TITLE: Studies of Surfaces and Interfaces on III-V Compounds Using UV and Soft X-ray Excitation

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OBJECTIVE: The objective of this work is to extend our knowledge of the bulk and surface electronic structure of III-V semiconductors, and their interfaces with metals, insulators, and other semiconductors, and to develop their application to a variety of electronic and opto-electronic device structures.

APPROACH: Our approach is to start with atomically clean semiconductor surfaces, often prepared by cleaving single crystals in situ under ultra-high vacuum (pressure = $10^{-10}$ torr) conditions. Surfaces may also be prepared by ion sputtering, heat cleaning, laser treatment, etc. These surfaces are then fully characterized by a variety of techniques, including: angle-resolved and angle-integrated ultraviolet (UPS) and X-ray (XPS) photoelectron spectroscopies (often using synchrotron radiation as the light source), Auger electron spectroscopy, low energy electron diffraction, contact potential difference measurements (using the Kelvin probe method), and photoluminescence. The chemical, electronic, and structural interactions of the semiconductor surface with adsorbates may then be studied by exposing the clean surface to gases or to atomic or molecular fluxes of some other substance. These exposures may be carried out on heated or cooled substrates, under laser irradiation, or influenced by a variety of other controlled perturbations.

PROGRESS: Although our work procedes on several fronts, in this summary we highlight three broad areas. Elaboration on these areas and delineation of our other efforts may be found in the publications listed below, and in our recent renewal proposal to the ONR.

Mechanism of Oxygen Chemisorption on GaAs

For both fundamental and practical reasons, we consider it very important to obtain a definitive understanding of the chemisorbed phase of oxygen on GaAs. This is the phase obtained with unexcited oxygen characterized by a completely resolved 2.9 eV As-3d shift and an asymmetric broadening of the Ga-3d peak with a shift of at most 0.7 eV. These shifts correspond to those obtained by Goddard's group (1) for oxygen attached to a surface As without breaking any back bonds. This was also our original suggestion for the chemisorbed oxygen. Problems with this model involved the dynamics of the break-up of the $O_2$ molecule.

Goddard et al (2) and Mark et al (3) suggested that this was done at defect sites with the oxygen uptake spreading outward from these sites. Our recent work shows that this is not the case. In addition, we have given definitive evidence that the model of Brundle et al (4), which assumes that there is no chemisorbed state -- only clusters of $As_2O_3$ and $Ga_2O_3$ -- is not correct. Finally, we have new evidence for a second major adsorption site where, in addition to an oxygen bonded to an As, there is an oxygen bridging between that As and a next nearest Ga (5).

Essential to arriving at these conclusions have been extensive experiments. These experiments have included the development of new valence band spectroscopy in which very low concentrations of adsorbed oxygen can be detected (0.001 monolayer) (5), thermal desorption, studies of the valence bands of $Ga_2O_3$ and $As_2O_3$, and adsorption of oxygen on disordered sputtered Ga-rich GaAs (110) surfaces. This work is part of the Ph.D. thesis of C.Y. Su, and will be published soon.

Mechanism of Adsorption of Column III and V Elements on GaAs

We have found that the column III elements do not bond "atomically", as predicted by all theorists who had considered this problem (6-9). This now appears to be accepted. This leaves open the very important question of how the metal is bonded to the surface. Recent theoretical estimates of the binding energy of column III elements to the surface by A. Zunger and W. Goddard et al for somewhat different models give a relatively small value of about 0.5 eV. From our work and the available calculations of column III molecules or two-dimensional islands on the surface, it is clear that metal-metal interactions are comparable to the importance of the metal-GaAs interaction.

It is clear that Sb (column V) forms an ordered overlayer. Skeath and Goddard have proposed detailed models (10). We intend to use angle-resolved photoemission to distinguish between these.

LEED work on column III and V overlayers has been carried out by our group in collaboration with A. Kahn of Princeton University. It has been definitively established that Brillson's report of ordered Al on GaAs at room temperature was incorrect (11). Additional studies have been made of the Sb on GaAs system, and this project has been turned over to Kahn. Duke et al are analyzing Kahn's data. At the present, Duke favors a model in which unconnected $Sb_2$ molecules are adsorbed on Ga sites. This model has been considered and discarded by Skeath and Harrison on the basis of bonding considerations. Again, angle-resolved photoemission will be used to help distinguish between this model and others.

Comparison of Our Work with that of Others

In general, very satisfactory agreement is obtained between our work and that of others. Previous disagreement between our work and that of Brillson et al (12) had caused some condusion; this has recently been resolved (13). Most significant is the agreement obtained by Monch and Gant (14), who measured the contact potential difference changes of a GaAs surface as a function of temperature, thereby locating the defect levels in energy and determining their density.

In their work, Brillson and co-workers used contact potential difference (Kelvin probe) and surface photovoltage (SPV) measurements to study metal-semiconductor interfaces. They conclude that Fermi level stabilization occurs over several monolayers of metal deposition, in conflict with our photoemission measurements which indicate complete stabilization for 0.1 monolayer. In their analysis, an interface "atomic dipole" layer was introduced to obtain agreement between their measurements, and larger, accepted Schottky barrier heights. This dipole, however, would be transparent to electron tunneling. Proper interpretation of their data, using the techniques of Monch et al (15), shows that Fermi level stabilization is indeed complete by 0.1 monolayer.

In their SPV measurements, they assumed that high intensity light was sufficient to flatten the semiconductor bands. If this was correct, their SPV would measure the band bending. However, analysis using the diode equation shows that 0.43 eV of band bending remained in their case (16). Thus, their measurements are not in disagreement with the accepted barrier heights, and an atomic dipole need not be introduced.

REFERENCE PUBLICATIONS


(1) J.J. Barton, W.A. Goddard III, and T.C. McGill, J. Vac. Sci. and Tech. 16, 1178 (1979).
(2) W.A. Goddard, private communication.
(3) P. Mark and W.F. Creighton, Thin Solid Films 56, 19 (1979); P. Mark, S.C. Chang, W.F. Creighton, and B.W. Lee, Crit. Rev. Solid State Sci. 5, 189 (1975).
(4) C.R. Brundle and D. Seybold, J. Vac. Sci. and Tech. 16, 1186 (1979).
(5) C.Y. Su, I. Lindau, P.R. Skeath, P.W. Chye, and W.E. Spicer, J. Vac. Sci. and Tech. 17, 963 (1980).
(6) C.A. Swarts, J.J. Barton, W.A. Goddard III, T.C. McGill, J. Vac. Sci. and Tech. 17, 869 (1980).
(7) E. J. Mele and J.D. Joannapoulas, Phys. Rev. Lett. 42, 1094 (1979).
(8) D. J. Chadi and R.X. Bachrach, J. Vac. Sci. and Tech. 16, 1159 (1979).
(9) J.R. Chelikowsky, S.G. Louis, and M.L. Cohen, Solid State Comm. 20, 641 (1976).
(10) Perry Skeath, I. Lindau, C.Y. Su, and W.E. Spicer, Proc. PCSI-8, J. Vac. Sci. and Tech., Sep. - Oct. (1981).
(11) See, for example, L.J. Brillson et al in Proc. 15th Int. Conf. Physics of Semicond. 1980 publ. in J. Phys. Soc. Japan 44, 1089 (1980), and ref. therein.
(12) L.J. Brillson and D.W. Kruger, Surf. Sci. 102, 518 (1981); and references therein.
(13) W.E. Spicer, S. Eglash, I. Lindau, C.Y. Su, and P. Skeath, presented at the 5th International Thin Films Conf., Israel (1981).
(14) W. Monch and H. Gant, to be published.
(15) H. Gant and W. Monch, J. Vac. Sci. and Tech. 18, Sep. Oct. (1981) and ref. therein; W. Monch and H. Gant, ibid. 17, 1094 (1980).
(16) T.C. McGill, J.O. McCaldin, and D.J. Smith, private communication.


PUBLICATIONS (RECENT)


1.) Column III and V Elements on GaAs (110); Bonding and Adatom-Adatom Interactions, P. Skeath, C.Y. Su, I. Lindau, and W.E. Spicer, J. Vac. Sci. and Tech. 17, 874 (1980).
2.) Oxygen Adsorption on the GaAs (110) Surface, C.Y. Su, I. Lindau, P.W. Chye, P.R. Skeath, and W.E. Spicer, J. Vac. Sci. and Tech. 17, 936 (1980).
3.) Unified Defect Model and Beyond, W.E. Spicer, I. Lindau, P. Skeath, and C.Y. Su, J. Vac. Sci. and Tech. 17, 1019 (1980).
4.) Fermi Level Pinning at 3-5 Semiconductor Interfaces, W.E. Spicer, P. Skeath, C.Y. Su, and I. Lindau, Proceedings of the XV International Conf. on the Physics of Semiconductors, Kyoto (Sep. 1980), J. Phys. Soc. Japan 49, (1980) Suppl. A, 1079 (invited paper).
5.) Use of Photoemission with Synchrotron Radiation ot Probe Surfaces on an Atomic Scale, W.E. Spicer, Prodeedings of the Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems Conference, Berkeley, Ca.
6.) Models of Column 3 and 5 Elements on GaAs (110); Application to MBE, P. Skeath, I. Lindau, C.Y. Su, and W.E. Spicer, JVST, accepted for publication as part of the PCSI-8 Proceedings, 1981.
7.) Bonding of Column III and V Atoms on GaAs (110), P. Skeath, C.Y. Su, I. Lindau, and W.E. Spicer, submitted to Solid State Comm. in March, 1981.
8.) Experimental Determination of the Bonding of Column 3 and 5 Elements on GaAs, P. Skeath, C.Y. Su, I. Lindau, and W.E. Spicer. The proceedings will be published as a special issue of the Journal of Crystal Growth, Fifth International Conference on Vapor Growth and Epitaxy, Fifth American Conference on Crystal Growth, pending approval by a committee at the conference.