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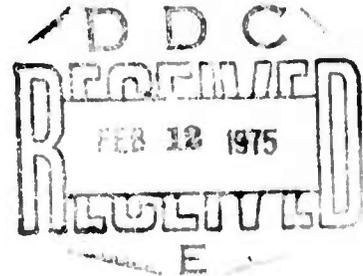
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## 1. Summary of Research Program

### A. Chemical and Physical Properties of Surfaces and Interfaces

The LRSM has an expanding and broadly based program of research on chemical and physical phenomena which occur at the surface of materials or at the interface between two materials. The long range goal of this program is to achieve the kind of deep understanding of such phenomena at the microscopic level which we now have about many important phenomena in bulk materials. Over and above the fundamental intellectual interest of the outstanding problems in this area, there are two major reasons for our thrust in this direction. The first is based on new capabilities: New theoretical and experimental techniques have recently been developed or are on the horizon which promise to make possible substantial advances in this field. The second reason is the growing urgency of the need to understand technologically important surface phenomena such as catalysis, which plays a crucial role in the energy and chemical industries, and a variety of surface phenomena which are assuming ever greater importance with the continuing miniaturization of electronic devices.

The primary goal of the Surfaces and Interfaces Program is to develop an understanding, on a microscopic level, of the bonding of and the interaction between adsorbed species on a solid surface. The core of the program is directed specifically to questions concerning the interaction of simple molecules, such as  $H_2$ ,  $CO$ , and  $C_2$ , with metal atoms of the late transition series when these atoms are in a variety of well-characterized surface environments. Such systems are simple enough to be amenable to experimental and theoretical analysis - both of which are imperative if progress is to be made - and at the same time are of considerable current interest in industrial processes. A variety of experimental and theoretical techniques are being employed by members of the program. One must study experimentally the structure of the bonding surface, the nature of reacting species, bonding configurations of reactants, the kinetics of the formation of surface species, etc. Theoretical effort must focus on the phenomena themselves as well as on the interpretation of experimental techniques and results.

### B. IV-VI Semiconductor Films and Surfaces

The purpose of this work is to explore and exploit several phenomena in semiconductors, especially lead chalcogenides. Emphasis is placed on possible device applications.

The importance of IV-VI compounds in infrared technology has long been appreciated. Optimum design of devices requires an adequate description of noise phenomena, which appear to be related to point defects in a complex way. Some of the newer applications of IV-VI devices to pollution monitoring are currently too expensive for large-scale deployment. A need therefore exists for a low-cost, moderate-performance system which may evolve from a combination of thin film growth and integrated circuit technologies.

### C. Heterojunctions of PbS-Si

This program is aimed at exploring heterojunction fabrication technology, the underlying mechanisms of heterojunction electronic characteristics, and problems of device geometry and topology of importance in the design of individual devices and device arrays.

The ultimate technological application of an IR-absorbing material is the detection and display of an image of an object which emits thermal radiation. Imaging technology in the visible and near-IR has undergone quantum improvements in reliability and economy via the development of charge-coupled devices. Far-IR imagers based on discrete IV-VI devices are both costly and frequently unreliable. The results of this research will contribute to the development of IR-CCD's in which photo-induced charge is produced in a IV-VI layer and the information processed in the silicon substrate.

## 2. Progress and Accomplishments

### A. Chemical and Physical Properties of Surfaces and Interfaces

The identification of molecular species on a surface, the nature of the chemical binding, and the underlying quantum mechanical structure of the substrate is being investigated using photoemission spectroscopy. The surface sensitivity of the technique, the fact that it can be used to study the high lying quantum states entering into bonding phenomena, and its non-destructive action on the surface itself combine to make it an exceptionally powerful tool. It can be used, for example, to monitor surface induced molecular conversion even in those situations where the species do not appear among the products in the gas phase. Work on dehydrogenation and C-C bond scission upon adsorption of  $C_2H_4$  on (110) W, and dissociation of CO on (100)W amply demonstrates the capabilities of the technique and illustrates some of what we have learned to date. Identification of species will be aided by using surface electromagnetic waves and newly developed infrared spectroscopy techniques to measure the vibrational frequency of the surface adsorbate complex.

The last six months have been spent designing and constructing an ultra-high-vacuum system for angular dependent photoemission studies of chemisorbed atoms. An energy analyzer system capable of collecting simultaneously all emitted electrons within  $120^\circ$  and  $\pm 2^\circ$  for any  $\theta$  and  $\phi$  has been built, as well as a sample holder which moves the sample with two degrees of freedom with respect to the light source. This system will be used to determine the spatial and energy dependence of the bonding orbitals for a chemisorbed atom or molecule. Experiments are underway at the "storage ring" at the University of Wisconsin as a high energy light source for the initial experiments with the above technique.

The proper identification of the energy levels of adsorbed molecular CO was accomplished by measuring the relative photoionization cross section as a function of photon energy from  $\hbar\omega = 20$  eV to 120 eV. This cross section measurements for CO on Pd and Ni was then compared to our measurements for gas phase CO. This identification of the energy levels of molecularly adsorbed CO will have considerable impact on theoretical calculations of chemisorption. First it indicates that CO is adsorbed in a localized bonding configuration similar to gas phase carbonyls and secondly it furnishes for the first time an experimentally determined system to check various theoretical models.

The properties of clean substrates are also being investigated with field emission spectroscopy. Work in progress is focused on Ni, Mo, and Si. It is known that field emission measures particular aspects of the surface density of states. Work in this area provides useful checks on theoretical models for metal surfaces. The geometry of the adsorbate and the location of the active site will be investigated by field ion microscopy, field desorption microscopy,  $\gamma$ - $\gamma$  angular correlation, infrared spectroscopy and angular-energy resolved photoemission spectroscopy. The latter technique shows great promise of being able to determine not only the symmetry of the bonding site but the spatial distribution of each orbital involved in the surface complex. The field ion microscope has been used to study diffusion on refractory metal surfaces. It will be used in the future to investigate similar phenomena on other transition metal tips as well as to study actual adsorption sites (active sites). In this regard, one should note that the tips employed tend to have all of the features existing on dispersed metal particles - various faces, edges, etc. - and that the microscope is capable of studying adsorption in any location.

Chemisorption and the associated modified chemical reactivity are being studied primarily by groups in chemistry and metallurgy. These groups share with the surface structure and theoretical groups a

common focus in exploring how chemisorption processes alter small molecule reactivity by directing the nature of reaction products, and altering the kinetics and mechanism for these fundamental reactions. These programs deal with adsorption, dissociation, recombination, and chemical reactivity of small molecules at metal and metal ion centers. Kinetic methods are widely used in studies such as modeling the surface adsorption and catalytic recombination of nitrogen atoms, examining the role of oxygen adsorption by copper and the nature of surface complexes in the surface initiated radical reactions of alkyl halides and amines, and in exploring high temperature adsorption and dissociation reactions of small molecules such as  $H_2S$ ,  $NH_3$  and  $CH_4$  on metals and metal oxides and sulfides. The interaction of small molecules ( $CO$ ,  $NO$ ,  $O_2$ ,  $H_2$ ,  $N_2$ ,  $N_2O$ ,  $SO_2$ ) with metallo sites ( $Mn^{II,III}$ ,  $Fe^{II,III}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ) in well-defined rigid ligand environments are being systematically examined. Varying the metallo site used in binding small molecules is observed to produce diverse electron distributions such as  $NO^+$ ,  $NO^-$ ,  $O_2^-$ ,  $O_2^0$ . The interrelationships of chemisorption-induced electronic changes and modified chemical activity are developing. A general model for the bonding of diatomic molecules with metallo sites has been applied to a series of metal ion centers. Chemisorption modified reactivity of oxygen and nitrogen oxides has been systematically examined. Different reactivities for metal bound  $NO^+$ ,  $NO$ ,  $NO^-$ ,  $(NO^{-2})$  have been recognized.

In order to gain some knowledge of the spatial distribution of electronic wave functions of surface atoms and atoms adsorbed on clean single crystal surfaces, we are attempting to measure the quadrupole hyperfine interaction of cadmium atoms adsorbed on clean single crystal tungsten surfaces as a function of coverage and substrate temperature with coverages as low as one 1/10 - 1/100 of a monolayer. The hyperfine interactions are measured by the method of integral and time dependent perturbed  $\gamma$ - $\gamma$  angular correlations using the isomeric state  $Cd^{111m}$ . The activity was produced in our Tandem Accelerator by bombarding Pd foil with 18 MeV  $\alpha$  particles. Experiments have shown that sufficient activity for the experiment can be prepared. An ultra high vacuum system suitable for the experiment has been designed and the parts are being built and assembled.

Solid-state electrochemical cell investigations using  $Ag_2S$  cathodes have been completed. As predicted, remarkably low overvoltages have been measured; however silver whiskers nucleate and grow at the electrode-electrolyte interface. Other promising sulfide cathode materials are now being examined. These include the ternary sulfide systems:  $AMS_2$  where A is Ag, Na or Li and M is Ta, Nb, Zr

or Ti. The  $MS_2$  sulfides have layered crystal structures, and Ag, Na, or Li atoms are positioned between the layers to form intercalated ternary compounds.

Surface electromagnetic wave studies have led to a new technique for probing surface binding. An analysis has been carried out of the use of the attenuated total reflection (ATR) method as an EM probe of adsorbed atoms and molecules on metal surfaces. We find that the electric fields of the surface EM modes which are excited at the active-interface exhibit a resonance peak when the reflectivity exhibits a resonance minimum and that the fields just outside the metal are appreciable larger than that of the incident bulk EM wave particularly in the infrared. The sensitivity of the ATR method should therefore, in principal, be greater than that of Greenler's (bulk EM wave) reflection-adsorption method. Using a simple model we have obtained an analytical expression for the electromagnetic field at the active interface in an ATR Otto (prism (P)/vacuum (V)/metal (M)) configuration which shows that for TM waves the peak magnitude of  $E_{\perp} / E_0$  in the vacuum at the active (metal/vacuum) interface for the "optimum" vacuum gap is proportional to  $\sqrt{\epsilon_p \epsilon_m / \epsilon_m} = \sqrt{\epsilon_p \omega \tau}$  where  $\tau$  is the electron scattering time. Thus the sensitivity of the ATR method for obtaining infrared and Raman spectra of adsorbed atoms and molecules can be increased by using single crystals of metals with sizeable  $\omega \tau$ . A further increase in sensitivity can be achieved by lowering the temperature of the metal to increase  $\omega \tau$ . Similar considerations apply to the Kretschmann (prism/metal/vacuum) configuration for which it will be advantageous to use epitaxially grown single crystal metal films. The ATR method will be used to investigate the IR spectra of molecules such as CO which are chemisorbed on metal surfaces.

Considerable effort in the program is focused on gaining a theoretical understanding of the basic phenomena as well as aiding in the interpretation of experimental results. Much of this work deals with the following types of problems: 1) the prediction and interpretation of angular resolved photoemission spectra of atoms and small molecules chemisorbed on transition metal substrates, 2) the development of self-consistent scattered wave calculations of the electronic structure of transition and noble metals in film geometry, 3) the investigation of the Born-Oppenheimer potential energy function for chemisorption and surface chemical reactions of small molecules on transition metal surfaces, and 4) the identification of those features of the substrate that govern its chemical reactivity. The rationale for these projects, in concert with the experimental program, is 1) to understand the geometry of the adsorption site(s) and directionality of the chemisorption bonds; 2) to provide a first principles understanding of the clean surface so that the parameters of approximate (LCAO) model Hamiltonians

can be fixed for use in the more complex problems of chemisorption and surface reactions; 3) to further the development of a quantum mechanical model for understanding chemisorption bonding, surface diffusion and surface chemical reaction involving small molecules on metal surface.

An example of the class of research directed toward the interpretation of experimental results would be work being done in our group on the theory of angular-resolved photoemission. We have developed a scheme for treating the effect of scattering of the outgoing photoemitted electron by the substrate, based on a multiple scattering theory similar to that employed in LEED or band structure calculation. The results can be interpreted in terms of a) the band structure of the substrate and b) the position of the adsorbate relative to the substrate as well as the symmetry of the core orbital (s, p, etc.). Having determined the adsorption site geometry, the angular dependence of the electrons photoemitted from levels involved in the chemisorption bonds can be treated, including final state effects, to gain information on bond symmetry and bond charge distribution.

We have succeeded in exactly solving a simple LCAO model for a dissociation reaction in which a diatomic molecule chemisorbs on a "bridge site" of a cubic substrate lattice and at the corresponding site on a gas phase complex composed of the same two substrate atoms. By modeling the hopping matrix elements in simple ways, one finds many of the observed characteristics of catalytic reactions; e. g., Brønsted relations relating the heat of adsorption and the activation energy for the reaction.

Realistic models of clean surfaces are an important prerequisite to studies of surface reactivity. To provide such models we are engaged in a program of self-consistent one-electron type calculations, using a modification of the scattered wave formalism appropriate to a film geometry. The surface electronic structure of thin films (5-7 layers) is expected to reasonably approximate that of a semi-infinite bulk solid, as indicated by jellium and LCAO calculations. Results to present include the energy levels of one and three layers of Cu. Self-consistency and extension to thicker films of Cu and Ni are being actively pursued.

Since calculations on simplified models show that the chemisorption bond is reasonably well localized in space (within the first or second coordination shell of the adsorption site) calculations of the electronic structure and potential energy function of adsorbates and surface reactants should exploit this simplification. We are developing

combined self-consistent scattered wave (SCSW) and LCAO techniques for treating such problems, where a "surface complex" (adsorbate plus first and possibly second substrate coordination shell) is treated by SCSW techniques and fit to an LCAO model Hamiltonian, with the full problem being then treated within an LCAO framework. The experimental side of our program requires accurate molecular orbital calculations as theoretical backup. We are engaged in standard SCSW calculations on small molecules to provide this assistance as well as to further our theoretical studies.

The theoretical model, developed during the earlier part of the year, for the angular distribution in photoemission spectra has been applied to the specific case of the layer compound 1T-TaS<sub>2</sub> in order to establish contact with recent experimental data. Preliminary numerical results reproduce the main observed features and thus allow a unique discrimination between the effects of the initial and final state in the photoemission process.

The development of a multiple scattering technique for calculating the electronic properties of solid surfaces is proceeding satisfactorily. We have performed preliminary calculations for a copper surface. The next step is to carry out self-consistent calculations for a nickel (Ni) surface. These results will be used to aid in understanding the chemisorption of simple molecules on Ni.

#### B. IV-VI Semiconductor Films and Surfaces

Our basic studies of the electronic structure of IV-VI compounds are almost complete. Work on the electronic structure of semiconducting alloys culminated in the development of a formalism based on an expansion of the coherent potential approximation (CPA). The formalism was used to obtain the first and only rigorously-based calculation of the electronic structure of  $Pb_{1-x}Sn_xTe$  with very successful results. Our calculations have also shown that the high pressure phase of CdS is an indirect gap semiconductor with a band gap of 1.5 eV. Initial calculations using the cluster technique have reproduced Pratt's Koster-Slater results for  $Pb_4Te_4$  and [Vacancy]  $Pb_3Te_4$ . Inserting a hydrogen atom to give [H]  $Pb_3Te_4$ , we confirmed the physical origin of the so-called hydrogen effect on the galvanomagnetic properties of chalcogen-rich materials. Energy band calculations on the Pb-chalcogenides, including PbPo, have solved the long standing puzzle of the lack of a regular trend in the energy band gap of these important materials. This irregularity has been shown to be directly related to the size of the Te atom with an associated anomaly in the lattice constant of PbTe. Further, it was shown that PbPo is a semimetal rather than a direct gap semiconductor as predicted before.

An important aspect of the IV-VI work involves the determination of how the electronic structure of a continuous film evolves from small molecules by studying the optical properties of matrix-isolated aggregates. Most of our studies on aggregates have been concerned with dilute matrices in which the predominant species are  $\text{MX}$  and  $\text{M}_2\text{X}_2$  ( $\text{M}$  = metal, e. g.,  $\text{Pb}$ ;  $\text{X}$  = chalcogen, e. g.,  $\text{S}$ ), although we have made some studies of the amorphous, high surface area film which is left behind when the matrix gas is removed. We have investigated the vibrational patterns of the ground electronic states of the "monomer" ( $\text{MX}$ ) and the "dimer" ( $\text{M}_2\text{X}_2$ ) molecules (germanium, tin and lead sulfide, selenide and telluride) by the use of infrared and Raman spectroscopy. We discovered that these matrix-isolated species emit strong luminescence when they are excited by laser radiation. Since the molecules do not rotate in the rigid matrix, the luminescence consists of simple vibronic band systems (i. e., transitions in which the molecule falls from a given vibrational level in the upper electronic state to a vibrational level of the ground electronic state). The emission bands are intense; we normally observe the luminescence from  $10^{-9}$  moles or less of the IV-VI compound. Several hitherto unknown electronic states have been discovered and characterized for each of the diatomic and tetratomic IV-VI molecules. By irradiating the sample with a single laser frequency (for example the blue line at 488 nm), we observe simultaneously emission from as many as five different excited electronic states with the luminescence covering the range from the ultraviolet to the near infrared. Obviously exciting strong luminescence in the ultraviolet with a visible light source involves a two photon absorption process. We have uncovered the role the solid matrix plays in the luminescence process and have found matrices in which the coupling between the host matrix and the guest molecules is minimal. Under these conditions the emission of light from the sample consists of very intense and very sharp spectral lines and we can observe the luminescence from individual isotopic molecules. In two cases we have been able to excite emission selectively from just one isotopic species. This has implications as to isotope separation methods.

Clean electroreflectance signals have been observed in  $\text{PbS}$ , using the MOS configuration on epitaxial films at 4 K. Major structure occurs at 2.063 eV and 3.1 eV, coincident with two thermorefectance peaks observed earlier. Thermorefectance spectroscopy is being employed for trace impurity diagnostics in  $\text{CdS}$  films on mica. Preliminary results suggest a new bound exciton line  $\sim 30$  MeV below the A exciton, which is associated with traces of chlorine in the cadmium starting material. This thermo-optic modulator technique is being pursued in conjunction with EPA scientists at Research Triangle Park.

They have expressed a need for a simple, cheap  $\text{SO}_2$  monitor as a result of the projected increased usage of high-sulfur fuels in the U. S. The modulation technique may ultimately be extensible to  $\text{SO}_2$  detection at 8.6 microns using a PbSnTe diode and PbS modulator.

Noise studies on IV-VI compounds have resulted in the observation of peaks in the integrated noise power as a function of temperature. These peaks appear to be associated with enhanced  $1/f$  noise produced by current carriers interacting with the lattice. We are pursuing the study of vacancy motion induced by the current, i. e., electromigration. The system to be studied is PbSe on  $\text{BaF}_2$ . A thorough investigation of PbSe on NaCl has been conducted already. The major difference between the two systems is that PbSe on NaCl is (100) parallel to (100) while the PbSe on  $\text{BaF}_2$  is (100) parallel to (111). In the latter case, the misfit dislocation density is appreciably higher and we anticipate a higher noise figure. This is observed. Additionally there is a peak in the integrated noise near 250 K. This peak is believed to be associated with the onset of vacancy motion. This temperature corresponds to an energy of 21.6 MeV which is very close to the LO phonon energy.

The change brought about in the electrical properties of the lead-chalcogenides upon exposure to atomic hydrogen have important implications for technological applications. Our theoretical calculations have shown that the effect is due to the occupation of Pb vacancies by H, and the resulting reduction of the holes created by Pb vacancy by one. Since these materials are usually heavily compensated, atomic hydrogen has effect on both n- and p-type materials.

The program of magnetoplasma measurements on single crystal lead telluride has continued. A large number of samples, over a range of carrier concentrations, have been prepared and reflectivity measurements made. The dielectric anomalies have been observed over the three frequency bands at 70 GHz, 140 GHz and 350 GHz. A circular polarizer for use at 70 GHz has been developed for use in transmission magnetoplasma measurements. A definitive quantitative picture of the unique lattice-dielectric (soft optic phonon) behavior of PbTe has been derived from microwave magnetoplasma and conductivity experiments. This material is an important infrared laser and detector material.

### C. Heterojunctions of PbS-Si

We have concentrated on developing ways of varying the composition so as to influence the responsivity of the heterojunction. We have uncovered what we believe is a unique and unparalleled means of studying the carrier concentration dependence of the PbS on the p-

properties of the heterojunction. The position of the Fermi level at the PbS-Si interface depends on the bulk doping of the PbS. As we have reported elsewhere, the sister compound PbSe can be reversibly doped by atomic hydrogen. The H is removed by a prolonged exposure to  $O_2$ . A study of the kinetics and details of this process on PbSe films has just been completed. Similar effects have now been observed on the PbS-Si system. As a result, the entire forbidden energy gap of both the PbS and Si can be scanned using appropriately doped Si substrates and a combination of H and  $O_2$  effects on PbS. What is particularly attractive about this study is the possibility of adjusting the PbS Fermi level continuously with either exposure to H or  $O_2$  and thereby determining what doping will produce the optimum photo-response. Subsequent permanent doping of the PbS to fix the Fermi level will require processing such as ion implantation.

The PbS-Si heterojunction is a unique system for studying a variety of electronic properties of heterojunctions. Studies on PbSe-H interactions have demonstrated that Pb vacancies when occupied by in diffusing atomic hydrogen, H, will change their charge state. Furthermore, recent work has shown that upon admission of oxygen, the hydrogen will out diffuse to the surface where it recombines with the oxygen and is removed from the system. What these results suggest is that the fermi level of the PbS in a PbS-Si heterojunction can be reversibly altered by a cycling in H and  $O_2$ .

We have initiated a study of the H and  $O_2$  effects on the PbS-Si heterojunction. In the back bias condition, appreciable decreases in the diode current were observed upon exposure to H but essentially no variation in the forward current was observed. These results are entirely consistent with the proposed band diagram and strongly indicate an absence of interfacial trapping levels. The reason is that as the PbS become increasingly n type, the number of holes decreases causing a decrease in the back bias current from the PbS. On the other hand, in forward bias the current from the Si is relatively unaffected by the charge density of the PbS.

A thorough study of the properties of PbS-Si heterojunctions at room temperature and 77 K was completed. Shifts in the band structure with temperature were quite evident. As a result, it was possible to calculate shifts in the electron affinity of PbS relative to silicon. The latter is known from photoemission studies. The effect of film thickness on diode behavior was also studied.  $D^*$ 's in the mid to high  $10^3 \sqrt{\text{cm}^2/\text{hg}}$  were obtained routinely. Injection from the PbS into Si was confirmed.