PHYSICAL REVIEW B VOLUME 43, NUMBER 17 15 JUNE 1991-I

Adatom-induced donor states during the early stages of Schottky-barrier formation: Ga, In, and Pb on Si(113)

P. Althainz, U. Myler, and K. Jacobi
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 1000 Berlin 33, Germany

(Received 18 December 1990)

We performed angle-resolved ultraviolet and soft-x-ray photoelectron spectroscopy for the early stages of Schottky-barrier formation of Ga, In, and Pb on Si(113) at room temperature. In the coverage region below 0.1 monolayer a band-bending behavior, typical for donor states, is found. The energies of the adatom-induced donor states in the band gap depend on the adatoms. The Schottky barrier reaches its final value at a coverage of about one monolayer. The values are 0.35 eV above the valence-band maximum for In and Ga and 0.425 eV for Pb. Measurements with Xe interlayers were made to verify that these interfaces are not reactive.

I. INTRODUCTION

The formation of metal-semiconductor interfaces is a subject of recent theoretical and experimental research. Upon deposition of metal atoms on semiconductors from far below the monolayer (ML) coverages to thick films, the Fermi level at the surface (E_{FS}) aligns at different energy positions in the band gap of the semiconductor. Charge which crosses the interface has to surmount the energy difference between this Fermi level and the appropriate semiconductor band (conduction-band maximum or valence-band minimum in the case of *n*-type or *p*-type charge carriers, respectively). The magnitude of the so-called Schottky barrier and its development with metal thickness is influenced by many different physical processes. Chemical interactions, defects, and metal-induced gap states are some of them. For comprehensive discussion of the various aspects of the problem see Refs. 1–5.

Recently some experiments on cleaved GaAs(110) surfaces at low temperatures[6–8] have stimulated the discussion about the metal adsorption process in the low-coverage region. On *p*-type samples an overshooting of the Fermi-level position at the surface was observed with increasing coverage. At coverages below one-tenth of a monolayer the Fermi-level position (E_{FS}) above the valence-band maximum (E_{VBM}) exhibits a maximum, after which it decreases until it reaches the final Schottky-barrier height. Theoretical models by Klepeis and Harrison,[9] Lefebvre *et al.*,[10] and Mönch[11] explain the pinning behavior at these coverages with adatom-induced surface states of donor character. According to these models the energetic position of the donor state should depend on the metal which is deposited on the semiconductor. Measurements on GaAs(110) show such a chemical trend in the observed pinning positions at low coverages.[11]

The absence of surface states in the band gap of cleaved GaAs(110) surfaces made it possible to detect the above-described effects. On the other hand, the chemistry of the GaAs(110) surface is much more complex than that of the covalent semiconducotrs since it involves the two different elements of the compound. Although the experiments on covalent semiconductors are complicated by the presence of surface states in the band gap, we have shown recently that the system Ga on *p*-type Si(113) is well suited for metal adsorption studies in the low-coverage region.[12] Adatom-induced surface states of donor character on a silicon surface were reported there for the first time.

In this work we present results of room-temperature adsorption of Ga, In, and Pb on *p*-type and *n*-type Si(113), extending the former results to other metals and to an *n*-doped substrate. A chemical trend of the induced donor levels at coverages of about 0.1 ML was found. The above-cited theories were therefore confirmed, and the results for metals on GaAs(110) are reproduced on a chemically simpler system. Although all three metals are known to give sharp, unreactive interfaces on silicon,[13,14] we proved this by a new method of gentle cluster depositon[15] by adsorbing the metals on top of a Xe interlayer and then depositing it on the Si surface through sublimation of the Xe.

After a short description of the experimental setup and the thickness calibration in Sec. II we present the band-bending behavior for Ga, In, and Pb adlayers on Si(113) as evaluated from Si 2*p* core-level measurements in Sec. III. The results are discussed in Sec. IV in the context of the above-cited theories.

II. EXPERIMENT

Photoemission measurements with synchrotron radiation were performed at the TGM 3 (toroidal grating monochromator) beamline at the Berlin electron storage-ring BESSY (Berlinger Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung). Photoelectron core-level spectra were taken with a hemispherical electron-energy analyzer (ADES 400, VG Scientific). The overall energy resolution including monochromator and analyzer was 300 meV at $h\nu=30$ eV and 400 meV at $h\nu=108$ eV. The Pb on Si(113) experiments were made at the TGM 6 Undulator/Wiggler beam line[16] at BESSY with another hemispherical analyzer (ARIES, VSW Scientific Instruments Ltd.). The resolution of this configuration was about 200 meV. All photoemission spectra were recorded in an angle-resolved mode at normal electron emission. The angle of incidence of the light was 45°. Equipment for low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) was present in our UHV chamber (base pressure 5×10^{-11} Torr). The preparation of the Si(113) samples [p-doped with 2.5×10^{17} (boron atoms)/cm^3 and n-doped with 2.3×10^{18} (antimony atoms)/cm^3] was as follows. After a chemical treatment[17] the samples were cleaned by cyclic sputtering and annealing at temperatures between 1100 and 1200 K in the UHV. A high surface-state intensity in the valence-band photoemission spectra and a 3×2 LEED pattern indicated a clean smaple.[17] The sample temperature was measured using a Pt/Pt-Rh thermocouple calibrated by an infrared pyrometer. The metals In (99.9999% pure, ALFA products), Ga (99.999% pure, BALZERS), and Pb (99.9995% pure, BALZERS) were evaporated from water-cooled ovens with effusion cells heated by electron bombardment. During evaporation the pressure never exceeded 2×10^{10} Torr. The evaporation rates were 0.25 ML/min for Ga and Pb and 0.5 ML/min for In. The sample could be cooled down to about 50 K. These low temperatures could not be measured by means of our Pt/Pt-Rh thermocouple, but we were able to condense xenon (99.99 vol%, MESSER GRIESHEIM) multilayers onto the sample.

III. RESULTS

All three metals exhibited layer-plus-islands growth mode with the substrate at room temperature. This was checked with Auger-electron spectroscopy (AES) and, in the case of Pb, with core-level spectroscopy. The plots of adsorbate-signal intensity versus evaporation time showed in all three cases a linear increase with a break after a certain evaporation time. Behind this break the slope of the curves indicated clustering. The ML coverage was defined to correspond to the evaporation time at this breakpoint. This was further supported through the amount of weakening of the Si signal from the substrate at this breakpoint. The AES results for Ga have been published.[12] The In and Pb metal layers showed the same behavior as described above. Our findings are in good agreement with other studies of Ga,[13] In,[13] and Pb (Ref. 14) growth modes on silicon. For the following all coverages are given in ML.

The LEED pattern showed no ordering of the adsorbed metal layers with the exception of Pb, which formed a 1×1 superstructure up to a coverage of one ML. Further investigations of the morphological structure of the Ga, In, and Pb adlayers on Si(113) are planned.

The change of band bending due to the deposition of metal onto the semiconductor surface was measured with core-level spectroscopy of the silicon $2p$ core-levels, as can be seen from Fig. 1. The spectrum in the lower part shows the emission from the Si $2p$ levels of the clean p-type Si(113) sample. After evaporation of 3 ML Ga the spectrum is shifted by about 310 meV to higher kinetic energies. This is completely due to band-bending changes since the energy of the incident photons was chosen to be 108 eV and therefore the components of surface core-level shifts and chemical shifts are negligible.[12] This choice of photon energy also allowed us to measure the Si $2p$ core level underneath the 3-ML-thick Ga film with a reasonably good signal-to-noise ratio. The spectra shown in Fig. 1 are the raw data. To evaluate the shifts of the Si $2p$ core level a linear background was subtracted and a separation of the two spin-orbit components was performed by means of a simple computer program.[18] Relative changes of band bending were thus measured with an accuracy of about ±20 meV. To determine E_{FS} at the clean surface we used the surface photovoltage measured at He temperature.[18] At low temperatures a flat-band condition is achieved under illumination with uv light. With core-level spectroscopy the shift of the spectra relative to their position at 300 K were measured and E_{FS} was determined. A correction for the finite sampling depth of the electrons was made. In our case the values for the difference between the Fermi level and the valence-band maximum ($E_{\mathrm{FS}}-E_{\mathrm{VBM}}$) were (595±25) meV and (620±25) meV for the p-type and the n-type sample, respectively.[18]

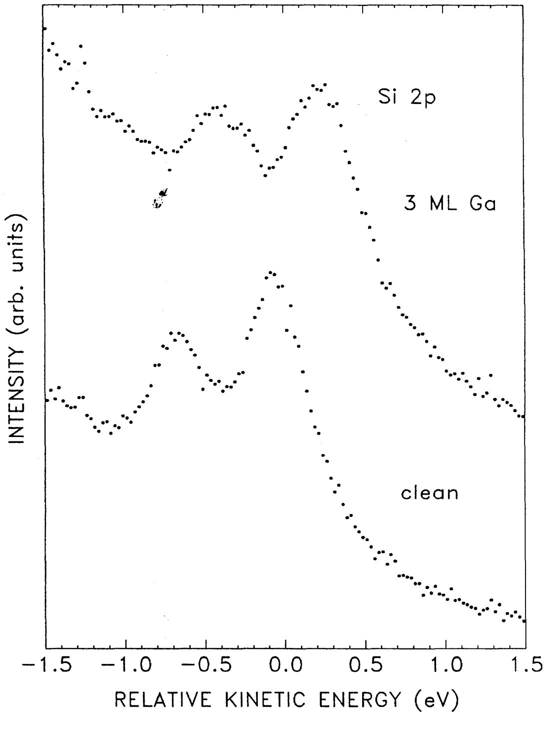

FIG. 1. Photoemission spectra of the Si $2p$ core level for the clean, p-type Si(113) sample and the sample covered with 3 ML Ga. The energy is given relative to the energy of the $2p_{3/2}$ component of the spectrum from the clean sample. The energy of the light was 108 eV.

From the Fermi-level position of the clean surface and the band-bending changes with increasing coverage the Fermi-level position in the band gap was derived. The data for Ga, In, and Pb are shown in Figs. 2–4. The change of E_{FS} with increasing coverage is quite similar for all three metals and for the *n*- and *p*-type substrates. At coverages below 0.1 ML E_{FS} moves up in the gap. For *p*-type samples this means an increase in band bending. This has been called overshooting.[12] For *n*-type samples the same move means a decrease in band bending before it increases again at higher coverages. Whereas the change of E_{FS} is the same for *p*- and *n*-type samples the underlying change in band bending is opposite. At about 0.1 ML E_{FS} reaches its maximum value in the gap which is 30 to 145 meV above the starting position for the clean surface. The final position of E_{FS}, i.e., the Schottky-barrier position, is reached at about 1 ML. Differences between the different metals can be found in the energetic pinning positions at 0.1 ML and in the values for the Schottky-barrier heights. At 0.1 ML coverage the Fermi-level pinning position was 745 meV (Ga), 700 meV (In), and 630 meV (Pb) above the energy of the valence-band maximum (E_{VBM}). The Schottky-barrier heights (*p*-type) are 350 meV (Ga and In) and 425 meV (Pb). The corresponding positions in Figs. 2–4 are marked by lines. Following the interpretation of our earlier measurements of Ga/Si(113) (Ref. 12) and some recent theoretical work[9–11] we assign the Fermi-level pinning positions at 0.1 ML coverage to adatom-induced surface states of donor character. These donor states follow a chemical trend in their energetic position, as will be discussed below.

The difference between Pb and the group-III metals Ga and In is revealed also in the metal core level spectra (Figs. 5 and 6). Note that the shifts of the spectra due to the band-bending changes were already substracted. With increasing coverage the In 4*d* core level is shifted to lower binding energies by 350 meV. A similar result was found for Ga with a shift of about 500 meV.[12] On the contrary, the Pb 5*d* core-level does not show such a shift. From 0.1 to 3.8 ML the position of the core level is constant within ±50 meV.

The results demonstrate some interesting properites of the Si(113) surface. The fact that such a small amount of metal as 0.1 ML is able to change E_{FS} in a reproducible manner is unique among the different silicon surfaces. Since up to now Si(113) has not been used as a substrate for SB formation, the question of its stability against surface disruption and metal interdiffusion arises. Although the Si 2*p* spectra show no sign of chemical intermixing we checked this question further by a new method of gentle adlayer deposition. The idea that the formation of metal clusters and islands releases enough energy to destroy chemical bonds at the surface was thoroughly discussed by Zunger.[19] Recently, Waddill *et al.* showed that the preparation of abrupt, defect-free interfaces depends in

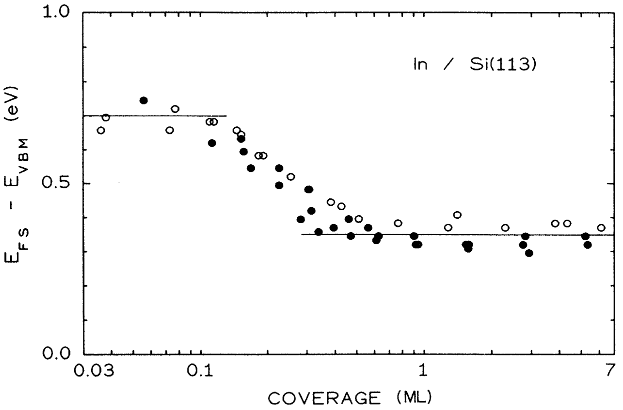

FIG. 3. Fermi-level position at the surface E_{FS} above the valence-band maximum E_{VBM} vs the In coverage. Solid circles represent measurements on *n*-type and open circles on *p*-type silicon.

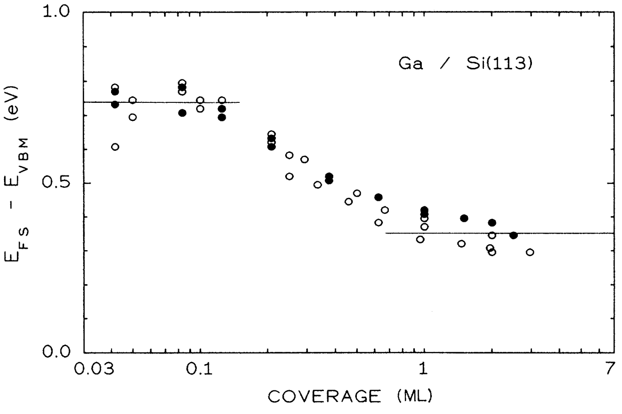

FIG. 2. Fermi-level position at the surface E_{FS} above the valence-band maximum E_{VBM} vs the Ga coverage in units of ML. Solid circles represent measurements on *n*-type and open circles on *p*-type silicon.

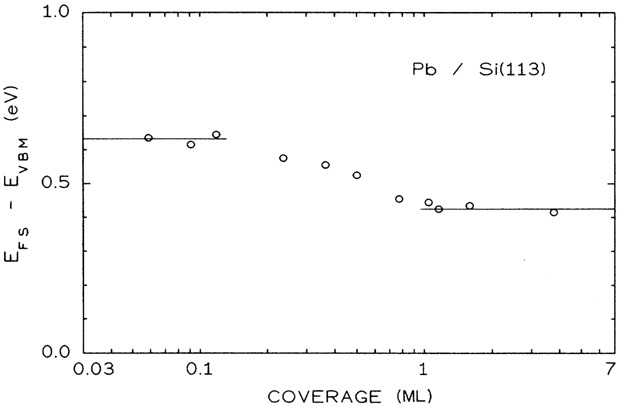

FIG. 4. Fermi-level Position at the surface E_{FS} above the valence-band maximum E_{VBM} vs the Pb coverage on *p*-type silicon.

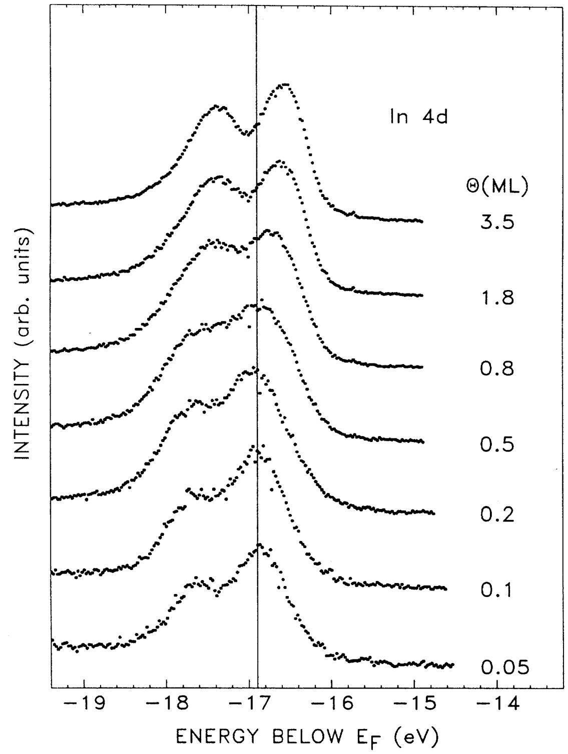

FIG. 5. Photoemission spectra of the In 4*d* core-level on *p*-type Si(113). Parameter is the In coverage Θ in units of monolayers (ML). The energy is referenced to the Fermi edge E_F. The In $4d_{5/2}$ peak of the metallic adlayer (3.5 ML) lies at 16.55 eV below E_F. The spectra have been shifted to correct for the band bending. Every spectrum is scaled to equal height to achieve a better visibility of shift in peak position. The energy of the light was 45 eV.

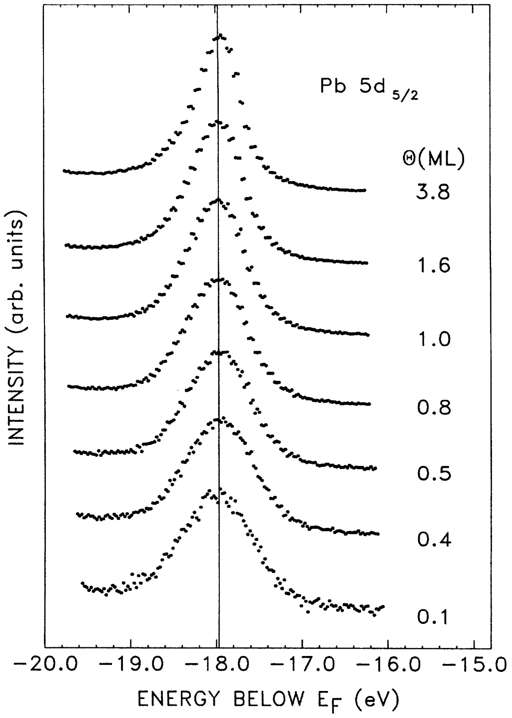

FIG. 6. Photoemission spectra of the Pb 5*d* core-level on *p*-type Si(113). Parameter is the Pb coverage Θ in units of monolayers (ML). The energy is referenced to the Fermi edge E_F. The Pb $5d_{5/2}$ peak of the metallic adlayer (3.8 ML) lies at 17.97 eV below E_F. The spectra have been shifted to correct for the band bending. Every spectrum is scaled to equal height to achieve a better visibility of the energy shifts. The energy of the light was 53 eV.

some cases on the prevention of this effect.[15] They used condensed Xe as an interlayer for the preparation of defect-free interfaces. Following this procedure we prepared metal-layers on silicon as follows. The sample was cooled down with liquid helium. Then about 60 L (1 L$\equiv 10^{-6}$ Torr s) Xe were condensed onto the cooled sample. This dose is equivalent to about 10 layers of Xe. After evaporation of the metal onto the Xe interlayer the sample was warmed up so that the Xe sublimed and the metal dropped to the Si surface. We believe that the latter took place in the form of metal clusters. The measurements of the Si core levels were made at room temperature. This procedure ensured that the energy which is released during cluster formation is absorbed into the thick Xe layer. In Fig. 7 Xe 4*d* core-level spectra for different Xe coverages are shown. The spectra are shifted to higher binding energies between 6 L and 66 L by 400 meV, which is due to the known distance-dependent binding energy shift.[20] The well-defined shift for doses larger than 6 L Xe indicates that a full ML of Xe is condensed first. After evaporation of about 1 ML In, the Xe multilayer is still present, which is proved by the topmost spectrum of Fig. 7. The broadening of this spectrum is due to charging of the metal on top of the isolating Xe layer. Figure 8 shows the band-bending behavior of In on Si(113) measured with the cluster-depositon technique. The final Schottky-barrier height is the same as for the case of normal deposition. Also the agreement in the low-coverage region between cluster deposition and normal deposition is fairly good. This indicates that at low coverage the adatoms are deposited atom by atom without forming clusters. The cluster-deposition technique was also used to examine the Ga/Si(113) system. The results are the same and not shown here. One therefore can conclude that the examined metal layers on Si(113) build sharp, unreactive interfaces.

IV. DISCUSSION

The results of band bending described above led to the assumption that adatom-induced donor states develop at coverages below 0.1 ML. A donor state supplies charge to the substrate and enlarges the positive charge at the surface and increases the band bending in case of a *p*-type sample (overshooting). For the *n*-type sample, the same positive charge of the donor state compensates partly the negative charge at the surface which increases the band bending. Therefore, both *n*- and *p*-type results indicate

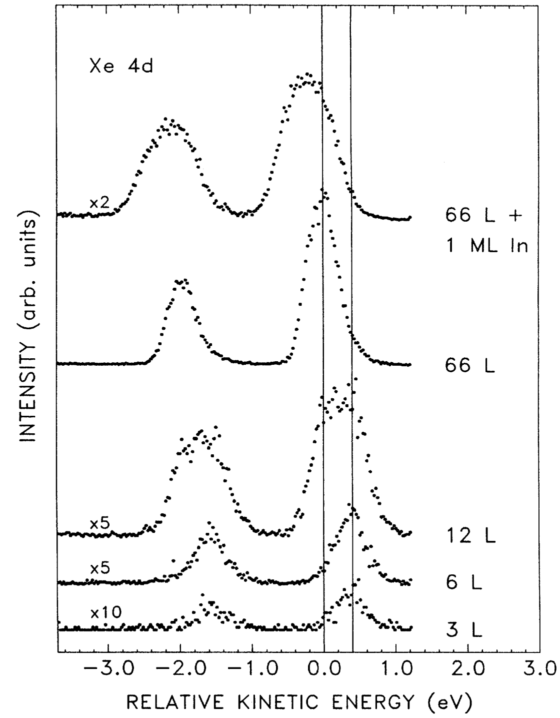

FIG. 7. Photoemission spectra of the Xe 4*d* core-level for different coverages of Xe and with In on top of a thick Xe layer. The energy of the light was 108 eV.

that a donor state is induced by the adsorbed metal atoms independent of substrate doping. The origin of these states can be explained by a model of Klepeis and Harrison.[9] For this model they assume that a single adatom forms an embedded surface "molecule" with adjacent substrate atoms. This surface molecule has filled and empty electronic states with donor or acceptor character,

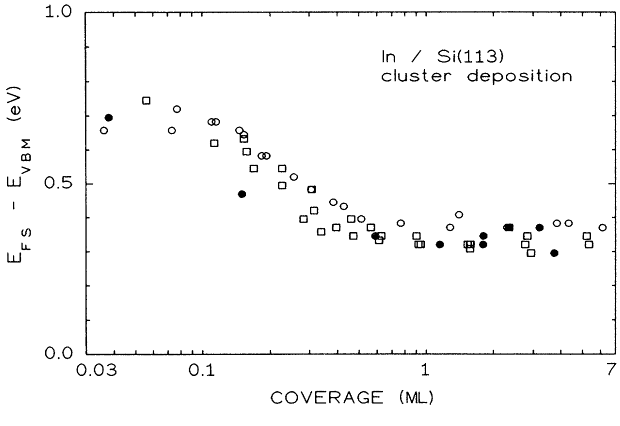

FIG. 8. Fermi-level position at the surface E_{FS} above the valence-band maximum E_{VBM} vs the In coverage. Solid symbols represent measurements on layers prepared by cluster deposition. Open symbols are for the values shown in Fig. 3. Circles represent measurements on *p*-type and squares on *n*-type silicon.

respectively. The presence of the surface shifts the donor state above the Fermi-level E_{FS} in the band gap of the semiconductor. In this case, every surface molecule donates one electron into the semiconductor until the band bending pins E_{FS} at the position of the donor level. After this no further donation of electrons occurs with increasing coverage. For the calculations a model of the surface structure is needed. Klepeis and Harrison used a tight binding approach to calculate the energies of donor levels for Al, Ga, and In on an ideal Si(100) surface. A bridging position of the adatom and a "seventeen atoms embedded molecule" was chosen.[9] It turned out that two kinds of donor levels could be possible: adatom-derived nonbonding metal states and substrate-derived silicon dangling-bond states. The calculated donor energies do not fit with our data, which is not surprising since our system is different from the calculated one. The model character of their calculations is also stressed by the authors.

It is reasonable that the chemical properties of the adsorbed metal influences the electronic structure of the embedded surface molecule and therefore the resulting donor level. Mönch compiled experimental data for different metals on GaAs(110) and found a weak dependence of the donor levels on the adatom ionization energies.[11] The atomic ionization energies of Ga, In, and Pb are 6.0, 5.8, and 7.4 eV, respectively. The trend of the low donor level of Pb in contrast to Ga and In therefore resembles the same chemical trend found by Mönch.[11] Actually, our values for Ga, In, and Pb on Si(113) lie exactly on the curve shown by Mönch for GaAs(110). The reversion of the trend for Ga and In is within the scatter of the data compiled by Mönch. It is surprising that the energies of the donor levels are the same for Si(113) and GaAs(110) although the ionization energy for Si(113) of 5.36±0.05 eV (Ref. 17) and of GaAs(110) of 5.82 eV (Ref. 21) differ by an appreciable amount. We believe that this discrepancy is released if one takes into account that the reconstruction of the GaAs(110) surface is very likely to be lifted during metal adsorption (see also below). This could change the ionization potential by 0.46 eV since the high electron affinity of the GaAs(110) surface, which is similar to the As-terminated GaAs(111) surface,[21] is quite obviously due to the reconstruction of the GaAs(110) surface which moves the As-surface atom outward and the Ga-surface atom inward.

The results of the metal core-level spectroscopy clearly showed the differences in the chemical behavior of the three metals. Table I lists the donor energy, the chemical shift in the low-coverage region, the atomic ionization energy, and the final Schottky-barrier height for all three metals. The chemical shift measured with core-level spectroscopy shows the same trend as the donor energies. Since the donor level of Ga-Si lies higher in the gap, more Ga-Si molecules transfer charge to the substrate. Therefore, more $Ga^{\delta+}$ species can be observed at the surface, which explains the larger shift to lower binding energies of the Ga core level with coverage compared to Pb. In this explanation we assume that with coverage the Ga-Si molecule breaks up and the Ga atom is incorporated into the metallic Ga clusters.

TABLE I. Donor energies, chemical shifts, and Schottky-barrier heights from this study compared to the atomic ionization energies for Ga, In, and Pb.

	Ga	In	Pb
Donor energy relative to the valence-band maximum in meV	745	700	630
Chemical shift to higher binding energy in meV	500	350	≈0
p-type Schottky barrier in meV	350	350	425
Ionization energy in eV	6.0	5.8	7.4

We believe that our results may be interpreted in terms of a chemical trend of donor levels of a surface molecule which consists of the adsorbed atom and a number of substrate atoms although we are not able to identify the local chemical bonding and the donor levels more precisely. The chemical trend needs further support by calculations based on atomic models of the adatom bonding configuration. In the case of alkali metals on GaAs(110) tight-binding calculations with a diatomic surface molecule by Lefebvre *et al.*[10] and Mönch[11] were carried out assuming the donor state to be the bonding state between the adatom and the Ga atom from the GaAs substrate. It is filled with two electrons if the surface is neutral. These computations reproduced the chemical trend found from the experiments as discussed by Mönch. On the other hand, a very recent theoretical work by Hebenstreit *et al.*[22] shows that the bonding of Na on GaAs(110) is ionic at a coverage of 0.5 ML. It seems that the final answer has not been given up to now.

The atomic structure of the 3×2 reconstruction of the clean surface is not solved up to now. The surface state intensity in the band gap must be very small; otherwise the donor levels would not be detectable. This agrees with the result that surface states could not be observed in the gap for the clean surface by photoemission.[17] We believe, therefore, that the pinning at the clean surface is due to defect states. This would also explain that the pinning position is the same within 25 meV for *p*- and *n*-doped samples.[18] The initial pinning around midgap for *p*- and *n*-type samples is also responsible for the similarity of the band-bending behavior for *p*- and *n*-doped samples and for the fact that 0.1 ML are necessary before the donor level stabilizes E_{FS}. At lower coverages it has to compensate for the charge in the surface state. Another explanation for the latter could be the formation of two-dimensional metal clusters of small size which donate only one electron each. Metals on GaAs(110) are able to pin E_{FS} at the donor energy with coverages of 0.01 ML and less.[6-8]

For the sytem Na on GaAs(110) calculations show that the change of the reconstruction of the clean surface plays an important part in the pinning of E_{FS} at coverages of 0.25 and 0.5 ML.[22] Since the reconstruction of the clean Si(113) surface vanishes upon adsorption of metals, probably the band-bending behavior from 0.1 to 1.0 ML is severely influenced by this process.

The values for the final Schottky-barrier heights are in good agreement with literature values for the low-index surfaces. The question of whether or not the Schottky-barrier height is determined by the metal-induced gap states (MIGS) cannot be answered by this work. We observed the metalization of the overlayer at 1.0 ML in photoemission where we saw the emission from the Fermi edge appearing in the gap. No conclusions on the local electronic structure can be drawn so far.

V. CONCLUSIONS

During the initial stages of Schottky-barrier formation on Si(113) an overshooting of the band bending with different amplitudes for different metals was found. This is interpreted to be due to adatom-induced donor states. The energies of these donor states in the band gap follow a chemical trend since smaller atomic ionization potential gives rise to higher-lying donor states in the gap. This is observed here for covalent semiconductors. Theoretical models explaining these states as surface "molecules"[9-11] are supported. The nonreactivity of the interface was proved with a method of gentle cluster deposition.

ACKNOWLEDGMENTS

We thank M. Bertolo and J. Schreiner for their help during some measurements at BESSY and P. Geng for constructing the sample holder and for technical assistance. The support by the BESSY staff is appreciated. This work was supported by the Deutsche Forschungsgemeinschaft (SFB6).

---

[1] F. Flores and C. Trejedor, J. Phys. C **20**, 145 (1987).
[2] I. Lindau and T. Kendelewicz, Critical Rev. Solid State Mater. Sci. **13**, 27 (1986).
[3] C. J. Brillson, Comments Cond. Mat. Phys. **14**, 311 (1989).
[4] R. H. Williams, Phys. Scr. **T29**, 209 (1989).
[5] W. Mönch, Rep. Prog. Phys. **53**, 221 (1990).
[6] K. Stiles, A. Kahn, D. G. Kilday, and G. Margaritondo, J. Vac. Sci. Technol. B **5**, 987 (1987).
[7] R. Cao, K. Miyano, T. Kendelewicz, K. K. Chin, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. B **5**, 998 (1987).
[8] M. Prietsch, C. Laubschat, M. Domke, and G. Kaindl, Europhys. Lett. **6**, 451 (1988); M. Prietsch, M. Domke, C. Laubschat, T. Mandel, C. Xue, and G. Kaindl, Z. Phys. B **74**, 21 (1989).
[9] J. E. Klepeis and W. A. Harrison, J. Vac. Sci. Technol. B **7**, 964 (1989); **6**, 1315 (1988).
[10] I. Lefebvre, M. Lannoo and G. Allan, Europhys. Lett. **10**, 359 (1989).
[11] W. Mönch, Europhys. Lett. **7**, 275 (1988).
[12] P. Althainz, U. Myler, and K. Jacobi, Phys. Rev. B **41**, 2849

(1990).

[13]D. Bolmont, P. Chen, C. A. Sébenne, and F. Proix, Surf. Sci. **137**, 280 (1984).

[14]G. LeLay, K. Hricovini, and J. E. Bonnet, Appl. Surf. Sci. **41/41**, 25 (1989).

[15]G. D. Waddill, I. M. Vitomirov, C. M. Aldao, and J. H. Weaver, Phys. Rev. Lett. **62**, 1568 (1989).

[16]W. Peatman *et al.*, Rev. Sci. Instrum. **60**, 1445 (1989).

[17]U. Myler and K. Jacobi, Surf. Sci. **220**, 353 (1989).

[18]K. Jacobi, U. Myler, and P. Althainz, Phys. Rev. B **41**, 10 721 (1990).

[19]A. Zunger, Phys. Rev. B **24**, 4372 (1981); J. Vac. Sci. Technol. **19**, 690 (1981).

[20]K. Jacobi, Phys. Rev. B **38**, 6291 (1988).

[21]W. Ranke, Phys. Rev. B **27**, 7807 (1983). We calculated the ionization potential by adding the band-gap energy of 1.42 eV to the electron affinity of 4.40 eV from Fig. 2 in this reference.

[22]J. Hebenstreit, M. Heinemann, and M. Scheffler (unpublished).