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**DYNAMIC PROCESSES AT SEMICONDUCTOR INTERFACES:
ATOMIC INTERMIXING, DIFFUSION BARRIERS, AND STABILITY**

FINAL REPORT

J.H. Weaver

15 August 1991

U.S. ARMY RESEARCH OFFICE

DAAL03-88-K-0093

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SUMMARY OF RESEARCH ACCOMPLISHMENTS

This report is the final report for ARO 25163-MS (DAAL03-88-K-0093).

Our research accomplishments are described below. Some of the work was highlighted in a feature article that appeared in Science (March 1991). A review chapter entitled "The Formation and Properties of Metal-Semiconductor Interfaces" was published by Springer-Verlag and another was submitted entitled "Atomic-Scale Chemistry of Metal-Semiconductor Interfaces." A total of twenty-six refereed papers or chapters were submitted or published, as listed elsewhere. Four graduate students completed Ph.D. studies and one completed his M.S. studies. Two outstanding undergraduates worked with us and have now matriculated at Penn and Stanford.

In our studies of interfacial phenomena, we continually sought to develop new ways to form interfaces. This allowed us to examine the role of kinetics and reaction pathways for surface processes, to gain fundamental new insight into interfacial phenomena, and to synthesize new, possibly useful interface structures. In one such effort, we developed a miniature ion source that allowed us to produce a flux of atoms that could be partially ionized. The ionized particles are then accelerated before impact on the clean semiconductor surface. The purpose of the experiments was to change the energy of the arriving flux, giving the ions sufficient energy to induce defect formation and to overcome any activation barriers for reaction. In another, we demonstrated that interfaces could be formed by cluster assembly (the deposition of clusters onto a surface). In a third, we developed a way of forming monolayer-to-multilayer films of oxygen-bearing species on surfaces so that oxidation processes and mechanisms could be explored in ways not previously possible. Each of these innovations has given new insight into thin film growth structures and stabilities.

During the first six-month period, our studies focused on the formation of interlayers of TiO_2 and CaF_2 on $\text{Si}(111)$ with subsequent growth of metal overlayers and the characterization of the electronic states of the interface. The goal was to examine interlayer integrity and stability against atomic intermixing. In studies with TiO_2 , we developed a procedure for interface formation that made it possible to investigate a large group of oxide interlayers, their stability, and their properties. Ti adatoms were deposited onto cleaved $\text{Si}(111)$ under conditions which led to oxide formation rather than the standard Ti-Si interaction and silicide formation. Such deposition showed that Ti-induced substrate disruption could be minimized while forming a stable overlayer. Our procedure involved adatom deposition in the presence of an activated partial pressure of oxygen. In this way, direct Ti-O reaction was enhanced and a stable TiO_2 layer was formed. This TiO_2 layer then served to protect the buried interface.

Studies of CaF_2 were undertaken because of the potential of CaF_2 as a high dielectric strength epitaxial overlayer on Si or GaAs. Our work examined the formation of metal overlayers on CaF_2/Si heterostructures, thus forming metal/epi-insulator/Si composites. For Au metallization, we found that the valence band offset for the CaF_2/Si heterojunction varied with annealing temperature and that Au deposition produced an upward shift of the CaF_2 bands, a flattening of the Si bands, and a large reduction in the valence band offset at the buried interface. We concluded that the movement of the Fermi level position at the Si surface and the variation of heterojunction band lineup correlated to the density of interface states and reflected charge redistribution and changes in interface dipoles. Extensive studies of Ti, Co, and Pd, on $\text{CaF}_2/\text{Si}(111)$ showed that the metal overlayer formed small clusters which grew and ultimately covered the CaF_2 surface. Au deposition produced sharp metal/insulator interfaces while signs of disruption were found for Ti, Co, and Pd adatoms. Comparison of the adatom-induced changes in the valence band features showed that the Fermi level position in the CaF_2 layer depended on the electronegativity of the metal overlayer. Annealing showed dramatic changes in morphology as metal-induced reaction with the Si substrate occurred and portions of the CaF_2 surface were exposed. We postulated that annealing induces the equivalent of blistering of the CaF_2 epi-layer as metal-substrate intermixing and reaction occurs.

During the second period, we developed the capability for low energy ion deposition onto surfaces. In feasibility studies of Ag growth on ZnSe(100) with the partially ionized beam, we found that acceleration to ~400 eV prior to deposition made it possible to induce substantial disruption of the ZnSe surface. It was then possible to directly compare results obtained by atom deposition and ion deposition, demonstrating that the latter led to Zn and Se release from the substrate and incorporation in the overlayer. Significantly, studies of the evolving Schottky barrier height showed effectively no change. From this, we concluded that surface disruption for ZnSe played a minor role in determining the barrier and, in turn, that defects were not important. Also in period two we undertook studies that involved the metal disilicides CoSi_2 , FeSi_2 , and MoSi_2 . Photoemission and low energy electron diffraction studies of silicides cleaved *in situ* made it possible to conclude that the surface was terminated by a single layer of Si because cleavage occurred within the bilayer along the [111] crystallographic direction for CoSi_2 and along [100] for FeSi_2 and MoSi_2 .

In the third period, we continued to focus on the interaction of low energy ions with surfaces. In particular, we examined In/GaAs(110), Bi/GaAs(110), and Ag/InP(110) interface formation, focusing on morphologies and band bending differences compared to conventional atom deposition. The results showed that the ions disrupted the substrate (In/GaAs and Bi/GaAs) and enhanced disruption (Ag/InP) and that three-dimensional growth occurred for both ion deposition and atom deposition. Measurements of Fermi level movement in the gap indicated slow approach to the same final position for ions and neutrals, almost independent of the amount of surface disruption. These results demonstrated that defects created during substrate disruption did not directly control band bending since the number of such defects was varied and band bending differences were slight. The second thrust involved feasibility studies of oxidation of GaAs at low temperature using condensed O_2 as the oxidizer. The goal was to better understand O - GaAs(110) interactions and surface oxidation. Since such interactions are inhibited at 300 K by the low sticking coefficient for oxygen and the activation barrier for reaction, we reasoned that we could alter the kinetics of the process by condensing multilayers of O_2 at 20 K. Feasibility experiments were very successful. Despite the enormous literature regarding semiconductor surface oxidation, no one had taken the approach of examining effects related to the amount of oxygen present, the photon flux, and the flux of secondary electrons.

During the fourth period, we continued to focus on the interactions of condensed oxidizing gases, O_2 , and N_2O with clean surfaces of GaAs(110). The goal was to develop an understanding of the mechanisms of oxidation. We completed studies of O_2 oxidation of GaAs(110) at 20 K that focused on the role of the photon beam itself in initiating reaction. Photoemission studies using the core levels of Ga, As, and O demonstrated that the topmost layer of As atoms was initially involved in a sequential two-step reaction to produce As^{1+} - and As^{3+} - like oxides. These reactions were mediated by secondary electron capture by O_2 , the subsequent dissociation of O_2 and then surface oxide formation. As^{5+} -like bonding configurations were formed when additional oxygen was condensed and exposed to photon irradiation. As the oxide thickened, it served as a diffusion barrier, and photon-stimulated desorption became important. Studies of Fermi level movement showed that band bending was strongly dependent on dopant concentration, O_2 dose, and light exposure, indicating band flattening due to surface photovoltages. Studies of N_2O interactions with GaAs(110) at 25 K using x-ray and ultraviolet photoemission demonstrated a direct correlation between the number of secondaries and the rate of reaction such that electron capture was necessary for the reaction to occur. N_2O dissociation produced O^- ions that reacted with GaAs to yield surface oxides.

During the fifth and sixth periods, we focused on the formation of surface oxides on GaAs(110), InP(110), and Si(111) and the stability of those oxides. The goal was to develop an understanding of the mechanisms of oxidation. Our results demonstrated the importance of electron capture as the first step in reaction, and they revealed the importance of kinetic processes. Studies of interfaces formed at 20 K by condensing O_2 , NO, and N_2O on InP(110) revealed striking differences in reactivity when heated, illuminated with visible light, or irradiated with soft x-rays. In particular, O_2 and N_2O desorbed without reacting when annealed but oxide-like In- and P-bonding configurations were thermally produced by NO. Visible light irradiation induced reactions for O_2 and NO at 20 K but not for N_2O on InP(110). Irradiation with 170 eV photons produced reaction for all three oxygen-bearing condensates. Investigations of the reaction cross sections for these systems demonstrated that

oxidation was mediated by the capture of photogenerated low energy electrons. For $O_2/InP(110)$, the extent of reaction depended on the amount of O_2 condensed on the surface. Hence, although the first stage of oxidation involved electron capture, the second stage involved diffusion through the oxide layer. Our results made it possible to determine reactive cross sections quantitatively. These studies of $InP(110)$ demonstrated the importance of electron capture and raised questions related to capture during electron irradiation from an external gun. We therefore undertook an investigation of negative ion formation for O_2 on $InP(110)$ during irradiation with electrons of energies between 1 and 8 eV. Detailed analysis gave reaction cross sections that depended on electron energy. These cross sections were much larger than those related to dissociative electron attachment and confirmed the role of negative ion formation. Once it was clear that negative ion formation was essential for oxidation, it was critical to determine the details of coupling of the electrons excited in the semiconductor with the affinity level of the oxygen molecules on the surface. To examine the coupling, we focused on O_2 on $GaAs(110)$ and showed that the surface reaction rate was strongly dependent on photon energy and substrate doping type. In particular, the low temperature reaction cross section was almost a factor of ten greater for p-type than n-type $GaAs(110)$, and reaction increased twenty-fold when the exciting photon energy increased from 1.7 to 1.97 eV. We showed that these differences reflected the energy distribution of the photoexcited electrons in the conduction band relative to the O_2 electron affinity level. Surface band bending and the photon excitation energy controlled the coupling of the levels.

Studies of the initial stages of oxidation of $Si(111)$ with condensed O_2 and N_2O also showed that reaction was induced by soft x-ray irradiation. For $O_2/Si(111)$, an SiO_2 phase was produced and its effective thickness increased with illumination. Intermediate oxides were observed and they also grew in thickness. Exposure of the oxidized surface to an intense photon beam produced structural changes in the film as annealing occurred. Our results showed that the defect-like Si^{3+} configuration converted to a SiO_2 -like configuration and a sharper interface developed. Studies of N_2O on $Si(111)$ showed slower initial reaction. From these studies, we concluded that the oxidation rate for the submonolayer oxide was determined by the availability of surface reaction sites and the cross section for electron capture. Growth for thicker films was also limited by oxygen diffusion through the existing oxide.

A second initiative during the final year of the project involved the synthesis of oxide layers on $GaAs(110)$ surfaces. We have produced Cr-oxide layers on $GaAs(110)$ in three different ways. When a Cr layer was grown on $GaAs(110)$ at 300 K and subsequently exposed to O_2 , the result was an inhomogeneous overlayer with oxidation enhanced by Cr-induced surface disruption. When Cr clusters formed by our Xe-buffer layer technique were deposited onto $GaAs$ and then exposed to O_2 , the result was a Cr_2O_3 -like species with small amounts of Ga_2O_3 . The third procedure involved Cr deposition onto an oxygen layer on Xe. This produced Cr_2O_3 out of contact with the semiconductor. The overlayer produced by deposition of the Cr_2O_3 clusters onto the surface was abrupt and there was no evidence of $GaAs$ oxidation. Finally, we investigated the stability of the Ga and As oxides grown at low temperature by the procedures discussed above. The results for Ti deposition showed the reduction of the Ga and As oxides in favor of the formation of energetically more stable Ti oxides. In contrast, Ti deposition onto an oxygen layer produced a Ti oxide, and the deposition of this oxide onto the buffered $GaAs$ surface produced no semiconductor disruption.

A parallel initiative was made possible by interactions with Ken Jones of the Fort Monmouth Laboratory. Previously, our work had shown novel Fermi level movement for cluster-assembled interfaces. In conversations with Ken, it became apparent that collaborative research could be undertaken that would combine the resources of his laboratory with the synthesis techniques of ours and the device characterization of Bob Mattauch's of the University of Virginia. As of this writing, a first set of measurements has been completed and a second series is underway. In each, the samples are prepared in Minnesota, their back surfaces are metallized at Fort Monmouth, a Au overlayer is then grown by us using cluster assembly, and then diodes are prepared and characterized. Ken has visited us in Minnesota, we have discussed the project, and we are all committed to see if anything novel can be learned. Note that this is a high-risk venture in the sense that we cannot guarantee a particular result. However, it represents an opportunity that must not be passed up because the result might be extremely important.

LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS GRANT PERIOD, INCLUDING JOURNAL REFERENCES:

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SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS GRANT PERIOD.

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F. Xu, Postdoctoral Associate (partial), now at University of Calabria

M. Vos, Postdoctoral Associate (partial), now at University of Western Ontario

T. Komeda, Postdoctoral Associate (partial), now at Texas Instruments, Japan

D.M. Hill, Postdoctoral Associate (partial), now at American Microsystems, Inc.

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G. Kroll, Graduate Student (partial), M.S.

J.P. Sullivan, Undergraduate (partial), B.S., now at Penn

M. Schabel, Undergraduate (partial), B.S., now at Stanford

During the course of this grant, five graduate students have earned their degrees. The two undergraduate students have gone on to pursue graduate studies.