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Metal-Induced Surface States during Schottky-Barrier Formation on Si, Ge, and GaAs

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We report evidence for extrinsic metal-induced surface states during the early stages of Schottky-barrier formation on Si(111), GaAs($\bar{1}\bar{1}\bar{1}$), Ge(111), and Ge(100). Results on Ge-(110) are related to those of Eastman and Freeouf for GaAs(110) and GaSb(110) and we propose a simple structural model to account for the anomalous results on (110) semiconductor surfaces.

Although the existence of surface states at the metal-semiconductor interface was proposed by Bardeen[1] in 1947 there has been little direct information about their spectroscopy and chemical origin until recently.[2,3] Eastman and Freeouf[3] have observed intrinsic-surface-state spectra on III-V semiconductors such as GaAs that *persist in the presence of a metal overlayer*. These authors were able to correlate the Schottky-barrier energies[4-6] with intrinsic-surface-state positions and suggested that the barrier height of III-V semiconductors is determined by *intrinsic surface states*. Our results in this paper show that this is *not true* for the (111) surfaces of Si, Ge, and GaAs. Intrinsic surface states on these surfaces are *removed* by the metallic overlayer and new states appear near the Fermi energy which are localized about the metal adatoms. These

extrinsic surface atoms pin the Fermi energy on (111) and (100) surfaces and determine the Schottky-barrier height. From ultraviolet-photoemission-spectroscopy measurements of bulk band-structure transitions of Si, Ge, and GaAs we deduce band-bending changes with final barriers, $\varphi_B = E_c - E_F$, of 0.75, 0.60, and 0.85 eV, respectively, in good agreement with Schottky-barrier heights measured by conventional capacitance-voltage measurements.[4-6,7] Similar metal-induced surface states occur within the band-gap energy range on Ge(100) surfaces but are much weaker on Ge(110) surfaces. The Ge(110) surface states occur at higher energies than on Ge(100) and Ge(111) and are not *completely* removed by metallic overlayers. A simple structural model is proposed for (110) surfaces in which only one-half of the "normal" surface at-

oms are bonded to metal adatoms. This model explains the present observed differences between (111), (100), and (110) surfaces as well as the Eastman-Freeouf result[3] of the insensitivity of surface states to overlayers on III-V (110) cleavage planes.

The primary experimental technique used in the present study is electron energy-loss spectroscopy (ELS) of transitions from core states to unoccupied surface and bulk states above the Fermi level.[8-11] This technique has previously been used to study intrinsic surface states on Ge,[8,9] GaAs,[9,10] and Si.[11] Although the energy resolution 0.5–0.8 eV for ELS[8-11] is not as high as that of photoemission partial-yield spectra,[3,12] essentially the same transitions are measured in both cases because of the localized core levels which have no energy–wave-vector dispersion.[8,9] In addition we performed photoemission-energy-distribution measurements[13] with an ultraviolet resonance lamp and with an Al $K\alpha$ x-ray source in order to observe occupied extrinsic valence-band surface states and to determine the core-level energies with respect to the semiconductor valence-band edge. The core levels were observed by x-ray photoemission spectroscopy and ELS for both the substrate and the metallic atoms. This determines (within a one-electron approximation) the unoccupied local density of states near both semiconductor and metallic atoms for the first time. Previous results determined only the density of states near the semiconductor atoms.[3,12] The experiments were performed in a multiple-technique ultrahigh-vacuum chamber which has been previously described.[14]

Typical ELS data for Si(111) and GaAs($\overline{1}\overline{1}\overline{1}$) surfaces are shown in Fig. 1. Curves a and b show ELS $3d$-core excitation for a ~1200-Å-thick Ga metal film and for ~1–2 Ga layers (2 Å average thickness) on Si(111).[15] Excitation from the Si $2p$ core state is shown in curves c and d for clean Si(111) and for the $\frac{1}{2}$-Å Ga overlayer. The partial Ga overlayer *removes* the intrinsic surface states shown by a shaded area and replaces them with extrinsic states localized near the Ga adatoms. The narrow line shape shown in curve b is nearly the same as the molecular excitonic line shape observed for clean GaAs(110) surfaces[9,10,12] and is quite different from the line shape for Ga metal (see Fig. 1, curve a). Similar ELS results for GaAs($\overline{1}\overline{1}\overline{1}$) with and without a ~2-Å In overlayer[15] are shown in curves e–g of Fig. 1. Because of the excitonic line shape observed for metal atoms near the metal-semiconductor inter-
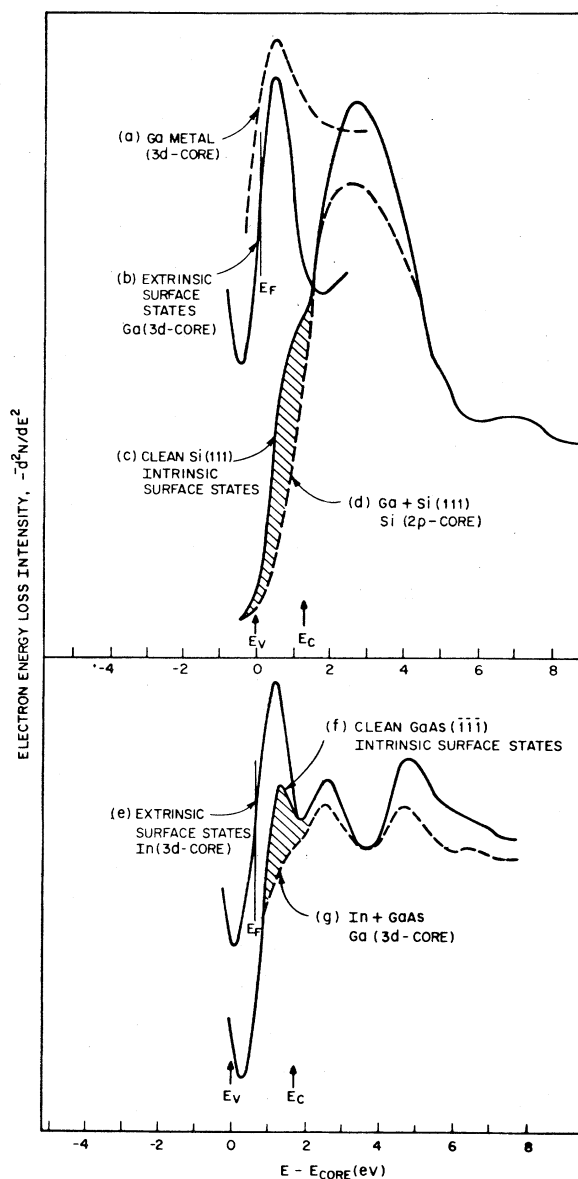

FIG. 1. Electron energy-loss spectra of core-level to unoccupied surface and conduction-band states. Note the *decrease* in intrinsic surface states (shown as shaded area) due to metal adsorption.

face we believe that the metal-atom electrons in this ~3–5-Å range are more nearly arranged in covalent semiconductorlike states rather than in a metallic electron gas. This concept is supported by changes in ultraviolet photoemission spectroscopy and in plasmon line shapes with metal layer thickness which will be reported later. These results for In overlayers on GaAs directly contradict those of Eastman and Freeouf for Pd and In overlayers on GaAs, GaSb, and GaP (110)

surfaces. This strongly suggests that their in-
terpretation of Schottky barriers involving only
intrinsic surface states of the clean semiconduc-
tor is correct only for (110) surfaces of III-V
compounds.

The energy scale of Fig. 1 was determined by
in situ x-ray photoemission spectroscopy with an
unmonochromatic Al $K\alpha$ photon source and cylin-
drical-mirror analyzer. The combined resolu-
tion (photon width plus electron width) is estimat-
ed to be ~1.3 eV. The Si(2p), Ga(3d), and In(4d)
core-level energies correspond to the weighted
average of the spin-orbit–split components. This
is appropriate since the present ELS resolution
of ~0.7–0.8 eV does not resolve the separate
spin-orbit components. The primary energy, E_p,
for ELS data of Fig. 1 was 100 eV except for the
Si(2p) transitions where it was increased to 190
eV. Similar results have been obtained for E_p in
the range 80–250 eV. The escape depth of the in-
elastically scattered electrons is ≲6 Å for the
data in Fig. 1, so that the ELS technique is quite
surface sensitive although the energy resolution
is somewhat lower than the partial-yield tech-
nique used by Eastman and Freeouf.[3,12]

Figure 2 shows ELS data for Ge (111), (110),
and (100) surfaces both clean and with Ga or In
metal overlayers. The ELS data for a thick
(≳300 Å) Ga metal film show a broad, steplike
threshold near the Fermi level while the thin
(~1–3 Å) interface transitions are sharper cor-
responding to a more localized molecular bond-
ing at the metal-semiconductor interface than
the metallic, electron-gas bonding in the pure
metal. The intrinsic surface states localized
near Ge atoms for (111) and (100) surfaces have
a broad distribution extending down to the va-
lence-band edge, E_v (for Ge $E_F \approx E_v$).[12] These
states are removed by a thin metal overlayer and
there is some attenuation of the bulk conduction-
band feature near 2.3 eV as shown by the dashed
curves. In contrast to this behavior Ge(110) has
somewhat ambiguous results as shown in Fig. 2,
curve e. The atomically clean surface shows no
clear surface-state peaks in the forbidden gap
but does show a broad shoulder extending from
midgap to the peak at 2.3 eV. This is similar to
an average of the Ga and Sb core-level results
reported in Ref. 3 and indicates that intrinsic
surface states occur at higher energies on this
surface. [The possibility of some residual sur-
face impurities on the clean surface is highly un-
likely. This sample was mounted on the same
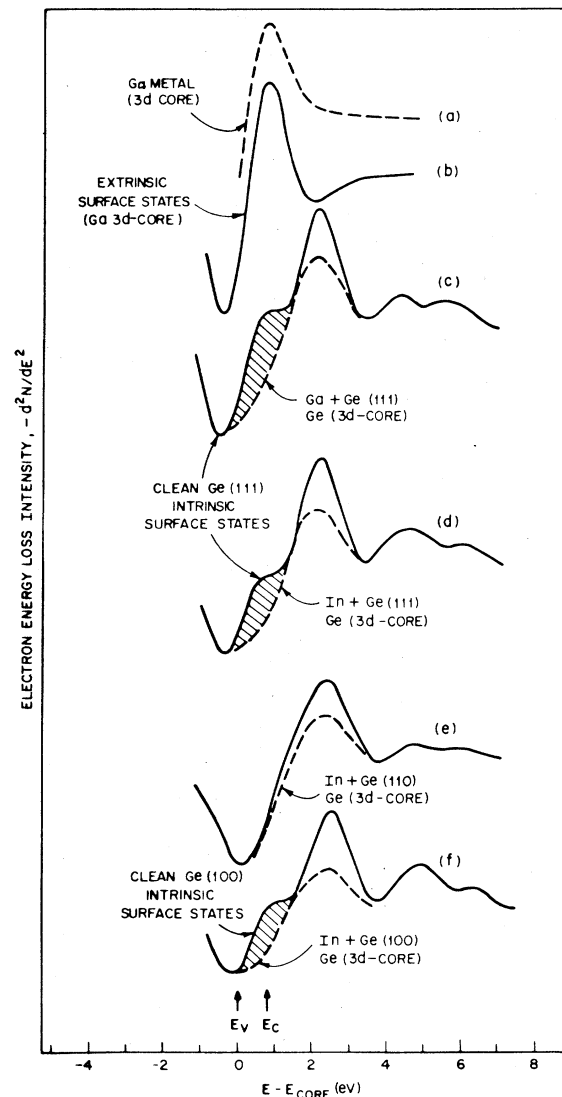crystal holder as the Ge(111) and Ge(100) sam-

FIG. 2. Electron energy-loss spectra of core-level to
unoccupied surface and conduction-band states for Ge
(111), (110), and (100) surfaces. Note the decrease of
intrinsic surface states (shown by a shaded area) due to
metal adsorption. The Ga-induced extrinsic surface
states show a sharper line shape than similar transi-
tions on Ga metal samples. Note the broad distribution
of intrinsic surface states on Ge(110) which overlap the
bulk conduction-band states.

ples and the same Ar^+-ion cleaning procedure
and annealing was applied to all three Ge sam-
ples simultaneously.[8,9,14] Thus the most likely
interpretation of Fig. 2, curve e, is that intrinsic
surface states overlap the first bulk conduction-
band peak. We interpret Figs. 1 and 2 as evi-
dence for some additional surface states in this
region for Si(111), GaAs($\overline{1}\overline{1}\overline{1}$), and for all *three*
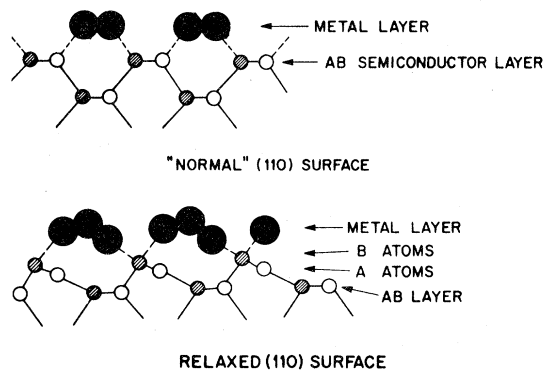
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FIG. 3. Geometry of metal-semiconductor interface for (110) surfaces. In the "normal" positions both atoms A and B can bond to metal atoms while for the relaxed structure only the atoms B are directly bonded to metal atoms and the atoms A retain their intrinsic surface states.

clean Ge surfaces since the metal overlayer produces somewhat more attenuation of this "bulk" peak than of the higher bulk peaks near 4.5 and 6 eV.

One can explain this different behavior of the (110) surfaces with a simple structural model shown in Fig. 3. If the two semiconductor atoms in the bulk unit cell (labeled A and B) assume bulklike positions then the dangling-bond surface states occur *below* the bulk conduction-band states[16] and metal layer atoms could easily bond to all surface sites A and B. This would give results for (110) surfaces similar to those of (111) and (100) surfaces. However, the present results along with those of Eastman and Freeouf[3] suggest that the (110) surface is anomalous for a large number of metal-semiconductor combinations. This behavior is likely to be due to surface relaxation of the sites A relative to the sites B as shown in the lower half of Fig. 3. The relaxed atoms (sites A) have a bonding which is sp^2-like rather than sp^3-like with a nearly empty p_z orbital (dangling bond) that is pushed to higher energies by the relaxation. In contrast the sites B have nearly filled sp^3-like dangling bonds (or lone-pair orbitals) which chemically bond to the metal overlayer. This bond will be only partially covalent since the geometry does not allow saturated bonds for all available electrons. The local atomic geometry at the first few metal-atom layers may be similar to that of the NiAs structure but this is not certain at present. However, the model for the relaxed surface does explain the lack of sensitivity of empty surface states to

metal overlayers for both Ge(110) and III-V-compound (110) surfaces and is probably a good zero-order approximation. There is additional support for this model in that the saturation concentration of oxygen on GaAs(110) is one-half monolayer[17] and that low-energy-electron diffraction intensities have a strong asymmetry which is quite different from that expected for the "normal" structure.[18]

In summary we have studied empty surface states and their relation to Schottky-barrier formation on (111)-type surfaces of Si, Ge, and GaAs as well as on Ge(100) and Ge(110). Extrinsic states localized near the metal adatoms *dominate* on (111)-type and (100) surfaces with the *intrinsic surface states removed by chemical bonding.*[19] However, on Ge(110) surfaces the intrinsic surface states seem to be insensitive to metal overlayers and intrinsic surface states play an important role similar to the one in III-V compounds. A simple geometric model is proposed for (110) surfaces in which only one-half of the normal surface atoms are involved in chemical bonding. The remaining sites retain most of the localized intrinsic surface states.

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though the qualitative concept of metal-induced surface
states agrees with experiment, the predicted barrier
height of the latter calculations is in error by a large
amount, 0.6–0.7 eV. This is probably due to their as-
sumed geometric model of substitutional replacement of
Si atoms by Al atoms.

Constancy of Minimum Metallic Conductivity in Two Dimensions*

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A scaling argument is used to demonstrate the existence of a minimum metallic conduc-
tivity with a universal value for two-dimensional random lattices. We present a summa-
ry of the results of a detailed numerical experiment which supports this suggestion and
indicates that the minimum metallic conductivity is $(0.12 \pm 0.03)e^2/\hbar$, in fair agreement
with some experimental results for inversion layers.

A description of the electronic properties of
disordered systems requires a firm basis for
characterizing the pure homogeneous disordered
state. This characterization has been hampered
on the one hand by calculations which are not eas-
ily related to experimentally measurable quanti-
ties, and on the other hand by experiments in
which sample preparation too often plays a deter-
mining role. This has meant that it is not easy
to distinguish one theoretical system from anoth-
er by the accuracy of its predictions, nor to tell
which approximations provide helpful simplifica-
tion and which produce misleading results.

Mott[1] argued some time ago for the existence
of a minimum metallic conductivity in disordered
systems, but his analysis has been subject to con-
troversy.[2] In this note we suggest that for two-
dimensional systems definite predictions can be
made about this quantity, which has been mea-
sured, for example, in silicon inversion layers.
In particular we present arguments not only for
its existence, but to show that, for noninteract-
ing electrons in a static two-dimensional random
potential, the minimum metallic conductivity
should have a universal numerical value, and we
find that value to be about $0.12e^2/\hbar$. This should
serve as a standard of comparison for theories
which take into account further aspects of physics
such as many-body effects.

Our analysis consists of two parts. We first
construct a scaling argument, a rather crude ver-
sion of those used in the theory of critical phe-
nomena[3]; the steps in this argument were almost
all in the paper of Edwards and Thouless,[4] but
their significance was not understood. This scal-
ing argument shows that the minimum metallic
conductivity has a universal value independent of
the details of the two-dimensional disordered
system. This being accepted, it is possible to
calculate its value using any convenient system,
and the tight-binding model with random site en-
ergies seems the most suitable for calculations.
We have numerically sampled small replicas of
tight-binding systems, varying the size of the
system to detect the positions of the mobility
edges, and varying the lattice structure and de-
gree of disorder to check the universality hypoth-
esis. In this note we give only a brief summary
of the results of these extensive calculations,
which are reported in full elsewhere.[5] Before
presenting our arguments we observe that the
Ioffe-Regel condition,[6] the importance of which
Mott[7] has repeatedly emphasized, leads to a two-
dimensional minimum conductivity in fair agree-
ment with what we obtain. According to simple
kinetic theory the conductivity of a two-dimen-
sional electron gas is given by

$$\sigma = 2ne^2\tau/m = (e^2/\hbar)k_F\lambda/2\pi,$$

where $\pi k_F^2/(2\pi)^2$ is the number of electrons n with