PHYSICAL REVIEW B VOLUME 33, NUMBER 6 15 MARCH 1986

Metallization and Schottky-barrier formation

Inder P. Batra*
IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

S. Ciraci†
IBM Research Laboratory, San Jose, California 95193

(Received 22 October 1985; revised manuscript received 2 December 1985)

Results of self-consistent electronic-structure calculations of aluminum deposited on Ge, as a function of metal coverage, provide strong evidence for overlayer metallization. At monolayer metal coverages, the overlayer changes into a (quasi-) two-dimensional metal characterized by a (modulated) ladder-type density of states. The origin of this transition is traced to the metal-semiconductor interlayer-distance relaxation upon metallization. Our results are in agreement with recent experimental observations, and have important implications for Schottky-barrier formation.

In spite of the recent progress made towards developing a microscopic understanding of the metal-semiconductor interfaces[1-8] and Schottky-barrier (SB) formation, the nature and origin of the electronic states responsible for the Fermi-level pinning are still not fully known. This is due to a large number of complicating factors which influence the Fermi-level position. The pinning, for example, may depend on geometrical structure, metal coverage and reactivity, chemical composition, doping and defect levels, interdiffusion, and surface orientation. It is perhaps a useless exercise to attempt to find a universal pinning mechanism.

Surface states invoked[9-11] at metal-semiconductor interfaces for pinning the Fermi level, in some cases, are eliminated[8] from the gap region owing to the surface reconstruction, and/or owing to the formation of chemisorption bonds.[12,13] The metal-induced states as put forward by Heine[14] require at least several metal layers on the semiconductor surface, and as such are not necessarily the pinning states because a SB gets established[15] at much lower coverages. It is now evident that in many metal-semiconductor systems, the sublayer and multilayer metal coverages lead to different pictures of the interface. The multilayer stage was investigated by Louie and Cohen[16] for an Al-Si junction. They were able to distinguish several types of interface states including metal-induced gap states identified as the pinning states. On the other hand, the binding configuration of metal atoms and chemisorption states have been emphasized in studies[17,18] involving monolayer coverages. In contrast to the chemisorption picture relevant at low coverages, Zunger[19] has proposed an alternate weakly interacting metal-cluster model for Al deposited on GaAs(110).

We believe that, depending on a particular metal-semiconductor system, more than one mechanism may be responsible for determining the position of the Fermi level (E_F) relative to the semiconductor band gap. More importantly, for a given system one may switch from one mechanism to another depending upon the coverage, especially if E_F is not strongly pinned. A crucial parameter[20] which governs the growth sequence may also play a significant role here. This is the so-called γ parameter which is the ratio of the interfacial binding energy to the binding energy of the overgrowth particles. If γ is of the order of unity, then at low coverages one may see the formation of chemisorption bonds. With increased coverage, the overlayer might metallize and relax outwards, resulting in weakening of chemisorption bonds and eventually to the preponderance of metallic states at the Fermi level. Such a picture has emerged from our Al-Ge prototype calculations and is qualitatively consistent with observations[21] on the Al-Si system; both systems have $\gamma \simeq 1$.

In this paper, we have studied the transition from the chemisorbed to metallic overlayer by calculating self-consistent charge density and local density of states for a commensurate Al-Ge interface. Our results present strong support[21] for the metallization of the overlayer, and its origin is the interlayer distance relaxation upon metallization. Furthermore, from this analysis we can bring together a number of concepts about SB formation, which are known in isolation, but have not been previously presented in a consolidated form. Our calculations are performed within the framework of local-density functional theory, applied in the momentum space formalism[22,23] using *ab initio* pseudopotentials.[24] The metal-semiconductor system is represented by a repeating slab geometry; other calculational details can be found elsewhere.[25]

The total energy calculations[20,25] for the prototype Al(001)-Ge(001) have favored the bridge site; it is about 1 eV lower in energy than the on-top site. For the bridge site, it was further noted that the metal-semiconductor interlayer distance, $R_\perp$, relaxed outwards significantly in going from half a monolayer (one Al atom per unit cell—$\theta = 0.5$) to a full monolayer (two Al atoms per unit cell—$\theta = 1$) coverage of metal. It should be noted that our calculations have used an ideal arrangement of the substrate atoms. There is some evidence[26] from low-energy electron diffraction experiments for Ag-Ge(001) that the fractional order spots do indeed disappear at $\theta = 0.5$. Moreover, the general conclusions drawn here are not sensitively dependent on such details of the calculations. Important physical consequences of the change in the value of $R_\perp$ in connection with metallization emerge upon performing charge-density and local-density-of-state (LDOS) analysis. Therefore, in Fig. 1 we show our calculated pseudocharge densities in the $(\bar{1}10)$ plane passing through Al and Ge atoms for the two coverages, $\theta = 0.5$ and 1. The charge densities were calculated self-consistently at equilibrium distances,[20,25] $R_\perp = 1.2$ Å for $\theta = 0.5$ and $R_\perp = 1.8$ Å for $\theta = 1$. The atomic positions are indicated below the charge-density contours.

 ©1986 The American Physical Society

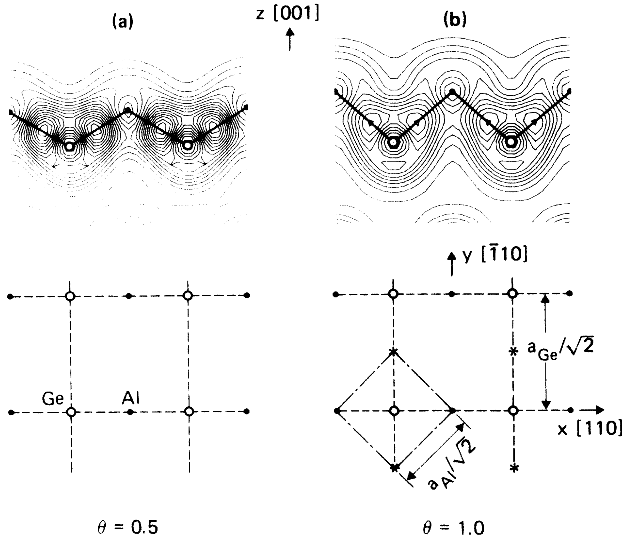

FIG. 1. Charge-density contours in the ($\bar{1}$10) plane of the Al(001)-Ge(001) interface corresponding to aluminum in bridge-bonded sites for $\theta=0.5$ and 1. The contour spacings are 0.005 a.u. Atomic arrangements are also shown for the two coverages; the stars and filled circles represent Al atoms, and open circles Ge atoms.

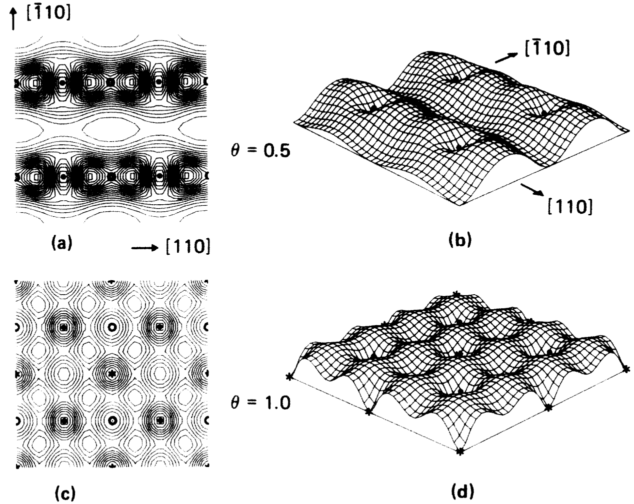

FIG. 2. Charge-density contours (spacings 0.0025 a.u.) and the surface maps in the (001) plane passing through aluminum atoms of the Al-Ge interface corresponding to aluminum in bridge-bonded sites for $\theta=0.5$ and 1. Notice the transition from anisotropic chemisorption state to metallization of the overlayer.

contours. The maximum charge density for $\theta=0.5$ reaches a value of 0.079 a.u. in the middle of the Al–Ge bond direction; the corresponding value for $\theta=1$ is only 0.056 a.u. suggesting a weaker bond. It is thus clear that at the higher coverage, the chemisorption bond has weakened and more charge is oozing out into the vacuum [see Fig. 1(b)]. This indicates the onset, where the directional covalent bonds begin to be replaced by more delocalized metallic-type[21] interaction. The chemisorption bonds are still visible at this coverage, but the metallic bonding can be clearly seen from the charge distribution. We may mention that in going to $\theta=1$, we have placed the additional Al atoms in an epitaxial relationship. The epitaxial geometry is found to be adequate from our force calculations leading to small forces acting on metal and semiconductor atoms at the interface.

The metallization of the aluminum overlayer is displayed more dramatically in Fig. 2. Here, we have plotted charge-density contours in the (001) plane passing through aluminum atoms. Also shown are the corresponding charge-density surfaces. For $\theta=0.5$, there is a valley parallel to the [110] direction showing lack of interaction between aluminum atoms along the [$\bar{1}$10] direction. However, the aluminum atoms located along the [110] direction show highly directed interaction mediated through the substrate. It is important to recall that the interatomic distances in both directions are identical. Hence, at the low coverage we see the formation of directional bonds responsible for such anisotropic behavior. The maximum charge-density contour has a value of 0.048 a.u. and occurs at a distance of $a_{Al}/4$ away from aluminum atoms along the [110] direction. The complete metal overlayer ($\theta=1$) shows a more isotropic charge density as is evident from Figs. 2(c) and 2(d). Maxima in charge density are now located along [010] directions, at halfway between nearest-neighbor Al atoms. The aluminum layer shows a tendency towards metallization, and chemisorption bonds with the substrate have weakened.

In Fig. 3, the LDOS at the Al overlayer for the two coverages under consideration are shown. New major peaks appear, in addition to the usual structure of the bulk Ge, and are connected with the interactions at the interface. At $\theta=0.5$, the Ge–Al–Ge bridge bonds are produced by the bonding combination of Ge-dangling bonds and Al sp^2 orbitals. The chemisorption states appear near the Fermi level and also at about 3 eV below it. The states connected with one sp^2 orbital overlap with the chemisorption bond states near the Fermi level, and contribute to the pinning at this coverage. States having the Al-$3p_y$ character would couple the metal atoms along the [$\bar{1}$10] direction, but since these states are unoccupied, the Al overlayer displays a nearly one-dimensional (1D) character. For $\theta=1$, the LDOS may be viewed as a modulation on top of the ladder-type density

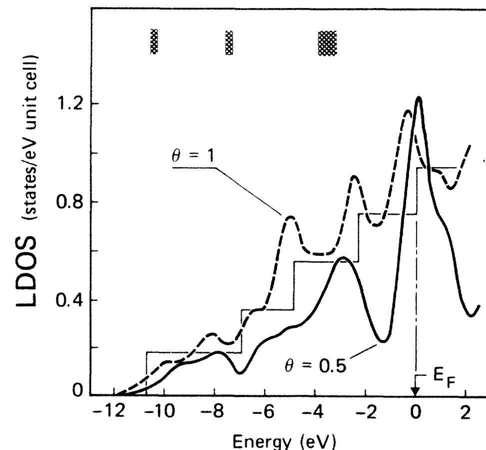

FIG. 3. LDOS at the Al layer for $\theta=0.5$ and 1, calculated by appropriately partitioning the slab. The ladder-type density of states is for the quasi-2D system with the same areal charge density as for $\theta=1$. The shaded zones indicate major structure of bulk Ge.

The maximum charge density for $\theta=0.5$ reaches a value of 0.079 a.u. in the middle of the Al–Ge bond direction; the corresponding value for $\theta=1$ is only 0.056 a.u. suggesting a weaker bond. It is thus clear that at the higher coverage, the chemisorption bond has weakened and more charge is oozing out into the vacuum [see Fig. 1(b)]. This indicates the onset, where the directional covalent bonds begin to be replaced by more delocalized metallic-type[21] interaction. The chemisorption bonds are still visible at this coverage, but the metallic bonding can be clearly seen from the charge distribution. We may mention that in going to $\theta=1$, we have placed the additional Al atoms in an epitaxial relationship. The epitaxial geometry is found to be adequate from our force calculations leading to small forces acting on metal and semiconductor atoms at the interface.

Our proposal to reconcile diverse viewpoints in SB formation is simply that the SB, at least in metal-covalent semiconductors, is fully developed only after a deposition of one to two monolayers[21] of metals and not at submonolayer coverages. With this ansatz, we can make the following observations. At submonolayers of unsupported metal films,[25] macroscopic metallic properties, e.g., work function, are drastically different from the bulk values. At one to two monolayers, on the other hand, we see[25] an evolution towards bulk properties. Inasmuch as it matters which metal is deposited[29] on a substrate for SB formation, one should at least have one to two monolayers of metal. Also, in those cases where nondirectional interactions are sought,[19] a metallized phase is a more likely candidate, rather than a chemisorbed layer.

In a recent study,[30] it was found that a seven-layer thick Al film exhibited a quasi-2D behavior. The states showed a free-electronlike solution in the (x,y) direction, but decayed into vacuum from both surfaces of the film. A similar behavior is expected from the states of a metal overlayer: The metal states may decay into the semiconductor, providing a preponderance of empty states across the gap. Consequently, without invoking either defect states or metal-induced states as described by Heine, a thin metal layer (one to two layers) is already capable of providing pinning states. We have thus also presented a theoretical confirmation of the novel finding[21] that in the Al-Si case the metallic character appears at coverages above one monolayer. The origin is traced to the interfacial distance relaxation upon metallization for the metal-covalent semiconductor system. The pinning states at one to two monolayers can also be thought of as a hybrid[16,29] of Bardeen[9] and Heine's[14] pictures, in which both the intrinsic surface states as well as the metal-induced states play a crucial role. Bardeen's picture by itself is inapplicable when intrinsic states are absent, e.g., in GaAs, and Heine's picture requires thick metal overlayers unnecessary for the SB formation.

We are grateful to Dr. A. Baratoff, Dr. E. Courtens, and Dr. K. H. Rieder for many constructive comments on the manuscript.

---

*Permanent address: IBM Almaden Research Center, San Jose, CA 95120-6099.

†Permanent address: Department of Physics, Middle East Technical University, Ankara, Turkey.

[1] *Thin Films and Interfaces,* edited by P. S. Ho and K. Tu (North-Holland, New York, 1982); *Thin Films and Interfaces,* edited by J. E. E. Baglin, D. Campbell, and W. K. Chu (North-Holland, New York, 1984).

[2] C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1984).

[3] R. Z. Bachrach, in *Metal-Semiconductor Schottky Barrier Junctions and their Applications,* edited by B. L. Sharma (Plenum, New York, 1984).

[4] G. W. Rubloff, in *Festkörperprobleme,* edited by J. Treusch, Advances in Physics, Vol. XXIII (Vieweg, Braunschweig, 1983), p. 179.

[5] A. Zunger, Thin Solid Films **104**, 301 (1983).

[6] R. H. Williams, Contemp. Phys. **23**, 329 (1982).

[7] L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982); M. Schlüter, Thin Solid Films **93**, 3 (1982).

[8] W. E. Spicer, I. Lindau, P. R. Skeath, and C. Y. Su, J. Vac. Sci. Technol. **17**, 1019 (1980); O. F. Sankey, R. E. Allen, S.-F. Ren, and J. D. Dow, *ibid.* B **3**, 1162 (1985).

[9] J. Bardeen, Phys. Rev. **71**, 717 (1947).

[10] A. Deneuville and B. K. Chakraverty, Phys. Rev. Lett. **28**, 1258 (1972); D. E. Eastman and J. L. Freeouf, *ibid.* **34**, 1624 (1975).

[11] E. J. Mele and J. D. Joannopoulos, Phys. Rev. B **17**, 1528 (1978).

[12] J. C. Phillips, J. Vac. Sci. Technol. **11**, 947 (1974).

[13] J. E. Rowe, S. B. Christman, and G. Margaritondo, Phys. Rev. Lett. **35**, 1471 (1975).

[14] V. Heine, Phys. Rev. **138**, A1689 (1965).

[15] G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B **14**, 5396 (1976).

[16] S. G. Louie and M. L. Cohen, Phys. Rev. Lett. **35**, 866 (1975); Phys. Rev. B **13**, 2461 (1976).

[17] J. R. Chelikowsky, Phys. Rev. B **16**, 3618 (1977); H. I. Zhang and M. Schlüter, *ibid.* **18**, 1923 (1978).

[18] J. E. Northrup, Phys. Rev. Lett. **53**, 683 (1984).

[19] A. Zunger, Phys. Rev. B **24**, 4372 (1981).

[20] I. P. Batra, Phys. Rev. B **29**, 7108 (1984).

[21] M. K. Kelly, E. Colavita, G. Margaritondo, J. Anderson, L. Papagno, D. J. Frankel, and G. J. Lapeyre, Phys. Rev. B **32**, 2693 (1985).

[22] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[23] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **45**, 1004 (1980); K. C. Pandey, *ibid.* **49**, 223 (1982).

[24] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 223 (1982); see also, D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[25] I. P. Batra and S. Ciraci, Phys. Rev. B **29**, 6419 (1984); J. Vac. Sci. Technol. B **3**, 427 (1984).

[26] J. R. Lince, J. G. Nelson, and R. S. Williams, J. Vac. Sci. Technol. B **1**, 553 (1983).

[27] F. K. Schulte, Surf. Sci. **55**, 427 (1976).

[28] P. Chaudhari, H.-U. Habermeier, and S. Maekawa, Phys. Rev. Lett. **55**, 430 (1985).

[29] J. Tersoff, Phys. Rev. B **32**, 6968 (1985); J. Vac. Sci. Technol. B **3**, 1157 (1985).

[30] S. Ciraci and I. P. Batra, this issue, Phys. Rev. B **33**, 4294 (1986).