$1/v^5$, where v is the velocity of sound, and the velocity of transverse phonon is only half of that of longitudinal phonon, it is therefore not surprising that the transverse mode will dominate if the matrix elements involved are at least comparable. All these factors considered, the experimental facts seem to be quite reasonable.

In summary, I report the observation of stimulated 29-cm^{-1} phonon in ruby. The single-frequency phonons are of transverse mode and propagate along the C_3 axis. Because the background phonons are negligible, the use of a conventional superconducting bolometer with great sensitivity is allowed. This phonon source is in principle tunable by an external magnetic field, and the linewidth is expected to be of the order of 0.02 cm^{-1}.[4] This intense, directional, tunable high-frequency phonon source may complement the superconducting tunnel junction as an alternative phonon source.[9]

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Unified Mechanism for Schottky-Barrier Formation and III-V Oxide Interface States

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Extensive experimental evidence indicates that the Schottky-barrier formation on III-V semiconductors is due to defects formed near the interface by deposition of the metal (or of oxygen). Detailed level positions are established and assigned to either missing column III or V atoms. This model also applies to formation of states at III-V oxide interface states.

One of the oldest unsolved problems in solid state physics is that of the mechanism of Schottky-barrier (SB) formation (see, for example, Refs. 1–6). An apparently unrelated problem is that of the states formed at the interface between a semiconductor and its oxides. Here, we analyze data of a relatively new type[7-10] from a large number of metals as well as oxygen-placed GaAs, InP, and GaSb and establish a new mechanism of SB formation. This is based on the formation of defect levels due to the deposition of the foreign atoms. The same mechanism applies to the states at the III-V semiconductor-metal interface.

A long-standing theory of SB assumes that there are surface states intrinsic to the ideal clean semiconductor.[11] These surface states are assumed to remain after application of the metal and to pin the Fermi level—thus, determining the barrier height and device characteristics. For the III-V compounds, this mechanism must be rejected since it has been definitively established[11] that there are no intrinsic surface states in the

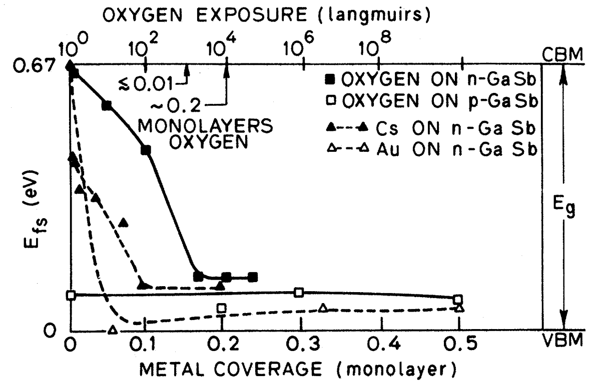

FIG. 1. The position of the surface Fermi level, E_{Fs}, for Au, Cs, and O on GaSb. Note that the final pinning position is little dependent on the adatom and that it is reached with much less than a monolayer coverage.

gap on the cleavage (110) faces on which the classical[1] Schottky-barrier height (SBH) experiment was performed and on which all the work reported here was also performed.

A second widely used approach introduced by Heine[12] is based on the SBH being due to states induced by the thick layer of metal placed on the semiconductor to form the SB. Recently, detailed calculations have appeared for the SBH due to this mechanism.[4, 5] The new experimental data,[7-11] shown in Figs. 1 and 2 and discussed below, raise grave questions about the applicability of this approach as well.

One aspect of the photoemission technique, used by ourselves in the SB studies, should be emphasized because it is critical in obtaining unambiguous data. This is the ability to measure *directly* the surface Fermi-level position, E_{Fs}, as metal or other atoms are placed on the clean semiconductor surface. We emphasize this point because other recent work appears to have fallen into difficulties[6] because of the use of techniques which do not directly measure E_{Fs}.

In Fig. 1, the movement of the surface Fermi-level position (E_{Fs}) is shown as either of two quite different metals (Cs or Au) or a nonmetal (oxygen)[13] is placed on the surface GaSb. There are two key results from Fig. 1: (1) The final pinning position is obtained with a low coverage (at most, 15% monolayer) of the foreign atoms, and (2) the SBH is essentially independent of an adatom despite the extreme difference in atomic orbitals of the adatoms. Similar behavior was observed on GaAs and InP.[7]

In Fig. 2, we show the final pinning positions obtained for a number of adatoms on the GaAs, GaSb, and InP. The coverages necessary to reach the "steady-state" SBH were approximately the same as those shown for GaSb in Fig. 1, i.e., 15% or less for the metals and a few percent for oxygen. Note again that the pinning position is essentially the same, independent of the adatom.[7-10] In all cases, it is clear that the submonolayer films do not contain three-dimensional islands[7, 14] and the data of Figs. 1 and 2 are impossible to reconcile to any theory based on a thick metal layer.[4, 5, 12]

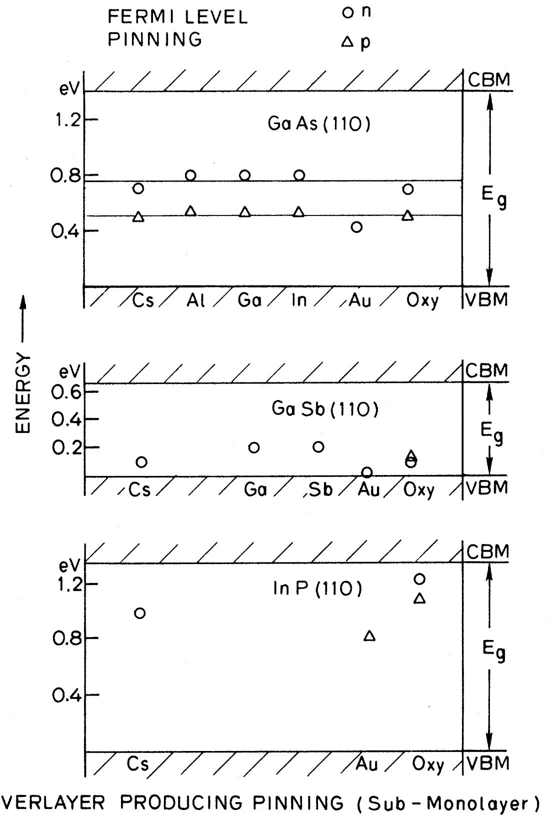

FIG. 2. The final E_{Fs} position for a number of metals and oxygen on GaSb, GaAs, and InP. Note that there is little dependence on the chemical nature of the adatom.

The atomic levels of Cs, Au, and O,[15, 16] for example, are so different that it is exceedingly difficult to see how they could induce states at approximately the same energy. These data forced us to conclude that the SBH was determined not by levels directly induced by the orbitals of the adatoms but by *levels induced indirectly* by the adatoms, e.g., defect levels. (It has been suggested that addition of oxygen to GaAs[15] will move the intrinsic empty surface states into the band gap; however, this would not lead to the pinning of *p*-type GaAs, as is found experimentally.

Direct evidence that defect levels may be formed near the metal-semiconductor interfaces was first provided by the results for Au overlayers on GaSb (110).[7] In this case, the Sb was removed from the GaSb and segregated to the Au surface. With all metals studied (In, Al, Ga, Sb, and Au), photoemission evidence was found for inclusion of the semiconductor material in the metal.[10] Sputter-Auger measurements made after the deposition of about 100 Å further confirmed this observation.

We suggest that the energy for this intermixing is at least partially provided by the heat of condensation of the metal atoms on the semiconductor surface. Only in the case of Cs on GaAs have direct measurements[14] of this been made. These show a heat of condensation of about 3-eV/Cs atom on clean GaAs as opposed to 1-eV/Cs atom on Cs metal. As mentioned earlier, Au in less than monolayer quantities does not form three-dimensional islands on the semiconductors studied here—thus, suggesting that the heat of condensation of Au on GaAs is comparable to or larger than that of Au on Au metal (4.5 eV/atom). Thus, there is convincing evidence that the heat of condensation will start a process which can produce defect levels near the semiconductor metal surface. This gives support to the conclusion drawn earlier that the adatoms produce pinning through a secondary mechanism, i.e., the formation of defect levels.

In Table I, we present details of the energy levels which we believe to be formed by the adatoms with the semiconductor at 293 °K. Associated with each level is a suggestion of the missing semiconductor atom with which it is associated. The defect is not necessarily a simple vacancy. More likely, it is a more complicated complex, e.g., for a missing Sb, a Ga atom may move into the Sb site, leaving a nearest-neighbor Ga vacancy.[17] However, because of their localized nature, centers due to both kinds of defects can exist in the same surface region. These complexes may change and grow due to formation of more complex vacancy configurations and/or interaction with the adatom if the sample is heated or otherwise sufficiently perturbed. However, there is little evidence that such treatment moves the levels by more than a few tenths of an electron volt.

TABLE I. Energy levels (measured from the valence-band maximum) due to defects produced by missing cations or anions. (*D*) and (*A*) indicate donors and acceptors, respectively.

	GaSb	GaAs	InP
Missing cation	⋯	0.55 (*D*)	1.2 (*D*)
Missing anion	0.1 (*A*)	0.75 (*A*)	1.9 (*A*)

The energy level assignments were made on the basis of the surface pinning levels of Fig. 2. The accuracy is ± 0.1 eV or better. The association with missing column III or V atoms was made principally for the following reasons. The 0.1 eV was assigned to missing Sb because of the long-standing association of such a level with an Sb deficit[17] and because of the preferential removal of Sb into the Au, the 0.9-eV level in InP with missing P because of the preferential movement of P into Au[7] and the reversal of E_{Fs} with oxygen exposure,[16] and the 1.2-eV level to missing In by process of elimination (confirmation of these InP assignments will be given presently in examining the work of others). For GaAs, the 0.75-eV level is assigned to missing As since this pinning position is associated with the defect state which often appears spontaneously with cleavage on many *n*-type samples[18, 19] (but never *p*-type samples), and As is considered to be most likely to leave the surface on cleavage.

The work of Farrow *et al.*[20] gives some verification for the InP assignments. They found that Au or Ag contacts with *I-V* characteristics consistent with a pinning at about 1.2 eV could be obtained on a P stabilized surface, i.e., a surface containing excess P; whereas, as Fig. 2 shows, pinning near 0.9 eV is normally obtained by Au and other metals on InP. Thus, In defects will dominate only if the formation of P defects is suppressed by P stabilization, consistent with our mechanism. Wieder[21] has recently reported metal-oxide-semiconductor (MOS) structures showing a strong maximum in interface state densities at 1.2 eV (the energy of interface states measured at oxide semiconductor interfaces of MOS structure agree[22] surprisingly well with those given in Fig. 2). Wilmsen and Wagner[23] have made sputter-Auger measurements on such structures and find In but not P in the thin "native" oxide region, indicating that the 1.2-eV level indeed is due to a In deficit. In contrast, Fritsche[24] has processed his InP MOS structures in quite a different way and obtains a sharp peak in interface state density at 0.9 eV. We attribute this to a preferential depletion of P from the InP with their processing.

The work above points out another key factor: The Fermi level can be moved between the levels shown in Table I according to the details of the interaction between the adatom and substrate and/or pretreatment of the semiconductor surface. This probably is the reason for changes in pinning position caused by different metals as observed by, for example, Williams *et al.*[25] and for the difference in interfaces seen in x-ray photoemission spectroscopy by Waldrop and Grant.[26] However, it should be noted that, within the model indicated by Table I, this variation is restricted by the energy positions of the defect levels.

Based on the mechanism of Schottky-barrier pinning suggested here, one can begin to visualize ways in which more control can be obtained of the SBH. For example, if one could vary the doping in the last few InP layers (for example, by evaporating about 10^{13} Be atoms/cm^2 on n-type InP and then diffusing them just below the surface) and, at the same time, minimize the defect formation on subsequent deposition of metal to form a practical Schottky barrier, the SBH maximum on n-type InP might be changed from its present value of about 0.5 to about 1.2 eV. The removal of P would be minimized by saturating a (111) or (100) surface with P.[20] In would then be evaporated to form the SB. By gentle annealing, after evaporation, the In deficit density might be reduced.

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