AD-A177 600 PROSPECTS FOR RESEARCH ON SEMICONDUCTOR MATERIALS SURFACES(U) ARMY RESEARCH OFFICE RESEARCH TRIANGLE PARK NC R W SHAW ET AL. 01 JAN 87 1/1

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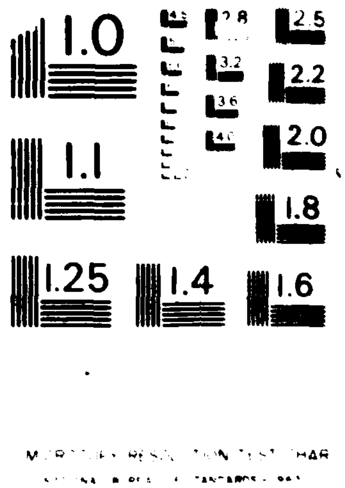
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U.S. ARMY RESEARCH OFFICE TECHNICAL REPORT
RESEARCH ON SEMICONDUCTOR MATERIALS SURFACES

12 NOVEMBER 1986
RESEARCH TRIANGLE PARK, NORTH CAROLINA

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188
Exp Date Jun 30 1986

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: U.S. Army Research Office; 6b OFFICE SYMBOL (If applicable): SLCRO	7a NAME OF MONITORING ORGANIZATION
6c ADDRESS (City, State, and ZIP Code): Research Triangle Park, NC 27709-2211	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING/SPONSORING ORGANIZATION; 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
1L161102BH57			

11 TITLE (Include Security Classification)

Prospects for Research on Semiconductor Materials Surfaces

12 PERSONAL AUTHOR(S)

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13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Workshop	FROM 86/11/12 TO ______	87/1/1	13

16 SUPPLEMENTARY NOTATION

The findings in this report are those of the authors and not official Department of the Army policies unless so designated by other documentation.

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Semiconductors, Heterojunctions, Semiconductor Devices, Surface Chemistry, Gallium Arsenides

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The workshop, "Prospects for Research on Semiconductor Materials Surfaces", was held at the Army Research Office, Research Triangle Park, NC on November 12, 1986. It was sponsored by ARO and organized by Robert Shaw, John Zavada, and Bernard Spielvogel. The workshop emphasized experiments to probe surface chemistry of semiconductor materials with the eventual goal of improved devices. Participants came from university, industrial, and Army laboratories and discussed current basic research activities, identified neglected research areas with high potential payoff, and developed specific research recommendations. This report provides the summary notes of the workshop.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION: Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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I. INTRODUCTION

We initiated this workshop following discussions among ARO staff in the Chemical and Biological Sciences Division and the Electronics Division about support of research on the chemistry of surfaces and interfaces of advanced semiconductor materials. We wanted to identify neglected research problems with high potential payoff in the production of improved devices and we were especially interested in the role of powerful new surface probes developed since the renaissance of surface chemistry and physics in the early 1970's. We believed that a well prepared, intensive discussion among active research workers from university, industry, and Army laboratories would provide a useful perspective from which to judge proposals for ARO support.

This report contains the summary notes from the discussions. The notes by John Yates (University of Pittsburgh) describe the workshop agenda and give the recommendations by the working group on "Semiconductor Bonding Fundamentals". The notes by William Beck (Martin Marietta Corp.) give the recommendations by the working group on "Fundamental Needs - Device Fabrication". We include the notes, "Problem Areas in MCT [HgCdTe] Long Wavelength Detectors", prepared before the workshop by Michael Martinka and used during the working group discussions.

II. SUMMARY NOTES - SEMICONDUCTOR BONDING FUNDAMENTALS

John T. Yates, Jr.
R. K. Mellon Professor of Chemistry
Director, Pittsburgh Surface Science Center

A one day meeting was held to bring together a small group of ARO-sponsored research workers to discuss future opportunities in the chemistry of semiconductor interfaces. The goals of the meeting as specified by ARO management are listed below:

- Review of current basic research
- Identification of research problems with high potential payoff in non-Si based semiconductor technologies.
- Emphasize problems relative to GaAs and HgCdTe technologies, with emphasis on device improvement.

Talks were given on the following topics:

- Molecular Beam Etching
  Pat Gillis, Hughes Research
- Interfacial Studies - II-VI and III-V Materials
  Len Brillson, XEROX
- Semiconductor Clusters
  Rick Smalley, Rice University
- Semiconductor-Metal Contacts (HgCdTe Films)
  William Beck and Guy Davis, Martin Marietta
- Army Needs for Advanced Semiconductor Materials - Associated Research Problems
  Ken Jones, ETDL

Following these five lectures, the group split into two small discussion groups whose general topics were:

Major Opportunity Areas - Semiconductor Bonding Fundamentals

Major Opportunity Areas - Fundamental Needs in Device Fabrication

The recommendations from the two Groups were discussed by the main group, and slight refinements were made. Below is a detailed summary of the basic recommendations in narrative-outline form:

Major Opportunity Areas - Semiconductor Bonding Fundamentals

A. Excitation of Surface Processes by Ion Bombardment

Problem - Reactive ion etching, RIE, involves the simultaneous combination of ion bombardment and reactive surface chemistry. It appears that RIE is a synergistic combination of at least three elementary processes, namely (1) active site production by ion bombardment of the surface, (2) electronic excitation of adsorbed species (halogen, CF_x, etc), and (3) local thermal excitation of activated surface chemistry due to the ion/solid collision.

Proposed Research - Careful experiments should be designed to separately test the importance of the three elementary processes in causing the RIE phenomenon. Deeper understanding could produce better geometrical control of the etching process.

B. Chemical Reactions with Semiconductor Surfaces

Problem - The chemical reactivity of semiconductor single crystal surfaces is virtually unstudied under controlled conditions using modern methods of surface science. Reactivity patterns should be explored for a wide range of semiconductor surfaces, and for a wide range of chemical compounds useful in processing these surfaces.

Proposed Research - Study all types of atomically-clean semiconductor surface reactivities with molecules used for different purposes in processing.

Examples:

1. Solvents - cleaning procedures - study reactivity using molecular beam dosing + surface spectroscopy of monolayer.

2. Organometallics (used for metal deposition and MBE processes). Study basic thermal and laser-induced degradative chemistry under controlled surface conditions.

3. Cleaning chemicals - HF, H_2O_2, etc. Study basic chemistry under controlled conditions.

C. Thermodynamic and Electronic Properties of Extremely Thin Films

Problem - Thin film interfaces are employed in junction fabrication as barriers for diffusion. These barriers can be 10Å or less in thickness, and their properties as materials may be governed strongly by the surfaces of the thin film interfaces.

Proposed Research - Both theory and experiment should be directed toward the understanding of electronic and thermodynamic properties of thin metal films in contact with semiconductors - i.e., Al/CdTe, Al/GaAs, Al/InP, Cu/CdS. How do the properties of the thin films converge to that of the bulk metal as thickness is increased?

D. Bulk Thermodynamic Properties of Compounds Important to Semiconductor Technology

Problem - Correlations of the interfacial behavior of rather esoteric materials with their bulk thermodynamic properties is a common feature in semiconductor materials science. Often, enthalpies of formation for a compound are in disagreement or are unknown. Particular problem materials are the metal arsenides. In addition, ternary phase diagrams are unknown or need refinement.

Proposed Research - A survey of the needs for this information should first be made followed by initiation of the proper measurements of bulk thermodynamic properties. A comparision to the properties of these materials in very thin film form should be made. Phase diagrams for 2-D systems may be compared to 3-D bulk phase diagrams.

E. Atomic Level Structural Characterizaton of HgCdTe Surfaces

Problem - Atomic level information about the structure of HgCdTe surfaces is not available. Indeed, the crystals now available have variable surface properties in different regions, and differ from sample to sample. The effect of sputtering on structure and stoichiometry is unknown.

Proposed Research - STM methods should be tried along with other surface structural methods (LEED, SEXAFS, NEXAFS). Careful studies of the relative sputter yields versus ion bombardment energy and angle would be useful. All factors affecting surface stoichiometry are of interest. A comparison of the surface structure and composition of bulk and epitaxial material would be useful in placing HgCdTe surface materials science on a firm footing.

F. Theory Linkage - Structure and Stability of Semiconductor Clusters - Relationship to Surface Reconstruction on Bulk Semiconductors

Problem - Semiconductor clusters (2-20 atoms) exhibit definite size dependent stability behavior which may be theoretically (electronically) explained by structural models which change significantly for neighbor cluster sizes. The same or similar stability factors in semiconductor clusters may also be at work in reconstruction processes on semiconductor surfaces, so that linkage of these entirely different areas through theory may exist. Also, soon-to-be-available photoelectron spectra of semiconductor clusters containing mostly surface atoms may be similar to photoelectron spectra for atomic surface layers on bulk semiconductors, suggesting that similar electronic descriptions may apply to both classes of materials.

Proposed Research - Keep an eye on experimental PES studies on clusters, especially for deeper sampling of the valence band. Get opinion of theorists about possible linkages suggested above.

G. Free Radical Chemistry on Semiconductor Surfaces

Problem - Free radical species are often postulated to cause RIE undercutting of masked areas. Except for H atom surface chemistry on semiconductors (partially explored) little is known about free radical surface chemistry on semiconductors.

Proposed Research - Employ selective methods to produce pure sources of particular free radicals and investigate their chemistry on semiconductor surfaces using surface spectroscopies which give information on bonding and structure. Thermal degradation processes for anchored radical species should be explored.

H. New Surface and Bulk Characterization Methods

Problem - The involvement of bulk H in determining the electronic properties of Si is well known. It is considered likely that similar effects may exist in GaAs and HgCdTe materials. In addition, bulk and surface defects are known to influence the behavior of GaAs and HgCdTe materials.

Proposed Research - Develop new physical and/or chemical methods to study H in semiconductors and to study bulk and surface defects.

III. Summary Notes - Fundamental Needs in Device Fabrication

William Beck, Martin Marietta Corp

A. Basic Issues Retated to Metal Contacts:

1. Additional process compatible surfaces (e.g., chemical etch),

2. More extensive characterization of pre-deposition surfaces to resolve conflicting results,

3. Wide-gap material, especially p-type,

4. Superlattices,

5. Good shallow contacts to GaAs and related III-V materials,

6. Dry etching of MCT and removal of Cd.

B. Basic issues related to molecular beam etching:

1. Develop low-energy ion and electron techniques to achieve

Minimal damage
Threshold behavior
Selectivity w/"simple" chemistry

2. Explore microwave plasmas for low-energy (minimum damage),

3. Determine the method of physical energy deposition (i.e. role of chemistry and sputtering vs temperature (local),

Use photo-ionization mass-spec as detector to avoid fragmentation,

Determine internal states of the product molecules (to check for thermal equilibrium on surface).

IV. PROBLEM AREAS IN MCT LONG WAVELENGTH DETECTORS

M. Martinka, CNVEO

SPECIFIC

1. Minimal sucess at activation of chemical dopants and their stability, radiation and thermal effects.

2. Process compatible surface passivation, etching, and metalization at the trial and error phase with some progressive improvement.

3. Few and conflicting experimental results on valence band discontinuity values needed for interface models.

4. Minimal efforts to reduce or qualify (ambient influence, temperature dependence, simultaneous alternate techniques, etc.) damage in normal surface and bulk analysis experiments. Few nondestructive efforts to monitor epitaxial growths.

5. In view of the stress on low temperature growth and processing, there is insufficient investigation of the resulting microstructure (nucleation, phase/anti-phase, low angle grain content, and clustering) and diffusion of growths, dopants, passivants and metalizations.

6. Minimal information on purity or purification work on the metalorganics suitable for MCT. Little experimental work on surface or gas phase reactions in MOCVD growth.

7. In view of the instability of MCT in chemical processing, there is little effort at in situ dry processing (laser assisted or active beam etching, pulsed laser material removal or anneal).

GENERAL

The level of effort in MCT is below that needed for a short term general breakthrough in materials and processes. However, progress in selected areas may be exploited for short term gain.

PROPOSED WORK

1. Co-ordinate separate UPS, XPS research on contact formation on MCT and add the complementary electronic characterization (I-V, C-V, contact resistance, noise) of the in situ produced contact. Yield handbook for in situ vacuum metalization of MCT. Subsequent goal is process compatible metalization handbook. For example,

Contact metal/substrate type and composition
Electronic characterization/ohmic, diode, noise, etc.
Substrate preparation/cleave, sputter, temperature
Method/evaporation, sputter, E-beam, etc.
Chemical and physical/reactive and nonreactive, intermetallic formation, interdiffusion, etc.

2. Similar longer term effort on valence band discontinuities after UPS, XPS techniques are qualified in terms of temperature dependence, strain dependence, etc.

3. The investigation of microstructure and lattice dynamics of MCT should be encouraged as it relates to lattice stability, dopant activity and stability, carrier lifetime and junction formation. All reasonable means (Raman, EXAFS, High Resolution Electron Microscopy (HREM), high resolution x-ray and topographic x-ray, far-infrared and ultransonic) should be considered to compare low and high temperature growths and dopant activation and stability.

Options:

a) Clustering in MBE and MOCVD layers versus LPE and bulk by an EXAFS/Raman comparative effort.

b) High resolution electron cross sectional lattice imaging of MCT/substrate, passivation and metalization.

c) Low angle grain structure via x-ray topography, low temperature CL, EBIC as compared to x-ray rocking curve data.

d) Investigate the diffusion, activation, and stability of chemical dopants by combining SIMS, EBIC, and perhaps at high concentrations EXAFS with Hall and calculated carrier concentrations and mobilities.

4. Address native and modified surface electronic structure to push process compatible passivations and etching out of the trial/error or proprietary phase. Various in situ surface and optical measures of cleaved and reacted surfaces may be compared with appropriate electronic measures. A starting point could be the current vogue in passivation, chemically generated CdS(60Å) on MCT, and a photoresist compatible etch; e.g., lactic acid (Br-methanol is not). Gas phase processes should be identified for in situ work.

Options:

a) Tunneling microscopy of surface bond states with ellipsometry for low energy, .6 to 6 ev, surface electronic structure of cleaved and reacted (gaseous exposure, metalized or etched) surfaces.

b) Suitable work configured about angle resolved UPS, ISS, LEED or possibly Reflection Difference Spectroscopy may also address these areas.

c) Submonolayer low abundance species at surfaces and interfaces may be investigated by Nonresonant Multiphoton Ionization of Desorbed Neutrals. A technique whose potential is high in quantitation, sensitivity, and spatial resolution relative to static SIMS.

d) Conduct C-V, DLTS, surface lifetime, and noise on suitable structures resulting from the above efforts.

e) Investigate possible nondestructive electronic information from photoreflectance.

5. Qualify and mininize damage due to current analysis techniques and investigate in situ optical nondestructive techniques to monitor epitaxial growth. Options:

a) As RHEED, Auger, and XPS are present in many MBE systems, some information on possible analysis induced damage is needed. Cooling samples and reducing active species in the vacuum chamber while monitoring the effects of E-beam and x-ray dose as a function of temperature may yield such information. Additional corroborative optical means such as ellipsometry, photoreflectance, and reflectivity may aide in the effort.

b) Investigate optical monitors for MBE and MOCVD growth along with absorption spectroscopy of the gas phase in MOCVD.

6. Investigate the purity of metalorganics used in the MOCVD growth of MCT.

7. Dry Processing of MCT. Options:

a) Investigate laser assisted or active species beam etching of MCT as hydrogen telluride and mercury are volatile with Hg liberated in reactions with active species. However, need to address the removal of Cd.

b) Investigate pulsed eximer laser adiabatic surface processes, material removal, surface cleaning, and shallow annealing and diffusion.

V. SUMMARY NOTES BY ARO

There is considerable agreement among the sets of recommendations of the two working groups and the notes by Martinka. Items A, B, of Yates' outline refer to the need for research on excitation of surface processes and chemical reactions; these correspond to Beck's A 1, 2 and B 3 and with Martinka's item 2 in his "Specific" list. In Beck's item B 1 and Martinka's item 4, they are both seeking to reduce damage. Yates' items E and F and Martinka's item 5 focus on the changed microstructure at interfaces. There are other areas of agreement and there are also special problems identified by the special perspectives of the working group on "Fundamentals" (e.g., thermodynamic properties of thin films) and the group on "Devices" (e.g., shallow contacts to GaAs). Jones' talk on Army needs emphasized the need for research on hetero-interfaces, contact metallurgy, etching damage, and chemical residues on surfaces.

This research area has interesting characteristics. Large numbers of devices are made without a clear understanding of their detailed properties. Understandably, industrial research is largely driven by the heavy investment in processes on the production line; but this hinders the exploration of new methods. Process engineers may not realize that experiments done under very clean conditions may provide fundamental information useful to them even though processing may not be done in clean conditions.

A tension exists between the need for research on advanced materials (e.g., GaAS, HgCdTe) and research on much better understood systems (e.g.,Si). As in other areas of research, the goal of the experiment should provide a guide; for example, in the study of energy transfer in reactive ion etching, one would start with simple, well characterized, model surfaces such as Si. On the other hand, understanding of the detailed chemistry of semiconductor-metal contact interfaces would require study of the semiconductor material of interest.

Studies of that semiconductor-contact chemistry in advanced materials (e.g., GaAs or HgCdTe) are made more complicated by their relatively low heats of formation and, consequently, their highly reactive surfaces and interfaces - an interesting problem in inorganic chemistry.

Another area of great interest for basic research with long term practical implications is the study of semiconductor clusters: chemical reactions, electronic structure, and synthesis of new materials.

Access to well characterized materials may create difficulties for scientists wishing to work in this research area. On the other hand, there are important problems to be solved - many of them identified in this report - and many of these problems can be attacked now, using commercially available materials and current experimental tools.

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