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Electron energy loss spectroscopy of the Si(111)–simple-metal interface

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New data are presented on the formation of Schottky barriers on Si(111) 7×7 with evaporated Al, Ga, or In metal. Electron-energy-loss spectra (ELS) have been taken as a function of metal overlayer coverage. The removal of clean surface state transitions has been observed at submonolayer coverage. The behavior of interface collective excitations of bulk-silicon-like transitions and of transitions from the metal core levels confirm the covalent character of the interface chemical bonds.

I. INTRODUCTION

A number of surface-sensitive electron-spectroscopy techniques have been applied recently to study the formation of Schottky barriers (SB) in semiconductors.[1-5] While ultraviolet photoemission spectroscopy (UPS) has been the most widely employed technique[1,2,4,5] only a few electron-energy-loss (ELS) results have been presented.[3,4] In this paper we would like to show that ELS provides very valuable information not obtainable from UPS on the early stage of the SB formation.

Already published results[1,2,4] show that the position of E_F (Fermi level) is mostly determined by the detailed properties of the region close to the interface. In particular E_F appears sensitive to the local density of states at the interface. New, metal-related interface states have been observed for the (111) and (100) surfaces of Si, Ge, and GaAs,[3-5] while the situation is less clear for the (110) surface.[1,3] The basic validity of the original Bardeen model[6] is thus confirmed. However, E_F does not depend on the "intrinsic" surface states of the clean semiconductor but rather on the "extrinsic" states related to the metal-semiconductor bonds. Theoretical models for SB's should then deal with the *microscopic* chemical properties of the interface. Some previous *macroscopic* theoretical approaches[7-11] are in agreement with the most recent experimental results.[1-5] For instance, the gradual "closure" of the gap proposed by Inkson[10] may correspond to an observed tailing of states from the semiconductor valence band into the gap.[2,4,5] However, no macroscopic model can provide a detailed description of the interface density of states. Consequently, no macroscopic approach can completely account for the new experimental results on SB formation.[1-5]

We report experimental results using electron-energy-loss spectroscopy on SB formation between silicon (111) 7×7 and the group-III metals Al, Ga, and In. Information has been obtained on the changes in collective excitations and in the joint density of states during this process. It has been shown[12] that the cross section for surface losses is nearly proportional to the imaginary part of the surface dielectric function. The difference between the dielectric function measured by ELS and the "optical" dielectric function, determined by surface optical transitions, is essentially due to the integration over a larger range of momentum transfer Δk in the two-dimensional Brillouin zone. For instance, a peak in the joint density of states as seen by ELS is really an average over a considerable region of wave-vector space. Usually, however, this does not prevent one from obtaining from ELS valuable information about the local density of empty and filled states.[13] Additional information is obtained by using a nondispersive core level as the initial state for energy-loss transitions. This technique has already provided valuable information about SB formation.[3] In the present case, the range of energy losses we study is wide enough to also cover transitions starting from core levels of In and Ga metal atoms. ELS is *more sensitive* than UPS to the spatial region near the surface. Previously reported[5] UPS data on the same junctions have provided information about the local density of filled states, the space-charge region and the surface electrostatic dipole. A two-step model of SB formation has been proposed in Ref. 5 on the basis of these UPS data. The present ELS results are not only complementary to these UPS data but also provide detailed information about the early stage of SB formation, covered by UPS.

The paper will be structured as follows. The experimental procedure will be described in Sec. II. The ELS results will be described in Sec. III and discussed in Sec. IV, while Sec. V will contain the conclusions.

II. EXPERIMENTAL TECHNIQUES

The experiment consisted of taking ELS data at each stage of the increasing metal coverage ranging between a fraction of a monolayer and 10–20 monolayers. Auger-electron spectroscopy and low-energy-electron diffraction (LEED) were also employed to characterize the surface before and after metal coverage. The ELS results were taken in the form of the negative second derivative of the energy distribution of the electrons reflected by the surface.[14,15] It has been shown[13] that the clean-surface-plasmon peak obtained in this way is nearly symmetric and this indicates that the negative second derivative provides a faithful representation of the loss function, i.e., of the surface ϵ_2 features when surface transitions prevail. The primary electron energy was 100 eV and the energy of the reflected electrons was analyzed by means of a cylindrical-mirror electron energy analyzer. All the experiments were carried out in a multiple-technique, ultrahigh-vacuum chamber described elsewhere.[15]

In-doped p-type and As-doped n-type, (111)-oriented silicon slices[16] with carrier concentration n and $p \sim 10^{16}$ cm^{-3} were cleaned by Ar-ion sputtering and annealed at ~700–850 °C for a few minutes. Upon slow cooling the samples exhibited sharp 7×7 LEED patterns. A metal overlayer was then deposited by means of a molecular-beam-epitaxy technique.[5] The metal was melted in a cylindrical oven giving a stable and collimated beam. An externally operated shutter controlled the metal deposition and the overlayer thickness was determined from the evaporation rate given by a water-cooled quartz thickness monitor. The results of this evaluation were checked *a posteriori* with standard interferometric techniques. During the evaporation the substrate temperature was below 110 °C and the pressure raised by less than a factor of 2 from its typical working value of 2×10^{-10} Torr. The Auger-electron spectroscopy data showed that the possible contamination of the 7×7 reconstructed surface and of the metal-covered surfaces was well below 10^{-2} monolayers of oxygen and carbon, the most common contaminants. LEED was employed to study the change in surface structure induced by the adatoms and some of the results have been reported in Ref. 4. They show that for a submonolayer metal coverage the 7×7 character of the surface is modified but not destroyed since only relative changes in the intensity of the spots are observed. On the contrary the LEED pattern is completely changed by annealing (~300 °C for 2 min) of the metal-covered surface. The second result is probably due to a diffusion of the metal overlayer and a subsequent roughening of the surface. Care should then be used while comparing results of different authors since similar small annealing is sometimes accidental and frequently occurs in preparing metal-semiconductor junctions.

III. ENERGY-LOSS SPECTRA

The main results we obtain with ELS are the removal of clean-surface spectral features at an early stage of metal coverage while the bulk-silicon features are almost unchanged, and the appearance of new metal-related peaks. Figure 1 shows a set of energy-loss spectra referring to

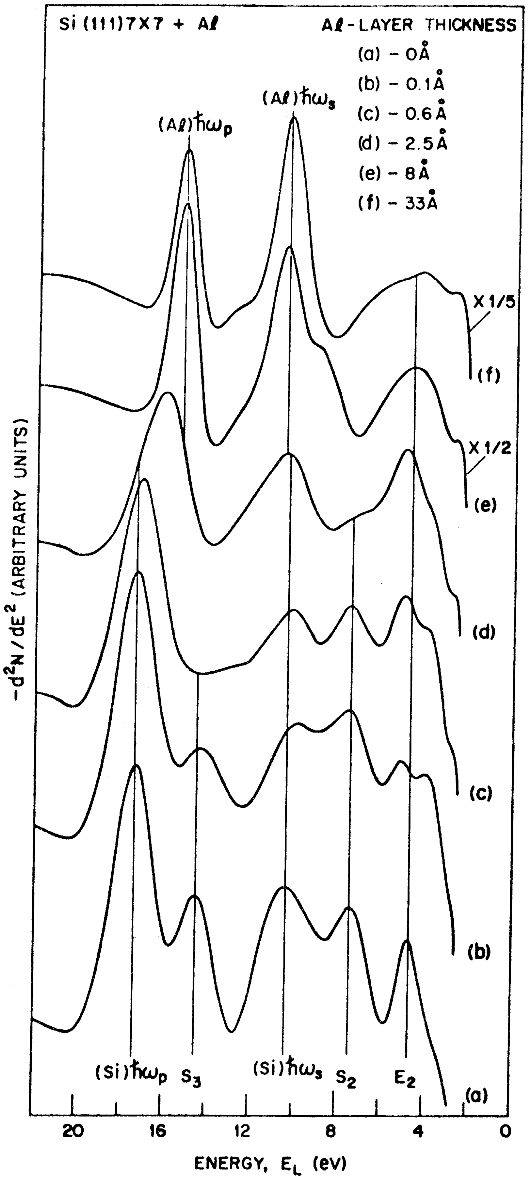

FIG. 1. (a) Second-derivative electron-energy-loss spectra for a clean silicon (111) 7×7 surface [curve (a)]; (c)–(f) increasing coverage with evaporated aluminum. The primary-electron-beam energy was 100 eV. The labeling of the different peaks is explained in the text.

the clean 7 × 7 silicon surface [curve (a)] and to the aluminum-covered sample with overlayer thicknesses between 0.1 and 33 Å. We estimate[5] that in our thickness scale one monolayer of aluminum roughly corresponds to 1.5 Å. All the features of the clean-surface spectrum have already been identified.[15] In particular the peak labeled in Fig. 1 as (Si)$\hbar\omega_p$ is due to bulk silicon collective excitations. The peak (Si)$\hbar\omega_s$ is related to the creation of surface plasmons. The peak E_2 is a one-electron transition related to the bulk-silicon band structure while peaks S_2 and S_3 are electronic transitions involving surface states. Two of the known low-energy-loss surface-state features have been hidden in Fig. 1 by the onset of the elastic peak S_0 appearing only in high-resolution-energy-loss spectra,[15] and S_1, lying at ~−2.0 eV.[14] One can see that the evolution of the energy-loss spectrum with coverage has almost ended at ~8 Å of Al overlayer (i.e., 5–6 monolayers) and intensity rather than shape modifications occur after that point. The main modifications leading from curve (a) to curve (e) are the following. The clean-surface-state features completely disappear after ~0.3 monolayer coverage for S_3 and ~2 monolayer coverage for S_2. The bulk-plasmon peak evolves from that of clean silicon (Si)$\hbar\omega_p$ to the onset of the peak labeled as (Al)$\hbar\omega_p$, due to the creation of bulk-metal plasmons.[17] The surface-plasmon peak of the clean silicon surface (Si)$\hbar\omega_s$ evolves to the onset of the sharp aluminum-surface-plasmon peak (Al)$\hbar\omega_s$. One should observe that the behavior of (Si)$\hbar\omega_s$ is strongly influenced by the decrease of S_2 and S_3. A tentative correction for this effect indicates that the intensity of (Si)$\hbar\omega_s$ slightly *increases* between (a) and (d). For curve (d) one has a superposition of (Si)$\hbar\omega_s$ and (Al)$\hbar\omega_s$. The main interband transition E_2 for clean Si(111) is substantially unchanged although slightly shifted to larger energy loss. A new metal-induced structure at ~4 eV is clearly resolved in curves (b) and (c) and it is superimposed to E_2 at larger coverages. Another metal-induced peak is observed at −2.8 eV.

Corresponding energy-loss spectrum behavior is observed when the overlayer metal is gallium (see Fig. 2) or indium (see Fig. 3). The estimated monolayer thicknesses are 1.5 Å for Ga and 2 Å for In.[18] The increased intensity of (Si)$\hbar\omega_s$ before the onset of the metal-surface plasmon is much more pronounced for gallium than for aluminum or indium overlayers. The apparent shift of (Si)$\hbar\omega_s$ which occurs in Fig. 2 between curves (a) and (d) is due to the removal of S_2. For curves (e) and (f) a new gallium-surface-plasmon peak arises whose position in energy is similar to that of (Si)$\hbar\omega_s$ after correction for the presence of the S_2 interband transition. Owing to better energy resolution the clean-surface peak S_1 not observed in Figs. 1 and 3 is present in the clean-surface curve (a) of Fig. 2. However, its apparent survival in curves (b)–(f) of Fig. 2 is misleading. Indeed, Figs. 1 and 3 where S_1 is absent for the clean-surface spectra show that a new structure appears between −2.5 and −3 eV after metal coverage. The peak around ~−2 eV in the upper curves of Fig. 2 must be identified with this new structure rather than with a surviving S_1 peak. Indeed Fig. 4 shows that its energy position differs by ~0.2 eV from that of S_1. Curve (b) of Fig. 3 shows that the corresponding structure induced by In coverage is at ~−2.7 eV. Transitions involving d-core levels of

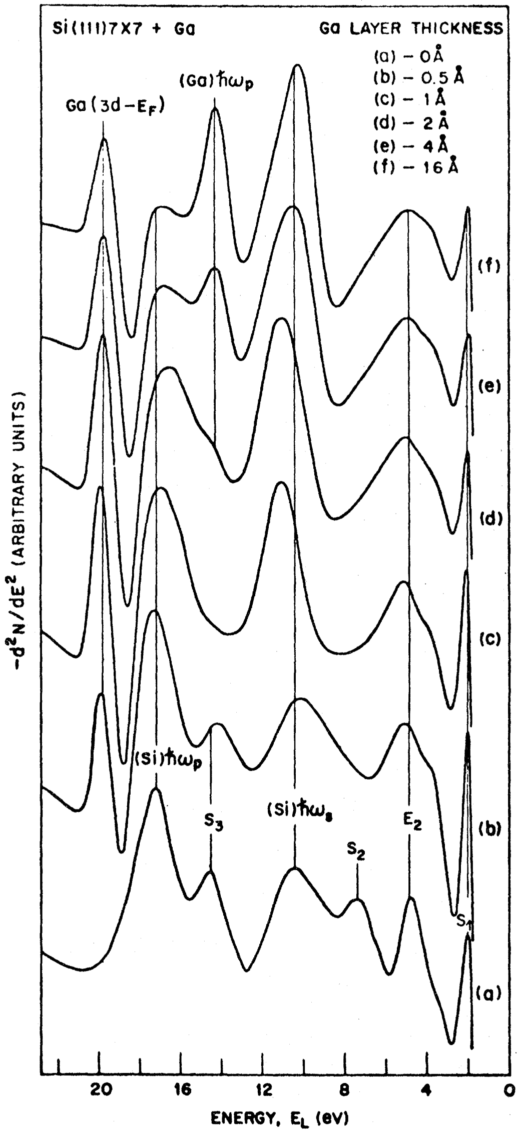

FIG. 2. ELS results for various gallium coverages.

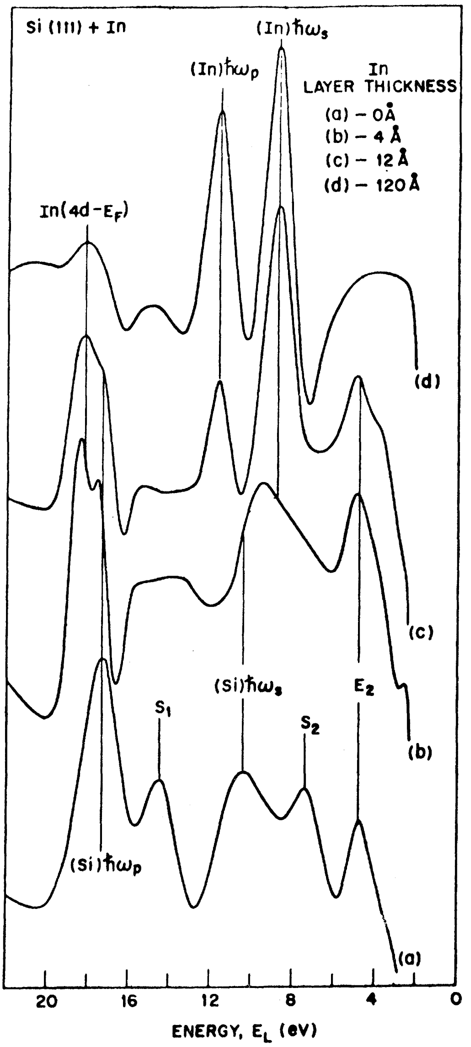

FIG. 3. ELS results for various indium coverages.

Ga and In also contribute to the spectra of Figs. 2 and 3 and the corresponding peaks are labeled as Ga($3d$-E_F) and In($4d$-E_F), respectively. Figures 2–4 again show that E_2 is still present after Ga or In coverage as it was after Al coverage. A new structure at ~−3.8 eV is superimposed to E_2 after Ga or In evaporation which corresponds to the one observed at ~−4 eV after Al evaporation.

The above experimental results for bulk and surface plasmon peaks are summarized by Table I which also reports previous results for comparison. We would like to emphasize that the similar nature of Al, Ga, and In overlayers is evident from the similar behaviors shown by Figs. 1–3. In summary the surface-plasmon peak (Si)$\hbar\omega_s$ is replaced by a much narrower metal-surface-plasmon peak. The clean-surface-state features disappear while the bulklike E_2 does not disappear and new metal-induced structures appear between −3.8 and −4, and −2 and −3 eV.

IV. EVOLUTION OF THE METAL-SEMICONDUCTOR INTERFACE

The present experimental results clearly show that the electronic states at the metal semiconductor interface are different from those of the clean silicon surface or from those one could expect at an *abrupt* junction. The transitions involving clean-surface states are removed by the metal. As we shall see all the new peaks appearing between −2 and −4 eV can be attributed to transitions involving metal-related states. The small changes in the bulk E_2 peak show that an "intermediate" region is present between metal and semiconductor.

Before discussing the ELS data in more detail, we wish to briefly comment on the question of the overlayer homogeneity. An "island" growth of the overlayer cannot be excluded *a priori* for our experimental conditions. Let us distinguish between two possibilities. The first one is that the overlayer grows only in limited regions of the semiconductor leaving significant portions of the silicon surface essentially "clean" for nominal average coverages up to many monolayers. This possibility can be ruled out by observing that the LEED patterns at low coverage[4] are not the weaker, *intrinsic* 7 × 7 pattern that should be given by the clean portion of the surface but *extrinsic* 7 × 7 patterns with coverage spot intensity quite different from the clean surface. All contributions from clean-surface states to UPS and ELS disappear after a fraction of the ion-metal-atom monolayer is deposited on the semiconductor surface. There is a

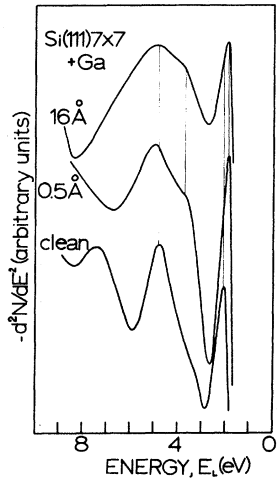

FIG. 4. Details of the spectra for the clean surface and two different Ga coverages in the low-energy-loss region.

TABLE I. Energy position of bulk and surface plasmons for Si, Al, Ga, In from our data and from the literature. (All energies in eV. Uncertainty ± 0.4 eV.)

	Si		Thick Al		Thick Ga		Thick In	
	$\hbar\omega_p$	$\hbar\omega_s$	$\hbar\omega_p$	$\hbar\omega_s$	$\hbar\omega_p$	$\hbar\omega_s$	$\hbar\omega_p$	$\hbar\omega_s$
Present data	17.3	10.4	15.3	10.6	14.3	10.3	11.7	8.8
Previous experimental values	16.9[a]	10[b]	15.0[c] 15.3[d]	10.3[d]	13.9[e,f] 14.2[g]	10.2[e,f] 9.9[g]	11.3[e] 11.5[g]	8.7[e] 8.2[g]

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second possibility that the metal overlayer starts growing with a uniform coverage of the clean surface, but then increases in thickness preferentially in some regions of the surface. Our data are somewhat ambiguous here and do not disagree with this common growth mechanism. Figure 5 shows that two different In overlayers with the same *average* thickness give spectra corresponding to different stages of the evolution shown in Fig. 3 and this indicates a difference in overlayer homogeneity. The possibility of an island growth of the second kind is not in contrast with our data nor with a two-step model of SB formation.[5] A clustering of this kind could in fact be the way in which the second step is carried out.

The disappearance of clean-surface-state transitions S_1 and S_2 after a small metal coverage indicates that the metal adatoms saturate the Si dangling bonds and remove the associated backbond states. This is consistent with the observed removal of empty clean-surface states in the gap[3] and of filled clean-surface states near the top of the valence band.[5] A pure dangling-bond surface-state model for the pinning of E_F is then incorrect for SB on Si(111). However, the hypothesis of pinning of E_F by interface states is still valid since new metal-induced interface states replace the clean surface ones.[3,5] As discussed above the metal overlayer also removes the S_1 clean-surface transition. A new peak appears in its place at slightly larger energy loss. This peak is due to transitions involving filled interface states created by the metal adatoms.[5] Since it appears in the spectra at a rather early stage of the coverage the initial states should be those created at 2.1–2.5 eV from the top of the valence band during the first step of Schottky-barrier formation.[5] This places the final states *within* the silicon forbidden gap in qualitative agreement with the results of core-level energy-loss spectroscopy. A quantitative agreement for the final-state position could also be claimed but it is not too meaningful due to the large uncertainty in both experiments.

The role of plasmons on the metal-semiconductor interface behavior is a long-time controversy.[8-10] A general criticism is that the models employed to calculate the interface dielectric function are too idealized to account for the real situation. It is clear from Table I that the initial and final stages

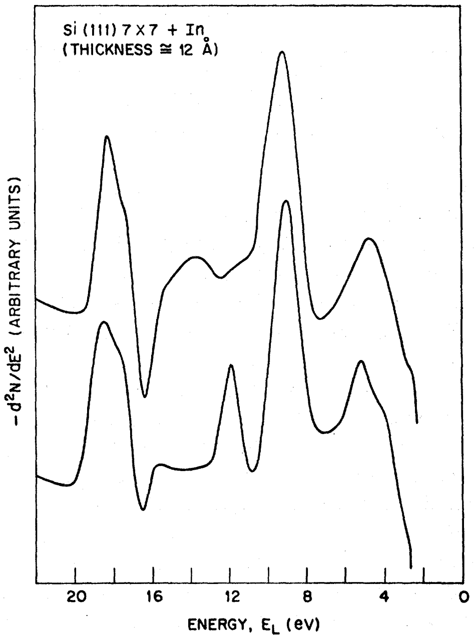

FIG. 5. Slightly different energy-loss spectra given by two different In evaporation with equal "average" thickness.

of our experiment correspond to the bulk-silicon, silicon-vacuum and bulk-metal, metal-vacuum plasmons, respectively. The increased intensity of the silicon-vacuum plasmon peak at very low coverages may be interpreted as an interference effect with the metal-vacuum interface.

A simplified model for low coverage would be a smooth metal film and a sharp metal-semiconductor interface. This gives[19] several plasmon modes including an *interface* plasmon whose energy is the root-mean-square average of the metal and silicon bulk plasmons in the zero-coverage limit. While the metal and silicon bulk plasmons are too close in energy for Si-Ga and Si-Al to see a peak between them, a structure seems to be present in Fig. 3 near the predicted position for Si-In (~14.3 eV). An interface plasmon at this energy is also predicted by the Inkson's many-body approach.[10]

Inkson's theory actually predicts *two* interface plasmon modes, the second at a much lower energy. Evaluation of this energy in our case gives 4.2, 4.0, and 3.3 eV for Si-Al, Si-Ga, and Si-In, respectively, which would agree with the position of the structure superimposed to E_2 after metal coverage. However, the observed interface transition at lower energy loss of 2–3 eV makes the stability of such low-energy plasmon questionable. Moreover the survival of E_2 after metal coverage shows that the actual interface is not too different from the bulk silicon and *cannot* be described by a sharp metal-semiconductor boundary. E_2 is indeed an interband transition related to the silicon band structure.[15] This means that the metal atoms at the interface are bonded to silicon in a way similar to the bulk silicon covalent bonds. Group-III atoms do behave in a similar way to Si atoms since they are substitutional impurities.

Phillips[20] has calculated the position of E_2 for hypothetic silicon–group-III "compounds" obtaining 5.0, 4.6, and 4.0 eV for Si-Al, Si-Ga, and Si-In, respectively. This theoretical trend in different "compounds" qualitatively agrees with that of the experimental position of the E_2 center of gravity for different metal-silicon interfaces (see Figs. 1–3).

We point out that the "interface" E_2 peak can be observed even for large nominal coverages due to the island growth discussed above. In this picture the peak superimposed to the low-energy-loss side of E_2 must be explained with a different interband transition rather than with a low-energy interface plasmon. The trend of this peak's experimental position in different interfaces is in qualitative agreement with that of E_1 calculated for the corresponding hypothetic metal-silicon compounds.[20] The peak observed around ~–14.5 eV for In-Si may still be interpreted as an interface plasmon. Indeed this is a reasonable energy for the free-electron plasma frequency of an "intermediate" region with free-carrier concentration between the metal's and semiconductor's.

We observe that the "covalent" character of the interface bonds is supported by several experimental facts[3-5]: For example, by the shape of Ga($3d$-E_F) transitions shown in Fig. 2 and In($4d$-E_F) transitions shown in Fig. 3. These peaks are due to transitions between metal d-core levels and final states lying near E_F. It has been pointed out[4] that the "excitonic" line shape observed at intermediate coverages is due to final states which are due to covalentlike bonds between silicon and metal atoms. It is clear in Fig. 3 that this "extrinsic" line shape is different from the "bulk-metal" line shape [see curve (d)].

Our present data confirm that strong changes in the local density of states are caused by the metal coverage and that the interface electronic transitions and collective modes cannot be described in terms of an abrupt metal-semiconductor junction. This is further evidence that a suitable theory of the metal-semiconductor junction has to be based on the chemical properties of the interface. Andrews and Phillips[21] recently connected the barrier height of transition-metal–silicon junctions to the formation of a strongly bonded silicide compound at the interface similar to the covalent interface bonds suggested in the present work. A calculation of the local density of states has been carried out by Louie and Cohen[22] on the basis of a jellium-semiconductor model for the Al-Si junction. Some of their conclusions are confirmed by our data such as the covalent character of the interface bonds but their model does not completely account for the experimentally observed changes in the local density of states. A substantial theoretical effort is probably required to provide a sophisticated "chemical" description of a specific metal-semiconductor interface but this effort does not seem to be beyond present capabilities. On the other hand, more experimental information about the changes in the local density of states may be provided by different experimental techniques such as high-resolution ELS[15] or optical measurements.[23]

V. CONCLUSIONS

We have carried out a step-by-step ELS study of Schottky-barrier information in silicon (111) 7 × 7. The results of these experiments corroborate and extend previous experimental results about the removal of clean silicon surface states by metal adatoms and about the covalent character of chemical bonds at the metal-semiconductor interface. An "intermediate" region appears between metal and semiconductor giving rise to interface plasmons and one-electron transitions which replace the clean-surface ones. Some of the one-electron transitions are much more similar to those of bulk silicon while others imply metal-induced localized states. The need for a "chemical" theory with structural details of particular interfaces instead of a "macroscopic" approach with parametrized interface properties of Schottky-barrier models is emphasized.

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