is associated with one onset of the strong, sharp higher-energy peak. This peak is considerably narrower than the K_1 density-of-states feature of bulk metals and indicates that the chemical bonds established at this stage may be much more covalent than for a pure metallic region. On the other hand, the large number of electrons (almost seven per unit cell) and the strong tailing of states into the gap indicate that the interface region formed at this stage is still more similar to a metal than to a semiconductor. The formation of this "intermediate" region introduces a strong density of new states in the gap, causing the pinning of E_F in a new position and saturating its shift. The SB height ΔV is determined by the subsequent change in the space charge due to the new distribution of interface states at the semiconductor surface. The quasicovalent character of the chemical bonds explain the presence of a surface dipole that lowers the work function. It is hard to evaluate the surface dipole per atom, since at high coverage the interaction among individual dipoles is too strong,[6] and at low coverage there is interference with the dipoles of metal atoms bonded during the first step of SB formation. Extrapolation to zero coverage of the ϕ-vs.-thickness derivative[6] gives a lower limit of ~0.2 electrons Å/atom.

For the first step of SB formation the energy position of the UPS peak indicates that the Si-metal bonds established at this stage are more covalent than for subsequent thicker metal layers. The peak intensity corresponds to a surface density of filled states of 10^{14}–10^{15} cm^{-2}. The first layer of metal atoms are probably chemisorbed as substitutional impurities in the silicon lattice with strongly localized bonds. Another possibility is that they chemisorbed in order to fill free-surface vacancies. The presence of ordered vacancies has been proposed as a super-lattice model,[36] and preliminary LEED results[16] on the Si-Ga interface indicate that the 7×7 character is slightly modified, but not destroyed by the metal overlayer.

The two-step SB formation process proposed here may be compared with several different theoretical models for metal-semiconductor junctions. The local character of the junction properties and the clear correlation between pinning of E_F and changes in the local density of states indicate that the Bardeen's idea[5] is basically correct. However, the surface states pinning E_F are not intrinsic to the clean semiconductor surface but extrinsic, i.e., due to the chemical bonds formed with foreign atoms on the semiconductor surface. On the other hand, the spatial dependence of the local density of states we deduce from experiment can be hardly described as a smooth tailing of free-electron-metal wave functions[6,20] into the semiconductor. Alternative "macroscopic" approaches[7,10-13] do not appear adequate to treat such a localized system, although some of their predictions are consistent with our data. For instance, the tails of filled states into the gap[6] is qualitively similar to the gap closure proposed by Inkson.[11,12] The "intermediate" region formed at that stage acts to smooth the transition between the large gap semiconductor and the complete gap closure in the bulk metal. The tendency to form strong covalent interface bonds will of course depend on the strength of the bulk covalent bonds and will decrease with increasing ionic character in qualitative accord with Ref. 4.

The results of the first theoretical efforts to take into account the "chemical" properties of the junction, and to describe a particular interface have been recently published.[19,20,37] Andrews and Phillips[37] have presented a model to account for ΔV_B on the basis of a "chemical" approach when strong chemical bonds are expected between metal and semiconductor. Louie and Cohen have carried out a pseudopotential calculation of the system Si–"jellium" Al.[20] The concept of gradual tailing of states in the gap is confirmed by their results, although their model is not yet able to provide a correct, detailed description of the local density of states as determined by our data.

V. CONCLUSIONS

The most important points established by our UPS study of the Schottky barrier formation on Si(111) 7×7 are (i) the local character of the junction properties and (ii) the correlation between the changes on the local density of filled states and those in E_F and ϕ. The characteristics of two new metal-related UPS peaks lying close to the top of the valence bands are consistent with a two-step process for the formation of the SB junction. The first layer of metal atoms are chemisorbed in a covalent way, as interstitial impurities or at surface vacancies. The subsequent adatoms are bonded in a less covalent but still nonmetallic way, and probably form a thin "intermediate" region that "bridges" between the silicon and metal parts of the junction. Presently available theoretical models do not provide a detailed description of the chemical bonds at the interface whose importance is emphasized by our data. The details of this description require a much more difficult theoretical treatment than simply correlating chemical trends in barrier heights and other macroscopic properties. However, the computation capabilities recently developed to describe clean surfaces[19] will probably allow a more accurate theoretical description of Schottky barriers in the near future.

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*Fellow of the Italian National Research Council, Gruppo Nazionale di Struttura della Materia.

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[22] Essentially no different data were obtained from differently doped samples. We observe that the position of E_F at the clean surface does not change too much from p- to n-type samples at these carrier concentrations, and the bulk properties of silicon do not appear to be *directly* influencing the SB properties.

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[27] Two kinds of electrical measurements are currently used to evaluate the SB height: (i) extrapolation of C^{-2}-V characteristics and (ii) linear extrapolation of forward I-V characteristics. Small discrepancies between the results of the two methods have been explained (Ref. 2) by an additional bending of the conduction-band minimum opposing the bending caused by space charge; this effect is predicted by both Heine's (Ref. 6) and Inkson's (Ref. 12) approaches. In our case we define ΔV_B as the distance between the minimum of the bulk conduction band and the bulk-silicon peak around -5 eV, minus the distance between the same peak and the Fermi level at the interface. Our ΔV_B should then correspond to the result of the C^{-2}-V extrapolation and the data we quote in the text (Refs. 2 and 3) have been taken in this way.

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