COLUMBIA UNIVERSITY

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UNIVERSITY RESEARCH INITIATIVE PROGRAM

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September 15, 1989 - September 14, 1990

INTERFACIAL AND THIN FILM CHEMISTRY IN ELECTRON DEVICE FABRICATION

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The fourth year's progress on the Columbia URI program on Interfacial and Thin-Film Chemistry in Electron Device Fabrication is reported. Progress has been made in three broad areas: MBE Growth and Devices, Laser Surface Interactions, and Fundamentals of Processing Gas/Surface Interactions. Examples of specific results include the first study of laser-assisted Cl_2 etching of copper; many new tunnelling and optical devices in layered semiconductors; a new 2-phase 2DEG-CCD; seminal studies of the Si-YBaCuO system; and the first observation of thin film growth by photoelectron injection.

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strain
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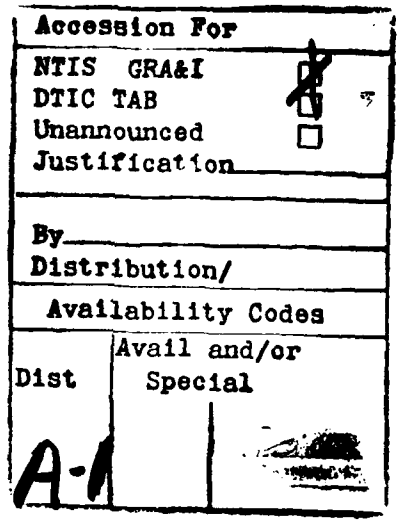

ABSTRACT (Block 19 Report Documentation Page)

The fourth year's progress on the Columbia URI program on Interfacial and Thin-Film Chemistry in Electron Device Fabrication is reported. Progress has been made in three broad areas: MBE Growth and Devices, Laser Surface Interactions, and Fundamentals of Processing Gas/Surface Interactions. Examples of specific results include the first study of laser-assisted Cl_2 etching of copper; many new tunnelling and optical devices in layered semiconductors; a new 2-phase 2DEG-CCD; seminal studies of the Si-YBaCuO system; and the first observation of thin film growth by photoelectron injection.

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I. DIRECTOR'S OVERVIEW

A. Introduction

This year's Navy URI program has yielded a rich variety of new findings in the fundamentals of surface processing and growth for electronic devices. The laboratory productivity reflects the fact that new instrumentation and faculty, brought in large part by the ONR program, are now in place and fully operational.

With regard to the areas of materials chemistry during advanced processing, Flynn and Herman have used advanced optical diagnostics to study chlorination reactions for semiconductor or metal surfaces. Chlorine-based reactions are key chemical pathways to etching metal (copper for packages and advanced IC's) and semiconductors. Flynn has examined the chemistry of hot atoms of importance in gas phase plasma reactor reactions using diode lasers, and Herman has studied the micro-Raman effect of chlorine-surface products. In other experiments, Osgood and Flynn have also found that electron-initiated reactions and collisions are a key phenomenon in UV-enhanced oxidation of GaAs and in the subsequent dynamics of products and reactants from UV-photodissociation of gas-phase reactions, respectively.

Some of the most complex interfacial reaction studies in our program are the most important from a practical point of view. In particular, Turro has investigated the mechanistic details of reactions which occur in novel photoresist materials in a collaboration involving IBM East Fishkill; this work involves the photochemistry of photopolymerization initiators used in these photoresists.

Key research has also been done in devising new applications for novel heterostructure devices. In particular, Yang and Fossum have both developed important collaborations with Wang to develop a new HBT concept (Yang) and a new 2DEG-CCD detector (Fossum). In addition, Wang himself has continued not only to grow superb and unique heterostructures, but also to develop and demonstrate several exciting new device structures. These include a GaAs MQW

optical-waveguide modulator on Si, an electron-hole plasma screened optical switch, and finally, several resonant interband tunneling devices.

New optical surface diagnostics studies have also been initiated. Osgood has developed new UHV techniques for the study of metal-alkyl surface reactions which use total internal reflection spectroscopy. Herman has made use of a high pressure diamond anvil to study SiGe strained MQW's. Finally, Wang in his study on plasma screening, used both Raman scattering and photoluminescence to determine the carrier density necessary to screen the internal electric fields in the GaSb/AlSb heterostructure.

Finally, Auston and coworkers have made significant progress in understanding and developing the practical applications of femtosecond techniques for generating submillimeter waves at semiconductor surfaces. The technique does not require electrical contact to the material and is capable of measuring the sign and magnitude of the space charge fields at semiconductor surfaces. It can also be used to measure the internal fields of strained-layer superlattices.

B. Objective

The objective of this URI research program is "to form an interdisciplinary research center to study several prominent classes of interfacial reactions which are important in the fabrication of submicrometer circuits and devices."

The ONR/URI funding has enabled Columbia to establish this new interdisciplinary research center on campus, the Microelectronics Sciences Laboratories (MSL). This center draws from the resources of three departments--Chemistry, Electrical Engineering, and Applied Physics. It has directly enabled three well known scientists to initiate their university research careers at Columbia: Professor Wen Wang, Professor Irving Herman and Professor David Auston. In addition, two new junior professors have initiated research in the surface chemistry of electronics materials. Their research has been aided indirectly by the equipment and research orientation at Columbia established by the ONR program: Professor Robert White, polymers for packaging (Department of Electrical Engineering) and Professor Brian Bent, the surface chemistry of CVD

growth (Department of Chemistry). We are currently planning to integrate these researchers into our complementary JSEP program.

The ONR program has been aided substantially by matching industrial gifts or complementary research programs in the area of our research program. These programs include funds for the surface chemistry of polymeric materials for packaging and metal CVD growth, and processing for pressure sensors. Contributing members to our program include Kulite Semiconductor, Hughes Research, IBM, and DuPont.

Both Professor Osgood and Herman have continued their numerous industrial interactions on research in laser processing and diagnostics. In this last year, the most notable new emphasis is in patterned CVD growth of aluminization and ultrashallow doping of GaAs. In this area, they have interacted with IBM, SRC, and Bellcore. Osgood has initiated a new program in laser-assisted semiconductor surface chemistry with IBM, and Herman has continued in his development of new direct-write diagnostics, also in collaboration with IBM. In addition, also in the area of laser diagnostics, Professor Flynn has had extensive interactions with Jim O'Neill at IBM East Fishkill on the use of diode laser diagnostics of plasma processing. Professor Turro has continued his collaborations on the mechanisms of photoresists with IBM scientists at East Fishkill and Almaden.

C. Capital Equipment Purchased in FY 89/90

RD200/CCD Raman Detection System	$31,150.00

D. Naval Research Laboratory Interactions

Professor Wen I. Wang continued collaboration with Dr. Ben Shanabrook (NRL) on the optical properties of (111) GaSb/AlSb multiple quantum wells. As a result, three papers were presented or published. In addition, Professor Wang continued collaboration with Dr. Robert J. Wagner (NRL) on the properties of two-dimensional holes in modulation-doped p-type AlSb/GaSb

heterojunctions. As a result, a paper was presented at the March meeting of the American Physical Society- (R.J. Wagner and W.I. Wang, "Hole Cyclotron Resonance in GaSb/AlSb Multiple Quantum Wells," Bull. Am. Phys. Soc. 35, 825 (1990)).

As part of a recently initiated program by Professor Yang and Dr. Ma, Drs. Wulff and Reeves of NRL agreed to measure the electrical and magnetic properties of specimens of high T_c superconducting devices in their system, testing for very high sensitivity in thin film applications. We have sought collaborative interactions with NRL in this connection. High T_c thin film samples of $Y_5B_6Cu_{11}O_y$ have been shown to contain a superconducting anomaly up to 160° K. Resistive specimens measured at Columbia University indicated a transition in this range. Professor Yang, Dr. Weinman and Dr. Ma visited Washington, where the NRL staff were kind enough to retest our samples. Columbia is pursuing the possibility that an unstable phase transition is responsible for our resistive measurements. Dr. Wulff offered to help us build a similar test system for thin films, and this will be pursued.

Professor Flynn had discussions in 1990 with Dr. Jane Rice of the Naval Research Laboratories, in the area of chemical and collision dynamics. His past interactions with NRL have included a visit to the Naval Research Laboratories where he gave a seminar in 1988 and service on the Navy Scientific Evaluation Panel in Washington in 1988. Professor Herman had discussions with and sent his publications to O. Glembocki at the Naval Research Laboratory.

E. IBM Program

The ONR-URI program at Columbia has been matched with Columbia's IBM Program in Electronics Materials and Materials Processing. This original match has continued to have concrete intellectual feedback into the ONR program. For example, Professor White's program (supported only by IBM) in polymer interfacial chemistry has provided added emphasis in our emerging interest in the complex materials of electronic packaging area. His program together with work being done in Professor Auston's and Bent's group have recently been given additional support by IBM for other areas of packaging research.

More recently, a decision has been made by the Microelectronics Sciences Labs to use a significant amount of the IBM grant to construct a new system for the growth of SiGe alloy material. This system will be constructed as part of the UHV-MPS system purchased by the ONR contract. The research to be done on these in situ deposited alloys will involve surface processing and device fabrication. The apparatus will include a several electron-beam evaporator, UPS lamp (for surface diagnostics) and a heatable substrate. The apparatus will not only extend Columbia's surface science capability but will allow growth of Group IV as well as the III-V semiconductors (presently in Professor Wang's lab).

In other areas, Professor Flynn has collaborated with Dr. Phaedon Avouris, IBM Watson Laboratories, Yorktown Heights, NY, regarding efforts aimed at scanning tunneling microscope studies of surface photochemistry and the use of lasers to enhance the sensitivity and selectivity of the STM process. Professor Turro has continued baseic investigations of the photochemistry of models of polyimides with Dr. Kelvin Welsh of IBM at East Fishkill, and Dr. Nigel Hacker at Almaden. Finally, Professors Herman and Osgood also had many discussions concerning their work with S. Gilliespie, W. Natzle, J. Hu and D. Podlesnik at IBM, East Fishill, and have visited them this past year.

II. PROGRESS REPORTS

A. MBE GROWTH AND DEVICES

1. Heterostructures Grown by Molecular Beam Epitaxy

Professor Wen Wang, Principal Investigator

a. We have demonstrated the first GaAs multiple quantum well (MQW) optical waveguide modulator on Si substrates. The modulators were operated at wavelengths of 890-910 nm, with greater than 20 dB modulation for a reverse bias of 2.5 V. This performance is at the state-of-the art level. All previous reports used vertical incidence geometry, which does not place stringent requirements on heterointerface smoothness, and that structure is not ideally suitable for integration. Waveguide geometry is better for integration with Si-based electronics since one can etch V-grooves on Si to adapt optical fibers. The results were published in Appl. Phys. Lett. 57, 1078 (1990).

b. We demonstrated optical induced screening of the strain-induced electric fields in the (111) GaSb/AlSb multiple quantum wells. Theoretical studies have indicated that strained-layer multi-quantum wells grown in the (111) axis exhibit band structures that are modified by built-in electric fields that arise from the piezoelectric effect, while those grown on (100) substrate will not. If these internal electric fields can be screened by optically generated carriers (electron and hole pairs), these (111) strained-layer quantum wells can be used as optically-controlled optical modulators and switches. Right now, other than the GaAs/AlGaAs quantum well SEED device invented by D.A.B. Miller of AT&T Holmdel, there is really no other semiconductor-based optical-controlled optical switch. We have demonstrated experimentally by photoluminescence and Raman scattering for the first time that strained-induced internal electric field (61 kV/cm) in (111) GaSb/AlSb multi-quantum wells can be screened completely by a plasma density of 10^{12} cm^{-2}. The bandgap of this material

system matches the 1.3 and 1.55 mm wavelengths of the fiber optical communication system. The results will be published in the Phys. Rev. B November issue,1990.

c. A new mechanism for negative differential resistance was demonstrated in broken gap heterostructures of InAs/GaSb/InAs and GaSb/InAs/GaSb in follow-up to our previous studies of interband tunneling in InAs/AlSb/GaSb double barrier structures. These structures represent the zero barrier thickness limit of double barrier resonant interband tunneling structures we reported during last year and exhibit negative differential resistance due to electron/light hole coupling. For example, in a GaSb/InAs/GaSb structure, light holes in the GaSb valence band couple with a quasibound electron state in the InAs layer. Our results demonstrate that even in the absence of a true barrier region, confinement still occurs due to mismatch of the electron and light hole wave functions at the InAs/GaSb interface. The state in the well has a highly reduced lifetime due the absence of strong confinement. As a result, these devices exhibit high peak current densities. Furthermore, the fast intrinsic response of these structures implies that performance will be limited by the extrinsic resistance and capacitances of the device. Peak-to-valley ratios of 2:1(3.7:1 at 77K) have been observed in these structures, which are lower than what is typically observed in resonant interband double barrier structures. This reduction in peak-to-valley ratio is due to less efficient bandgap blocking in the absence of AlSb barriers. Nonetheless, these peak-to-valley ratios are the highest for single barrier devices and should be adaquate for high-speed applications which require the high current densities achievable in these devices. The results were published in J. Appl. Phys. **68**, 2854 (1990).

d. Resonant interband tunneling in InAs/GaSb/AlSb/InAs and GaSb/InAs/AlSb/GaSb structures has been observed for the first time. These structures offer large peak-to-valley ratios at higher peak current densities than previous double-barrier interband tunneling results. Room temperature peak-to-valley ratios as high as 20:1 were observed at peak current densities of 28 kA/cm^2. The highest peak-to-valley ratio observed at 80 K was 80:1 at 1.2 kA/cm^2. At these high current densities, these values represent the highest peak-to-valley ratios measured in polytype tunneling structures. The large peak-to-valley ratios are attributed to resonant interband tunneling with a confined state and bandgap blocking of nonresonant currents. Thus, these structures combine the high peak-to-valley ratios of double-barrier

polytype structures and high current densities of resonant interband coupling devices and once again demonstrate that even in the absence of a true "barrier," confinement of a quasibound state in the well region still occurs. Peak-to-valley ratios comparable to double-barrier structures are exhibited since bandgap blocking occurs in one bias direction due to the presence of an AlSb barrier. Also as with interband coupling results, the small total barrier thickness results in a well state with a very short lifetime and thus a device with a fast intrinsic response time. The high peak current densities and large peak-to-valley ratios achievable with this structure along with reduced parasitics associated with the material system make this structure an attractive candidate for high speed two- and three- terminal devices. The results are accepted for publication in Appl. Phys. Lett. Oct 8 issue, 1990.

e. We have observed multiple negative differential resistance regions in resonant interband tunneling devices. Vertically integrated polytype heterostructures of InAs/AlSb/GaSb have advantages for low-power high speed circuit applications of multistable components. The peak voltages are reduced by a factor of 2 compared to the AlInAs/GaInAs material system, while high peak-to-valley ratios of 4:1 (17:1) at 300K (77K) are maintained. We also proposed a high-density memory cell that uses the multiple NDR regions of a resonant tunnel diode.

ONR PUBLICATIONS FOR THIS WORK UNIT:

K.F. Longenbach, L.F. Luo, and W.I. Wang, " Resonant interband tunneling in InAs/GaSb/AlSb/InAs and GaSb/InAs/AlSb/GaSb heterostructures." to appear, Appl. Phys. Lett., Oct. 8, 1990.

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K.F. Longenbach, L.F. Luo, S. Xin and W.I. Wang, "Resonant tunneling in polytype InAs/AlSb/GaSb heterostructures." Invited paper at the Sixth International Conference on Molecular Beam Epitaxy, San Diego, CA. August, 1990; to be published in J. Crystal Growth, 1991.

J.I. Song, D.V. Rossi, S. Xin, W.I. Wang, and E.R. Fossum, " A resistive-gate planar-doped AlGaAs/GaAs 2DEG CCD for III-V IR detectors." sub. to Appl. Phys. Lett., July, 1990.

B.V. Shanabrook, D. Gammon, R. Beresford, W.I. Wang, and R.P. Leavitt, "Optically induced screening of the strain induced electric fields in (111) GaSb/AlSb quantum wells," papers presented at the 20th Int. Conf. on the Physics of Semiconductors, Thessaloniki, Greece, August 6-10, 1990.

B.V. Shanabrook, D. Gammon, R. Beresford, and W.I. Wang, "Optical induced variability of the strain induced electric fields and band structure in (111) GaSb/AlSb quantum wells," Bull. Am. Phys. Soc. 35, 572 (1990).

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R. Beresford, L.F. Luo, and W.I. Wang, "Interband tunneling through single barrier InAs/AlSb/GaSb heterostructures," Appl. Phys. Lett. 56, 952 (1990).

R. Beresford, L.F. Luo, K.F. Longenbach, and W.I. Wang, "Resonant interband tunneling through a 110 nm InAs quantum well," Appl. Phys. Lett. 56, 551 (1990).

W. Hansen, T.P. Smith III, J. Piao, R. Beresford, and W.I. Wang, "Magnetoresistance measurements of doping symmetry and strain effects in GaSb/AlSb quantum wells," Appl. Phys. Lett. 56, 81 (1990).

J.-I. Song, D. V. Rossi, S. Xin, W. I. Wang, and E. R. Fossum, "Large Bandwidth (13 KHz - 1 GHz) Planar-Doped 2DEG-CCD with High Transfer Efficiency at Room Temperature (abstract)," to appear, IEEE Trans. Electron Devices, November 1990.

J. I. Song, D. V. Rossi, S. H. Xin, W. I. Wang and E. R. Fossum, "A Resistive-Gate AlGaAs/GaAs 2DEG CCD with High Transfer Efficiency at 1 GHz," sub. to IEEE Trans. Electron Devices, May 1990.

J.-I. Song, D. V. Rossi, S. Xin, W. I. Wang, and E. R. Fossum, "A Resistive-Gate $Al_{0.3}Ga_{0.7}As$/GaAs 2DEG-CCD with High Charge Transfer Efficiency at 1 GHz," sub. to IEEE Trans. Electron Devices, May 1990.

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2. High Performance GaAs Charge-Coupled Devices

Professor Eric R. Fossum, Principal Investigator

GaAs CCD's are important in many demanding signal processing applications because of their high speed, low noise and radiation hard capability coupled with their compatibility with III-V electro-optic devices. Potential applications include radar signal processing, spatial-light modulator (SLM) multiplexers, high-speed readout for acousto-optical tunable filters (AOTF), fast-in/slow-out signal acquisition for high-speed sampling, and for multiplexers in advanced IR, UV and X-ray image sensors. Because of the emergence of III-V LWIR detectors, we have focussed on CCDs for monolithic multiplexing of these detectors.

During the past year, a breakthrough in III-V CCDs was accomplished. The first resistive-gate two-dimensional electron gas (2DEG) CCD was demonstrated, and it exhibited very good performance. The first 2DEG-CCD was fabricated completely at Columbia. The material layers (GaAs, AlGaAs) were grown by MBE under the direction of Professor Wang, and had a uniformly-doped AlGaAs layer. The room temperature CTE exhibited by this device had a charge transfer efficiency greater than 0.9997 at frequencies up to 1 GHz (our test station limit). Dark current was high however, and limited low frequency operation to 13 MHz.

A planar-doped AlGaAs layer structure was then investigated. The resultant CTE was 0.9997 and it had reduced dark current, enabling low frequency operation to 130 kHz. The origin of the dark current was then investigated theoretically and by experiment. It was shown that thermionic-field emission across the AlGaAs layer dominates dark current behavior and excellent agreement between experiment and theory was obtained over a wide temperature range. A new p-i-n doped AlGaAs structure has been proposed to further reduce dark current. This work has been performed, in part, in collaboration with NASA/JPL (Dr. J. Maserjian).

A new 2-phase 2DEG-CCD was invented and demonstrated for the first time. A 2-phase device has simplified clocking requirements compared to the 4-phase devices described above,

and eliminates power dissipation in the resistive-gate during integration of images, significantly enhancing low temperature performance.

The 2DEG-CCD concept has also been investigated for the InAlAs/InGaAs/InP material system as well, in collaboration with Professor Wang, and with IBM Research (Dr. P. Kirchner and Dr. J. Woodall). Buried-channel CCD configurations are also under investigation. Such a CCD would serve as a monolithically integrated high QE SWIR image sensor since the cut-off wavelength of InGaAs extends significantly beyond that of silicon.

ONR PUBLICATIONS FOR THIS WORK UNIT

J.-I. Song, D. V. Rossi, S. Xin, W. I. Wang, and E. R. Fossum, "Large Bandwidth (13 KHz - 1 GHz) Planar-Doped 2DEG-CCD with High Transfer Efficiency at Room Temperature (abstract)," to appear, IEEE Trans. Electron Devices, November 1990.

J. I. Song, D. V. Rossi, S. H. Xin, W. I. Wang and E. R. Fossum, "A Resistive-Gate AlGaAs/GaAs 2DEG CCD with High Transfer Efficiency at 1 GHz," submitted to IEEE Trans. Electron Devices, May 1990.

J.-I. Song, D. V. Rossi, S. Xin, W. I. Wang, and E. R. Fossum, "A Resistive-Gate $Al_{0.3}Ga_{0.7}As$/GaAs 2DEG-CCD with High Charge Transfer Efficiency at 1 GHz," submitted to IEEE Trans. Electron Devices, May 1990.

J.-I. Song, D. V. Rossi, S. Xin, W. I. Wang, and E. R. Fossum, "A Resistive-Gate Planar-Doped AlGaAs/GaAs 2DEG CCD for III-V IR Detectors," submitted to Appl. Phys. Lett., July 1990.

E. R. Fossum, J.-I. Song, and D. V. Rossi, "Two-Dimensional Electron Gas Charge-Coupled Devices (2DEG-CCDs)," submitted to IEEE Trans. Electron Devices, August 1990.

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3. Interface Chemical Modification of Metal on Superconductor-Semiconductor Systems

Professor E. S. Yang, Principal Investigator

Research Scientists, X. Wu and Q. Y. Ma

a. AlGaAs/GaAs Heterostructure-Emitter Bipolar Transistor

Over the past year, we have fabricated a new structure of heterojunction bipolar transistor (HBT) in which the base-injected carriers are confined by band offset inside the emitter so that a high injection efficiency is maintained. This transistor combines the merits of homojunction transistor and the conventional HBT, and it is simple to fabricate.

Figure 1 shows the band diagram of the new device. Compared with a conventional HBT, the heterojunction is moved away from the emitter-base junction. However, the carrier injection mechanism is the same as in a homojunction transistor. The influence of the conduction-band discontinuity is minimized since it is pushed into the quasi-neutral region of the emitter where the hole reflection barrier still exists, blocking the base-injected carriers into the emitter.[1]

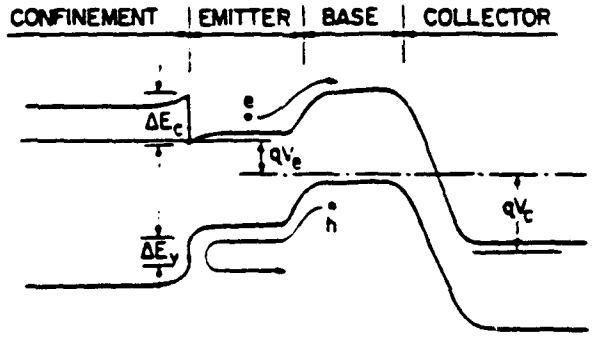

Figure 1. Energy-band diagram of the heterostructure-emitter bipolar transistor. Compared to a conventional heterojunction bipolar transistor, the heterointerface is moved into the quasi-neutral region of the emitter.

[1]L. F. Lou, H. L. Evans, and E. S. Yang, "A heterojunction bipolar transistor with separate carrier injection and confinement," IEEE Trans. Elec. Dev. 36(9), 1844 (1989).

The transistor was made of AlGaAs/GaAs materials. The sectional structure of the device, grown by molecular beam epitaxy, is shown in Figure 2. AuGe/Ni and Pt are used for the emitter and base contacts, respectively. One of the typical common-emitter characteristics of this device is shown in Figure 3. A differential current gain of about 28 is observed at a collector current of I_C=70mA, corresponding to an emitter current density of 1100A/cm.[1] This result is very good considering that a doping ratio of 10 between the base and the emitter was used. With such a high doping ratio, a gain of only about 0.1 would be expected in a homojunction transistor. It proves that the idea of carrier confinement indeed works. Compared with conventional HBT's, this transistor exhibits a very low offset voltage (V_{offset} < 0.2 V). This advantage is attributed to the use of a homojunction for emitter current injection. Such a homojunction results in another benefit: the gain of the transistor was found to be very uniform across the wafer. It suggests that the gain of this device is not sensitive to the base doping fluctuation. In addition to the common-emitter current gain, the breakdown voltage of the transistor has been measured as well. The average BV_{CEO} is measured to be 1.5 V. Such a value of BV_{CEO} is difficult to achieve in homojunction transistor with a similar short base.

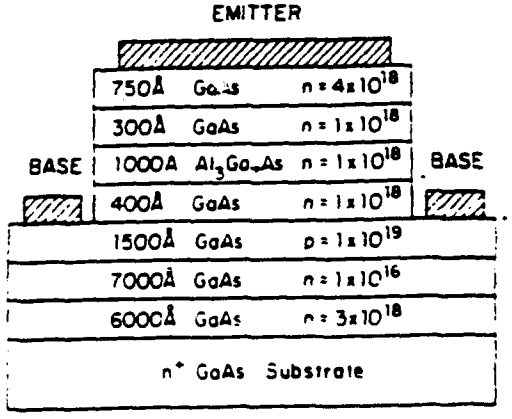

Figure 2. Schematic structure of the heterostructure-emitter bipolar transistor with a 400 Å n-GaAs confinement layer.

[1]X. Wu, Y. Q. Wang, L. F. Luo, and E. S. Yang, "An AlGaAs/GaAs heterostructure-emitter bipolar transistor," IEEE Elec. Dev. Let. 11(6), 264 (1990).

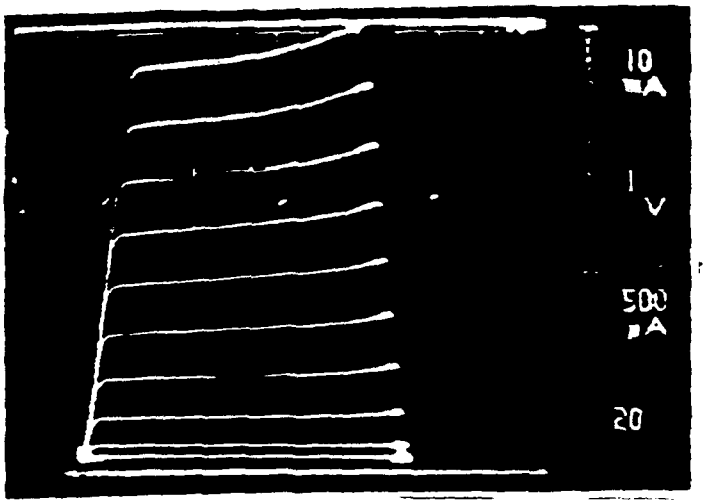

Figure 3. Common-emitter characteristics for the heterostructure-emitter transistor, which shows a current gain of ~ 28 at I_c = 70 mA and an offset voltage less than 0.2 V.

b. High T_c Superconductor Interfaces

We have continued high temperature superconducting (HTS) thin films work in collaboration with Dr. C. A. Chang of IBM Watson Research Center. Our goal is to understand the interfacial problems between HTS materials and normal materials (metals and semiconductors) which will allow us to develop superconductor-semiconductor hybrid devices and HTS interconnects. The project has been carried out in the following areas.

(1) Properties of Metal-YBCO Interfaces and Proximity Effect

An important obstacle for microelectronic applications of $YBa_2Cu_3O_7$ (YBCO) high temperature superconducting materials is the development of stable, low resistance metal contacts to the material. The proper choice of contact metal and surface preparation are crucial to achieve the necessary resistivity and stability.

We have investigated metal contacts to YBCO superconducting thin films by X-ray photoelectron spectroscopy (CPS) and electrical characterization.[1,2] Metals (Ti, Cu, Sn, Nb, Au, Pd) were deposited onto sputter-cleaned YBCO films in an ultrahigh vacuum chamber. XPS was performed in situ immediately after the metal deposition. The results of XPS indicate that the reactive metals (such as Ti, Cu, Sn, and Nb) react strongly with oxygen, forming an oxide layer at the interface and a non-superconducting layer due to depletion of oxygen in the surface of the YBCO. These layers reduce the current flow drastically and cause a large contact resistivity at the interface.

For Au contacts, no significant reaction was observed at the Au/YBCO interface. More interestingly, the contact resistance for Au (R_c) has the same temperature dependence as the YBCO film resistance, as shown in Figure 1. That is, it decreases linearly with temperature from 300 K to 82 K, and then drops dramatically at 79 K, similar to the point where the film becomes superconducting. At 77 K, the contact resistance can approach zero, leaving only the resistance of the metallic contact material. This is due to the proximity effect at the Au/YBCO contact.

The proximity effect is a phenomenon in which the Cooper pairs in a superconductor diffuse across the superconductor-normal material (N-S) interface to form an induced superconducting layer in a normal material. The induced superconducting region is characterized by the coherence length of the material, and it depends strongly on the quality of the interface and on the normal material chosen. The coherence length of the YBaCuO system is on the order of a few angstroms or a few tenths of angstroms, depending on the orientation. In comparison, the coherence length of a metal reaches a few hundred nm at 77K.[3] A good metal-YBCO interface could not only extend the coherence length of YBCO for Josephson tunneling junction

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[1]M. T. Schmidt, Q. Y. Ma, L. S. Weinman, X. Wu, E. S. Yang, and Chin-An Chang, "Chemistry and Resistance at Metal Contacts to $YBa_2Cu_3O_7$ High T_c Superconducting Thin Films," presented at AVS 36th National Meeting, Boston, MA (October 1989); to be published in AIP Conf. Proc.

[2]Q. Y. Ma, M. T. Schmidt, L. S. Weinman, E. S. Yang, and Chin-An Chang, "Studies of thin metal contacts to high T_c superconducting films," presented (post-deadline paper) at APS Meeting, Anaheim, CA (March 1990).

[3]Q. Y. Ma, "Physical and Material Properties of High T_c Superconducting Thin Films," Ph.D. thesis, Columbia University, May 1990.

applications, but also prevent the YBCO surface from degradation. The formation of even a very thin insulator or interface disruption can inhibit the contact from showing proximity effects to the superconductor.

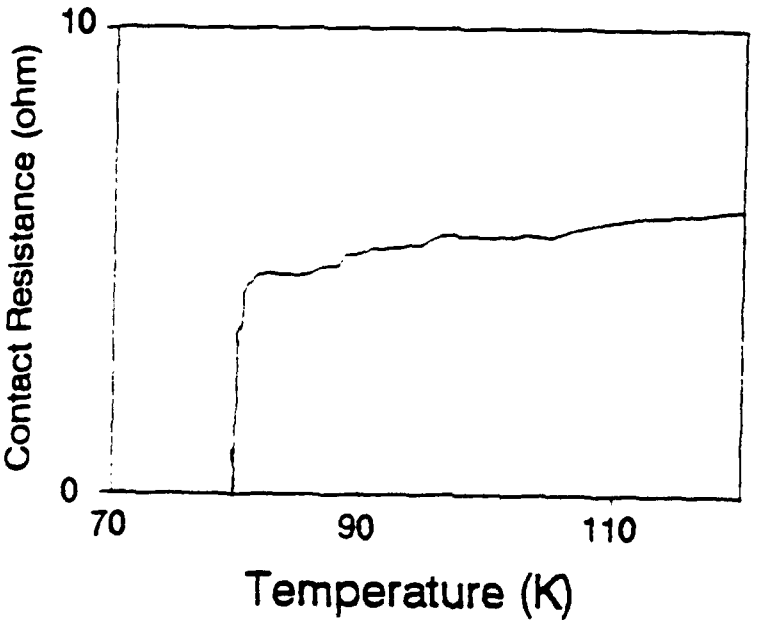

Figure 1. Temperature-dependent contact resistance of a Au/YBCO film interface.

Au does not react with YBCO as indicated by XPS. Thus, a good contact is expected for Au/YBCO interfaces. Confirmation of the proximity effect can be made from a current-voltage (I-V) relation of a metal-superconductor contact. Figure 2 shows the I-V curves of a Au/YBCO contact. At 300 K the curve is linear, indicating a resistive relation. However, at 77 K there is a superconducting current flow through the contact, even at a zero voltage bias.

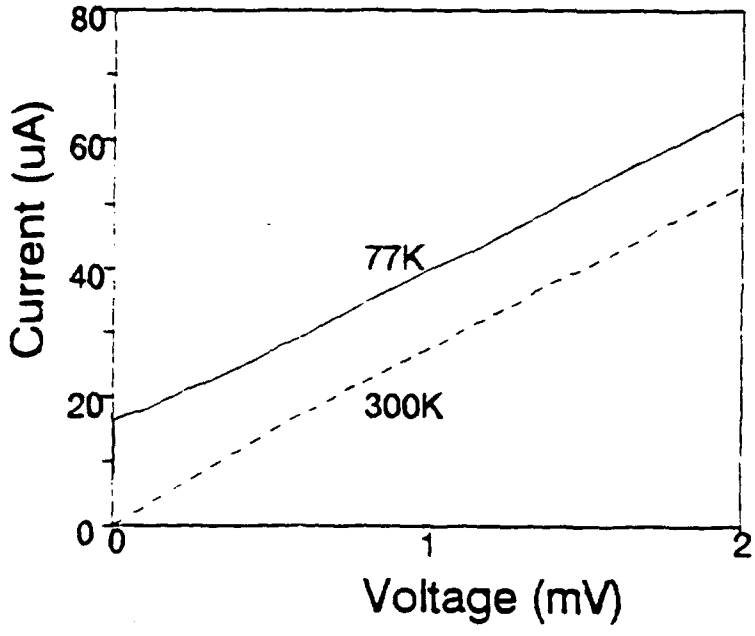

Figure 2. Current-voltage relations for a Au/YBCO contact measured at 77 K and 300 K.

(2) HTS Interconnects on Si Substrates

An important application of high temperature superconductor (HTS) to electronics is the development of superconductor-semiconductor hybrid devices and superconducting interconnects. This requires the formation of HTS structures on a semiconductor substrate. Technically, it is much more difficult than on an insulating substrate. Most semi-conductors, except silicon, cannot withstand high temperature processing needed for making the HTS films. For a silicon substrate, due to the large difference in lattice constant and thermal expansion coefficient between silicon and YBaCuO materials, the interdiffusion and reaction at the Si-YBaCuO interface destroy the superconductivity of the film.[1,2] Furthermore, patterning of HTS films usually involves chemicals that degrade the surface of the HTS material.

[1]Q. Y. Ma, X. Wu, M. T. Schmidt, E. S. Yang and Chin-An Chang, "Interdiffusion between Si substrates and YBaCuO films," Physica C 162-164, 607 (1989).

[2]Q. Y. Ma, E. S. Yang and Chin-An Chang, "Rapid thermal annealing of YBaCuO thin films deposited on SiO2 substrates," J. Appl. Phys. 66, 1866 (1989).

We have studied material properties of a Si-YBaCuO intermixed system. We found that silicon reacts strongly with oxygen and forms silicon oxides during the high temperature process. The oxide destroys the crystalline structure of the YBaCuO material, and the mixed film becomes insulating. We also found that a metal buffer layer can reduce the film-substrate interaction. Thus, a superconducting thin film is formed on a silicon substrate. We chose Au as a buffer because Au could effectively reduce the silicon diffusion[1] and Au was found to be nonreactive with YBaCuO. In fact, the film conductivity was improved through intermixing with a Au layer. Furthermore, Au can be used as a good electrical path between the HTS interconnects and the semiconductor active devices.

These results led us to fabricated HTS interconnects on silicon substrates using the Si-YBCO intermixing technique.[2,3] On a silicon substrate, a thin layer of Au was first evaporated and patterned using photolithography. A YBaCuO film was then deposited by e-beam evaporation and annealed in a rapid thermal processing system. After high temperature annealing, the patterned feature became superconducting, separated by Si-YBaCuO intermixed areas which are insulating. We have demonstrated superconducting micron-sized line structures with T_c of 73 K.[4] This patterning technique is especially useful for making high T_c superconducting interconnects and devices on a Si wafer.

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[1]Q. Y. Ma, X. Wu, M. T. Schmidt, E. S. Yang and Chin-An Chang, "Interdiffusion between Si substrates and YBaCuO films," Physica C 162, 607 (1989).

[2]Q. Y. Ma, G V. Treyz, C. Shu, E. S. Yang and Chin-An Chang, "A novel method for patterning YBaCuO superconducting thin films," Appl. Phys. Lett. 55, 896 (1989).

[3]Q. Y. Ma, E. S. Yang, G. V. Treyz, C. Shu, R. M. Osgood, Jr., and Chin-An Chang, "Use of Si-YBaCuO intermixed system for patterning of superconducting thin films," presented at the MRS 1989 Fall Meeting, Boston, MA, (Nov.-Dec. 1989); to be published in the proceedings of the MRS 1989 Fall Meeting.

[4]Q. Y. Ma, C. Shu, E. S. Yang, and Chin-An Chang, "Patterning of High T_c Superconducting Thin Films on Si Substrates," presented at the Symposium, "Superconductivity Applications for Infrared and Microwave Devices," of OE/Aerospace Sensing Conf., Orlando, CA (April 1990); to be published in OE/Aerospace Sensing Conf. Proc.

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Q. Y. Ma, E. S. Yang and Chin-An Chang, "Rapid Thermal Annealing of YBaCuO Thin Films Deposited on SiO2 Substrates," J. Appl. Phys. 66, 1866 (1989).

Q. Y. Ma, M. T. Schmidt, L. S. Weinman, E. S. Yang, and Chin-An Chang, "Studies of Thin Metal Contacts to High Tc Superconducting Films," presented (post-deadline paper) in APS 1990 March Meeting in Anaheim, CA.

Q. Y. Ma, C. Shu, E. S. Yang, and Chin-An Chang, "Patterning of High Tc Superconducting Thin Films on Si Substrates," to be published in Proc. of the OES/Aerospace Sensing Conf, Orlando, CA, April 1990.

B. LASER SURFACE INTERACTIONS

1. Laser Surface Interactions and In Situ Diagnostics of Surface Chemistry During Electronic Processing

Professor Richard M. Osgood, Jr., Principal Investigator

Associate Research Scientist, Dr. Michael Schmidt

Postdoctoral Fellows, Dr. Quinyun Yang and Dr. Xiaoge Zhang

a. Introduction

During this past year, this research program has concentrated on three separate investigations: ECR Plasma and UV-induced oxidation and oxide removal (surface cleaning) of GaAs; metal alkyl surface chemistry on well characterized semiconductor surfaces; and laser photoelectrochemical etching of SiC. In the first investigation, we have used UHV diagnostics in the form of high resolution XPS and He^+ISS to study UV enhanced oxidation and the chemistry of oxidation and reactive surface cleaning by an ECR plasma source (from IBM). The investigation has had two major successes: 1) the first clear indication of thin film growth enhancement by photoelectron injection, and 2) a new method of low temperature oxide removal and surface preparation on GaAs surfaces. This project has been undertaken with important cooperation with Professor Yang who shares the usage of the UHV system. Our work on metal-alkyl spectroscopy has focused on the design and construction of a new UHV system which combines infrared total internal spectroscopy and time-of-flight spectroscopy, as well as more conventional probes. As of this report we are one month from our first experiment on this apparatus. The final project involves an electrochemical study of several SiC-aqueous solution systems in order to realize photoelectrical chemical etching of SiC. This study was undertaken in collaboration with Kulite Corporation in New Jersey. The electrochemical study result is a new method for extremely rapid etching of SiC.

b. Fundamental Study of Photooxidation of GaAs

We have carried out extensive investigations of the photoenhanced oxidation of GaAs surfaces and the low temperature removal of GaAs-oxides with electron cyclotron resonance (CER) hydrogen plasma. The ECR plasma work is performed in collaboration with W. M. Holber at IBM T. J. Watson Laboratory, who designed and donated the custom made source we have mounted on our UHV surface analysis system, and J. Forster and D. V. Podlesnik of the IBM General Technology Division. The following discussion highlights some of the important conclusions we have established in this work.

The ultraviolet (UV) photochemistry of semiconductor surface reactions has been of intense interest for both fundamental and practical reasons.[1-4] This interest originates in part because these surfaces represent prototypical covalently bounded systems whose experimental methods of preparation and whose crystallographic structure are known in precise detail. In addition, semiconductor surfaces present an excellent opportunity to study systems in which chemical reactions can proceed via either direct photoexcitation of adsorbate molecules, or by excitation of the semiconductor to create either thermalized or excited electron-hole pairs. Since the optical absorption depths of UV light in semiconductors can be extremely short, i.e. 50 Å,[5] both energetic and thermalized free carriers are efficiently provided in the near-surface region of semiconductors.

It has been previously clearly established that the initial oxidation of a GaAs surface can be enhanced by visible-light creation of electron-hole pairs. These studies have shown that the presence of photons above the band-gap energy of GaAs (1.43 eV) leads to an increase in the sticking coefficient of molecular oxygen on GaAs by about three orders of magnitude.[6] The enhanced sticking coefficient has been attributed to carrier-induced chemistry. Photogenerated

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[1]R. M. Osgood and T. F. Deutch, Science 227, 709 (1985) and references therein.
[2]T. J. Chuang, Surf. Sci. 178, 763 (1986) and references therein.
[3]M. T. Schmidt, D. V. Podlesnik, H. L. Evans, C. F. Yu, E. S. Yang, and R. M. Osgood, Jr., J. Vac. Sci. Technol. A6, 1446 (1988).
[4]Ph. Avouris and R. E. Walkup, Annu. Rev. Phys. Chem. 40, 173 (1989) and references therein.
[5]H. C. Casey, D. D. Sell, and K. W. Wecht, J. Appl. Phys. 46, 250 (1975).
[6]W. G. Petro, I. Hino, S. Eglash, I. Lindau, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. 21, 405 (1982).

carriers formed with visible illumination are thought either to increase oxygen adsorption through charge transfer, as mentioned above for other compound semiconductors, or to assist in the dissociation of O_2 through carrier recombination,[1] or the formation of negatively ionized adsorbed oxygen.[2] Whatever the mechanism, GaAs oxidation enhancement with visible photons has been shown to saturate near one monolayer (ML).[3,4]

In our work, we describe a sharp increase in the photoenhanced oxidation rate of GaAs in the presence of deep-UV radiation ($4.1 < h\nu < 5.1$ eV). In contrast to the previous experiments with visible light, the deep-UV light reaction enhancement occurs at oxide coverages > 1 ML, allowing the oxide coverage to exceed several ML. Our results suggest that in addition to affecting the adsorption and dissociation of oxygen on the GaAs surface, deep-UV photogenerated carriers can also stimulate the reaction by enhancing the mass transport of the oxidant to the GaAs/oxide interface where the oxidation reaction occurs.

The photon-energy threshold for the process is in close agreement with the threshold for internal photoemission of electrons into GaAs-oxide, a process which would greatly increase the electron density at the surface of a thin GaAs-oxide. This increase in the carrier density at the surface could have a large effect on O_2 adsorption and oxidant transport, through electron attachment to O_2 to form negative oxygen ions at the oxide surface. Our experimental observations are consistent with this photogenerated increase in the electron concentration in the oxide. Similar processes would be expected to occur in thin layers of products from other electronegative reactants, such as fluorine or chlorine on semiconductor surfaces.

Our work on oxide removal by ECR hydrogen plasma has large potential for molecular beam epitaxy applications. While MBE growth techniques have enjoyed great success for the fabrication of semiconductor materials with novel electrical properties, the regrowth of materials on

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[1]K. A. Bertness, P. H. Mahowald, C. E. McCants, A. K. Wahi, T. Kendelewicz, I. Lindau, and W. E. Spicer, Appl. Phys. A47, 219 (1988).
[2]W. Monch, Surf. Sci. 168, 577 (1986).
[3]K. A. Bertness, T. T. Chiang, C. E. mcCants, P. H. Mahowald, A. K. Wahi, T. Kendelewicz, I. Lindau and W. E. Spicer, Surf. Sci. 185, 544 (1987).
[4]V. M. Bermudez, J. Appl. Phys. 54, 6795 (1983).

previously processed wafers has not been extensively exploited. The main obstacle for GaAs regrowth is that standard growth preparation involves thermal cycling of a substrate to ~600° C to remove surface oxides and other contamination. Besides its inefficiency in removing carbon contamination, this thermal processing degrades the sharp interfaces grown by MBE, especially in the case of superlattice quantum layer materials.

Several groups have found that hydrogen plasmas can be used to effectively remove surface contamination (oxygen and carbon) from GaAs resulting in well ordered surfaces at much lower temperatures than standard techniques.[1-3] The ability to etch, effectively and selectively, GaAs-oxide on a GaAs substrate by a hydrogen plasma[4,5] has stimulated interest in its use for GaAs surface preparation and fabrication.

Although empirical methods for producing MBE growth surfaces with hydrogen plasma cleaning have been developed,[6-8] and several fundamental studies of hydrogen interaction with GaAs have been made,[9-12] the mechanism of the cleaning, and therefore the minimum thermal energy required, has not been determined. We have studied the reduction of the surface oxides on GaAs and the removal of contaminants, with particular attention to the effect of sample heating.

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[1]A. Takmori, S. Sugata, K. Asakawa, E. Miyauchi, H. Hashimoto, Jpn. J. Appl. Phys. 26, L142 (1987).

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[7]S. Sugata, A. Takamori, N. Takado, K. Asakawa, E. Miyauchi, H. Hashimoto, J. Vac. Sci. Technol. B6, 1087 (1988).

[8]N. Kondo and Y. Nanishi, AIP Conf. Proc. No. 167 (Presented at the 34th Nat. Symp. of the American Vacuum Soc., DG-ThA3, Anaheim, CA 1989) (American Institute of Physics, New York, 1988).

[9]O. M'Hamedi, F. Proix and C. Sebenne, Semicond. Sci. Technol. 2, 418 (1987) and references therein.

[10]For H ion effect see: M. Cherchour, F. Proix and C. Sebenne, Rev. Phys. Appl. 22, 285 (1987).

[11]For TDS study see: W. Mokwa, D. Kohl, and G. Heiland, Phys. Rev. B 17, 1816 (1984).

[12]For EELS study of H on GaAs see: H. Luth and R. Matz, Phys. Rev. Lett. 46, 1652 (1981).

In conclusion, ECR hydrogen plasma can effectively clean GaAs surfaces and produce an ordered surface at relatively low temperatures. Our results show that at room temperature, cleaning starts with As-oxide reduction and oxygen removal. Ga-oxide is removed slowly at room temperature, but mold heating expedites the reduction of Ga-oxide. In addition, heating (~ 200°C) subsequent to the hydrogen plasma process is required to remove effects of the hydrogen plasma exposure such as surface hydride formation. However, the reduced temperature used in this work to prepare a clean, stoichiometric, ordered surface suitable for MBE growth is much lower than standard MBE cleaning procedures and thus allows increased opportunities for MBE regrowth on previously grown structures.

c. UHV Study of Metal Alkyl Chemistry

A new UHV system for surface studies is being built and is near completion. The system, equipped with various surface science techniques, will be used to study the reaction of organometallic molecules and, in particular, the laser enhancement of these reactions on semiconductor surfaces. The first experiment will be on the reaction of $(CH_3)_3Ga$ on GaAs surface, which is an important step in growing epitaxial GaAs layers. The purpose of the experiment is to determine the detailed reaction pathway of $Ga(CH_3)_3$ dissociation on and the desorption of species other than Ga atom from the surface and the possible enhancement of the reaction by the use of laser light, which may lead to a low temperature growth process. The experiment will be carried out in collaboration with Professor R. Bersohn in the chemistry department and researchers at IBM (East Fishkill).

The system being built consists of three chambers: one UHV analysis chamber, one UHV reaction chamber and one high pressure reaction chamber. While the chambers can be isolated from one another by gate valves, a sample, which would be mounted on a heatable-coolable manipulator, can be transferred between them. This arrangement makes it possible for the sample to be first exposed to gases in the high pressure chamber under conditions similar to the ones employed in device manufacturing processes and subsequently studied by surface techniques under

UHV conditions. The system will be equipped with several surface analysis and cleaning techniques. Fourier transform infrared spectrometry will be used to do attenuated total reflection (ATR) measurements on semiconductor samples. A differentially pumped mass spectrometer will be used in thermal programmed desorption (TPD), laser induced desorption (LID) and time-of-flight measurements. In addition the system is equipped with a cylindrical mirror analyzer (CMA) with a coaxial electron gun for Auger spectroscopy, a rear view electron diffraction (LEED) apparatus and an ion sputter gun for surface cleaning. The combination of these techniques allows the surface conditions to be defined to the sub-monolayer coverage before an experiment is carried out and the detailed identification of surface species involved in the reaction of organometallic gases on semiconductor surfaces.

d. Rapid Photoelectrochemical Etching of SiC

This research effort represents a collaboration with Kulite Semiconductor, a local sensor company, with the intent of developing a class of new, high-temperature, pressure transducers. SiC is ideal for such high temperature devices because of its important properties such as a wide band gap (2.2 eV), high thermal conductivity, and high dielectric strength. However, SiC is a chemically inert material, making microfabrication in it particularly difficult. We have now achieved the first chemical etching procedure based on photoelectrochemical etching using a focused ultraviolet laser. The samples used were epitaxial n-type β-SiC ($10^{16}/cm^3$) grown by CVD at the NASA Lewis Research Center. Etching was performed in aqueous HF solution under an applied anodic potential. A frequency-doubled Ar^+ laser at 257 nm was focused to a few microns and scanned across the surface to produce microstructures. By varying the potential (0.4-2.0 V_{sce}) and the power density (5-5000 W/cm^2), etch rates between 1-100 μm/min were obtained. The effects of electrode potential and electrolyte composition on the morphology of the etched structures were also investigated. Auger analysis of the surface indicates that a thin (less than 10 Å) carbon rich layer exists on the SiC surface etched in HF solution, while there is a carbon incorporated SiO_2 layer on the surface if the SiC is illuminated in a non-HG solution. The

results suggest that etching proceeds through an anodic SiO_2(C) formation and chemical dissolution of the oxide by HF.

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2. In Situ Optical Diagnostics of Semiconductors Prepared By Laser Chemical Processing and Other Novel Methods

Irving P. Herman, Principal Investigator

Kinetic models were developed to help explain the kinetics of laser-assisted etching of copper films on glass by chlorine. Raman analysis of surface-bound CuCl and $CuCl_2$ products and the Cu_2O protective layer was reported last year. Raman analysis of the laser oxidation of Cu films to form very thin Cu_2O films began this year. Figure 1 shows a representative Raman spectrum of laser-fabricated Cu_2O.

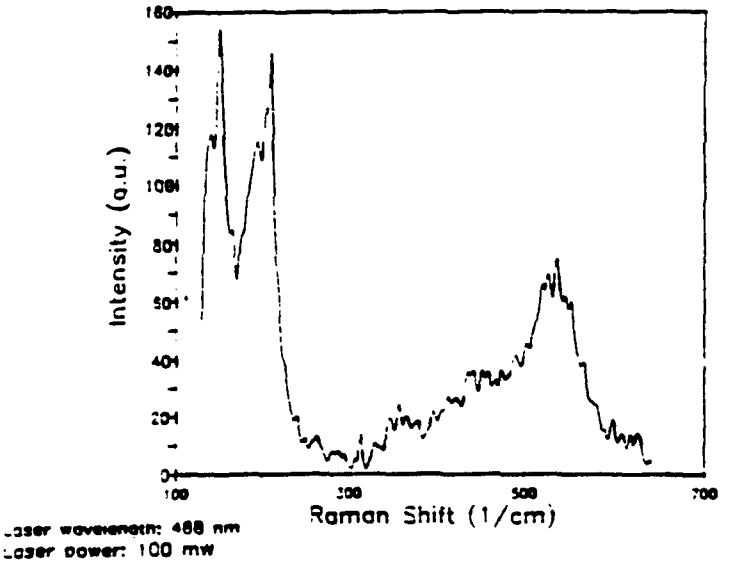

Figure 1. In Situ Raman spectrum of laser-fabricated Cu_2O showing the three prominent peaks.

Sometimes locally molten regions are formed in laser chemical processing of interfaces. For example, this is true in etching of Si by Cl_2 and in laser doping. To study this further, focused argon-ion laser radiation was used to form partially molten zones in c-Si and c-Ge. Raman scattering was used to measure the Γ point phonon frequencies and linewidths for solid material at the melting temperature, giving 481.7 ± 0.4 and 24.3 ± 0.3 cm^{-1} for silicon and 281.4 ± 0.5 and 14.1 ± 0.5 cm^{-1} for germanium. Polarization Raman spectra for Si are shown in Figure 2 for the

$z(x,y)\bar{z}$ configuration (b) normally allowed in c-Si and c-Ge and the normally forbidden $z(x,x)\bar{z}$ configuration (a). This solid semiconductor floating in the molten region is responsible for the lower frequency peak in (a) and the only peak in (b).

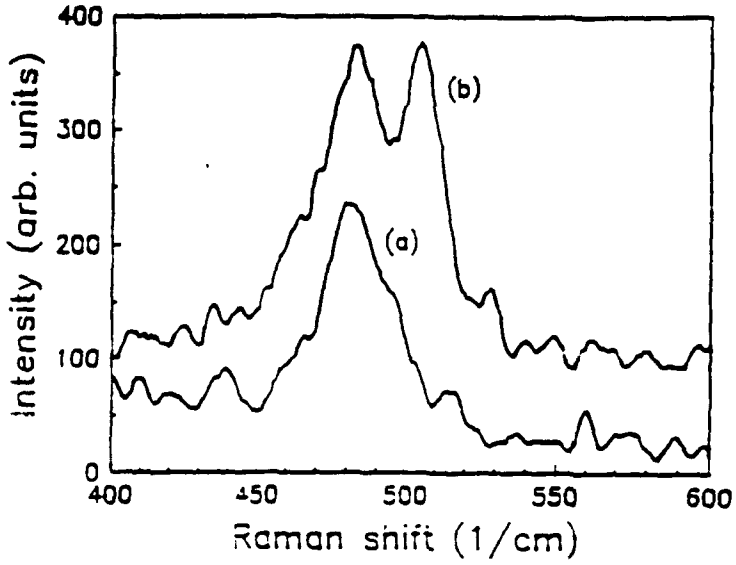

Figure 2. Raman spectrum of partially molten c-Si produced by cw laser heating: (a) $z(x,x)\bar{z}$; (b) $z(x,y)\bar{z}$.

The Raman spectrum of Ge/Si strained layer superlattices (SLS) depends on the strains in each layer; however analysis of these strains from the Raman spectrum is complicated by the effect of confined modes and possible surface roughness. Examination of the Raman frequencies vs. applied hydrostatic pressure can clarify the importance of strains and the interpretation of the Raman spectrum. We have examined the Raman spectrum of pseudomorphic (4 layer Ge/12 layer Si) x 25 SLS's, grown on c-Si by MBE at AT&T Bell Laboratories by J. Bevk, as a function of pressure in a diamond anvil cell (T=295 K). (This work was also supported by the Columbia JSEP program.)

Figure 3 shows typical spectra at ambient and elevated pressure and Figure 4 plots the Raman frequency for the c-Si substrate, Ge-Si interface features, and the Ge layers vs. pressure. The latter two are from the SLS; the SLS Si peak falls within the c-Si feature.

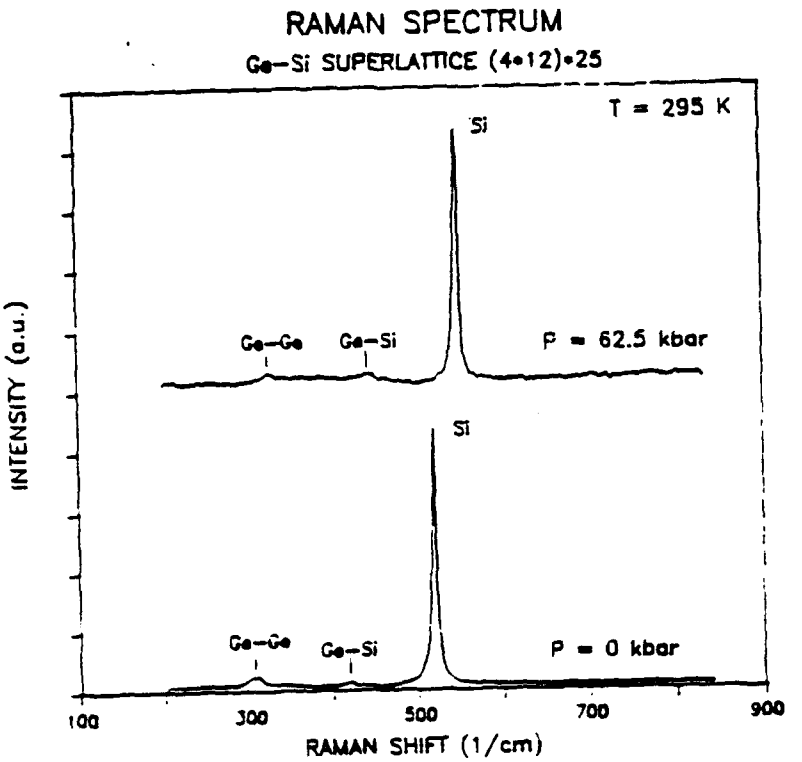

Figure 3. Raman spectra of Ge/Si superlattice at ambient pressure and at 62.5 kbar.

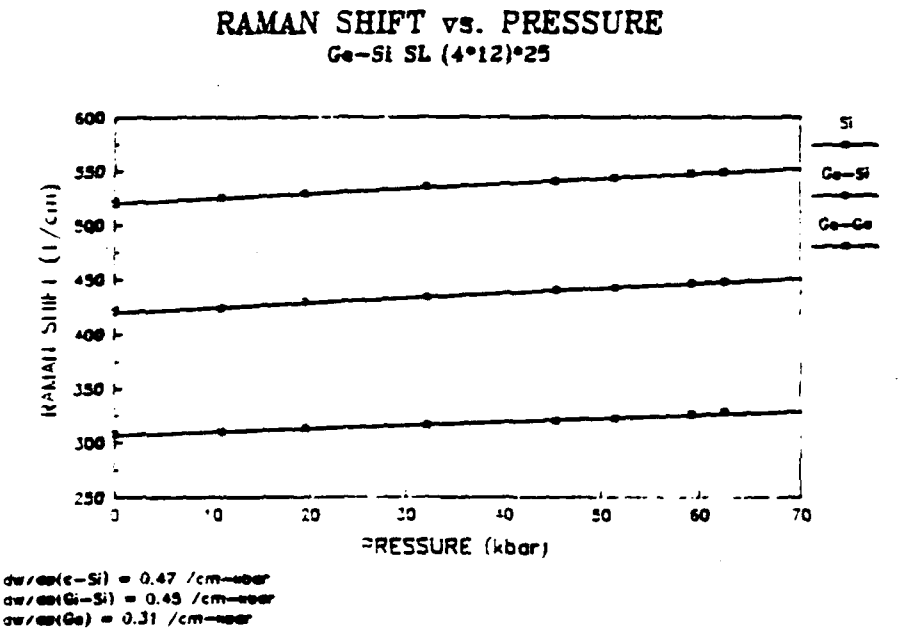

Figure 4. Variation of Raman shift of Ge/Si superlattice peaks vs. applied hydrostatic pressure.

Since Si and Ge have different bulk moduli, in general the stress and strain in the layers can change as the applied pressure (P) is changed. In this sample, the Ge layers are under compression, while the Si layers are unstressed. The slope dω/dp for the Ge feature is 0.31 cm^{-}

$^{-1}$/kbar, compared to dω/dP of 0.35 cm^{-1}/kbar for c-Ge. This is understood by examining the frequency of the Ge feature ω vs pressure P, which is:

$$\omega(p) = \omega_{Ge} + \left(q - \frac{C_{12}}{C_{11}}p\right)_G \frac{1}{\omega_o}\left(\frac{a^S}{a^G} - 1\right) - \left(\frac{p}{2\omega_o} + \frac{q}{\omega_o}\right)_G \frac{P}{(C_{11}+2C_{12})_G}$$

$$+ \left(q - \frac{C_{12}}{C_{11}}p\right)_G \frac{P}{\omega_o}\frac{a^S}{a^G}\left[\frac{1}{(C_{11}+2C_{12})_G} - \frac{1}{(C_{11}+2C_{12})_S}\right]$$

where p and q are the Ge deformation potentials, C_{11} and C_{12} are the elastic constants, a is the lattice constant, G refers to Ge, and S refers to Si. The second term on the RHS is the zero-pressure shift which, as mentioned above, is altered by other factors. The third term is the ordinary hydrostatic term in bulk Ge, while the last term gives the change due to the different elastic constants of the Ge and Si in the superlattice accounts for the difference in Ge slopes, when confinement effects are included. Because pressure tuning only changes the strains in the layers, this analysis proves that stresses are determined correctly using the standard elasticity model.

Early progress reports described the use of Raman scattering to determine the composition of Ge-Si alloys in situ and nondestructively. This year polycrystalline Ge-Si alloys were grown in an oven by the horizontal Bridgeman technique to study the phonon properties of these alloys vs. temperature. Raman scattering experiments are to be performed in the same oven. The polycrystallinity of the samples is of no concern because the grain size, ~10-20 μm, is very large from a scattering perspective. Raman spectra of representative $Ge_{1-x}Si_x$ alloys are shown in Figure 5 for x = 0.22 and 0.57. The results of this study will be very useful for in situ optical diagnostics.

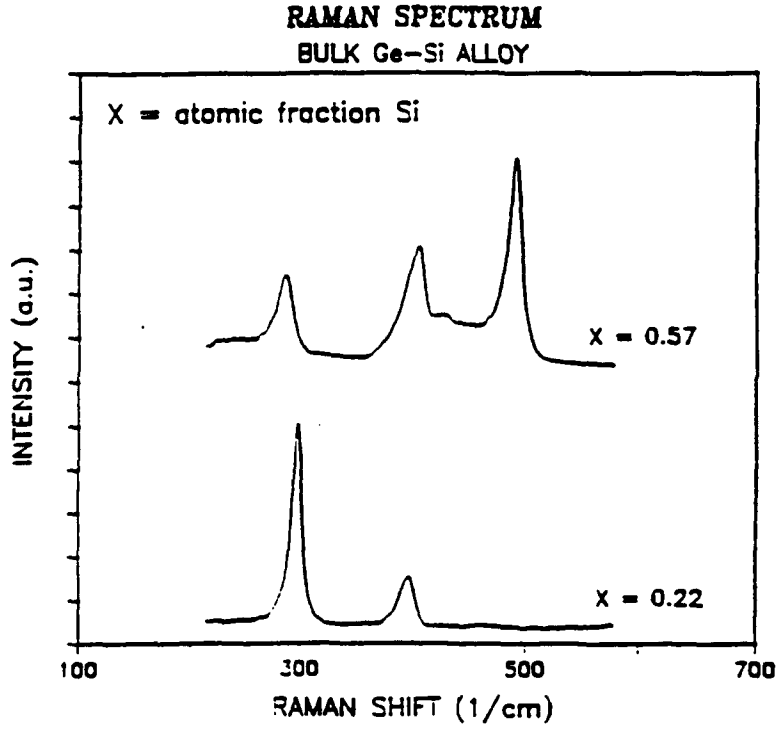

Figure 5. Raman spectra of two Ge-Si bulk alloys grown for phonon studies.

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3. Ultrafast Optoelectronic Measurements of Sufaces and Interfaces

Professor David H. Auston, Principal Investigator

Research Scientist, Xi-Cheng Zhang; ONR Fellow, Justin Darrow

Research Objective:

To develop new high speed optical measurement techniques to characterize the properties of semiconductor interfaces and surfaces.

Accomplishments:

We have continued research on the development of a new non-contacting method of measuring the properties of space-charge depletion layers at semiconductor surfaces. This technique, which uses femtosecond optical pulses, does not require any electrical contact to the material and is capable of measuring the sign and magnitude of the space charge fields at semiconductor surfaces. It can also be used to measure the internal fields of strained-layer superlattices. Last year we demonstrated the basic concept of this measurement approach.[1] This year we have extended the technique to the study of a wide range of semiconductor surfaces, including space charge depletion layers, metal-semiconductor interfaces, and strained-layer superlattices.

The technique is based of the fact that when a femtosecond optical pulse is absorbed at the surface of a semiconductor, a rapid photocurrent current transient is produced due to the internal field associated with the semiconductor surface or interface. This current pulse radiates as a femtosecond electrical signal and can be detected by time-resolved optoelectronic techniques that we have previously developed. The magnitude and sign of the radiated electrical pulse is determined by the sign and strength of the internal electric field. Our detection technique is extremely sensitive and can detect fields of a wide range of values without requiring large optical

[1] Pankove, "Optical Processes in Semiconductors", ch 18, Dover Publications, Inc. New York.

injected carrier densities. Typical injection levels in our experiments are 10^{13} cm^{-3}, which also ensures that the injected carriers act only as a probe and do not screen the field. This work is being performed in collaboration with Professors W. Wang and E. S. Yang.

The physical mechanism of generating an ultrafast electromagnetic wave from a semiconductor surface can be summarized as follows.[1] Basically, the ultrafast wave is the electromagnetic radiation from a transient photocurrent within the depletion layer of a semiconductor. As a femtosecond laser beam illuminates a bare semiconductor surface, photons are absorbed, creating electron-hole pairs. If there is a built-in field present near the semiconductor surface, the free carriers driven by the internal field are swept across the depletion layer and form a photocurrent normal to the surface. This transient photocurrent in the depletion layer radiates a subpicosecond electromagnetic pulse with submillimeter wavelength. The amplitudes of outward (pseudoreflected) radiated field, inward (transmitted) radiated field can be determined from the surface photocurrent by application of boundary conditions of the fields across the interface. If the optically illuminated semiconductor area is larger than the electromagnetic wavelength, the electromagnetic pulse is directional and diffraction-limited; it propagates in free space, and can be steered by varying the incident angle of the laser beam.[2] The radiation field, with a bandwidth from DC to 2 THz, does not depend on the long photocarrier lifetime. The illuminated surface radiates outward and inward radiated waves which satisfy a generalized Fresnel's law.

Samples have been selected from a variety of semiconductors which have bandgaps less than the incident photon energy (2 eV). Table 1 shows the peak amplitude of the radiated electromagnetic wave from some samples at room temperature where the amplitudes are normalized to that of the InP sample.

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[1]X.-C. Zhang, J.T. Darrow, B.B Hu and D.H. Auston, OSA Annual Meeting, postdeadline paper PD19, 1989; X.-C. Zhang, J.T. Darrow, B.B Hu and D.H. Auston, to be published in APL, Mar. 12, (1990)

[2]B.B Hu, J.T. Darrow, X.-C. Zhang and D.H. Auston, to be published in APL, Feb. 5, (1990); J.T. Darrow, B.B Hu, X.-C. Zhang and D.H. Auston, to be published in APL, Mar. 5, (1990)

Table 1

Sample	InP	GaAs	InSb	GaSb	CdTe	CdSe	Ge	Si	GaSe
Amplitude	100	28	8	2	33	11	7	0	0

Table 1: The amplitude of the outward radiated field of several samples from III-V, II-VI and group IV semiconductors at room temperature.

The Si and GaSe samples did not show a measurable signal because the absorption length in Si at an optical wavelength of 620 nm is approximately 10 times longer than that in InP and GaAs, causing few photogenerated carriers in the depletion layer to contribute to the radiation. The surface states of p-type GaSb sample locate near the valence band which do not change the Fermi level position significantly from the bulk level. Therefore the p-type GaSb sample shows a very weak radiated signal caused by the small band bending. The (100)-oriented semi-insulating iron-compensated InP, which shows the strongest signal in Table 1, has been analyzed by Auger spectroscopy and found to have a 15 angstrom oxide layer on the surface. Parameters which control the radiated field are the transient carrier mobility, the strength of the surface field and the width of the depletion region. The amplitude and sign of the radiation field directly reflect the integral of the surface field with the photogenerated free carriers within the depletion width. We have measured the amplitude of the radiated field as a function of temperature. An increase by a factor of approximately 3.4 in the amplitude of the radiated field was found for semi-insulating InP when it was cooled from room temperature to 80 K. This increase of the radiated field is expected from the increase of the carrier mobility. Small amplitude differences in the radiated fields effected

by the crystal orientation ((111) vs (100)) and crystal growth history (LEC vs epitaxial layer) from InP and GaAs samples are expected and have been observed.

Metal/semiconductor Schottky barriers have been used to verify that the surface field and transient photocurrent are normal to the semiconductor surface. The schematic illustration is shown in Figure 1. Forty Å thick gold films were evaporated on $n=5.3\times10^{15}$ /cm^3 and $p=6.8\times10^{16}$ /cm^3 GaAs (111) wafers. The wafers were chemically cleaned and heated in ultrahigh vacuum to 550 °C to produce clean surfaces prior to gold deposition in the same vacuum system. The heating also served to anneal indium on the back of the sample to provide an ohmic contact. The Schottky samples show good rectifying behavior in I(V) measurements. Therefore, a bias on the Au film results in a uniform modulation of the electric field at the semiconductor surface.

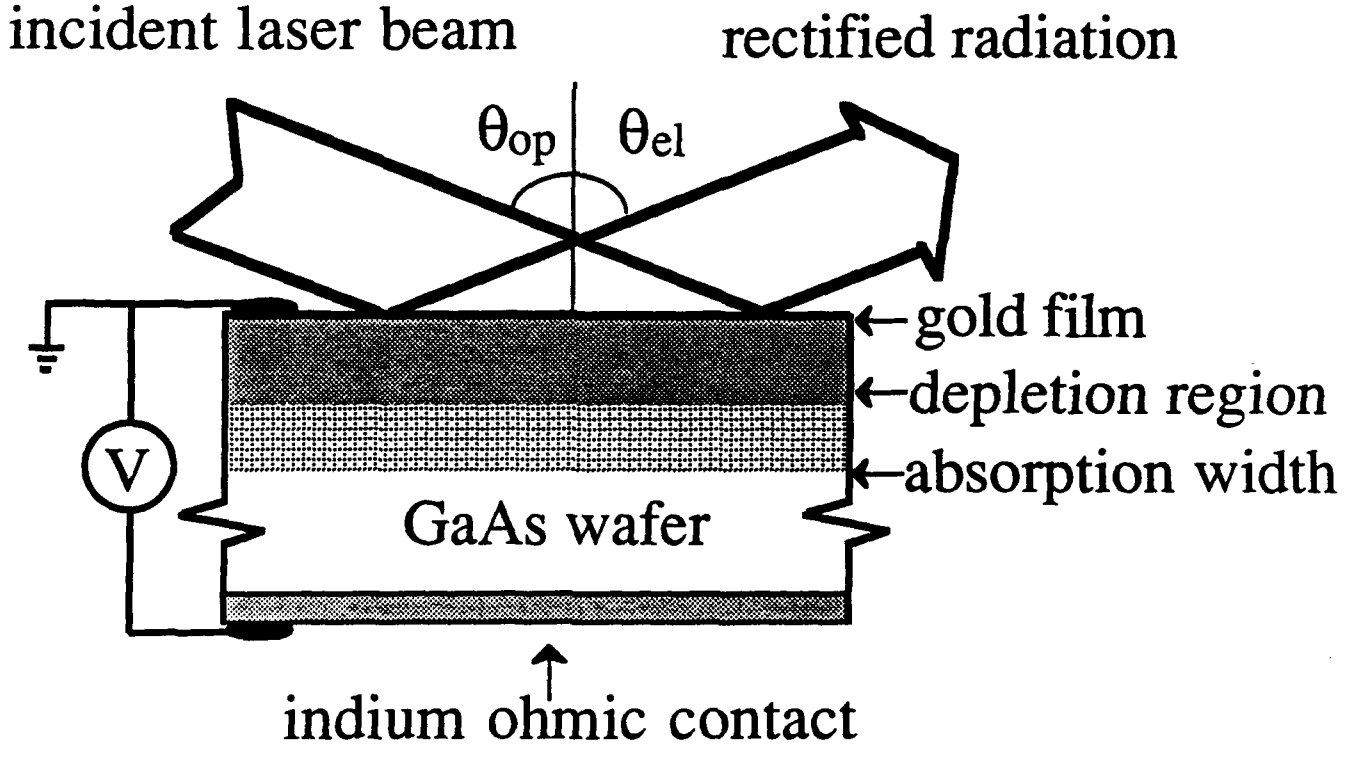

Figure 1: Schematic illustration of the outward radiated field from a Au/GaAs Schottky Barrier with an external bias. The incident angle of the laser beam θ_{op} is close to the GaAs Brewster's angle and the outward angle θ_{el} of the radiated field is close to the optical spectacular angle. For GaAs samples with a high doping level (>10^{16} /cm^3), the depletion width is less than the photon absorption width.

Figures 2(a) and (b) show the amplitude of the radiated signal from n-type and p-type GaAs with a 40 Å Au film vs the applied bias voltage. The radiated field of n-type GaAs at zero bias is about 5 times stronger than that of p-type. The radiated field shows an increase at a moderated reverse bias on the n-type sample and saturates at higher reverse bias. Basically, the reverse bias enhances the internal (built-in) field and increases the depletion width, while the forward bias cancels the internal field. The direction of reverse bias (as well as forward bias) of n-type and p-type Schottky barriers is opposite. Therefore, with the rise of the substrate potential, the surface field of the n-type sample increases (reverse bias) and more radiated signal is achieved; meanwhile the p-type sample shows a less radiated signal following a similar analysis.

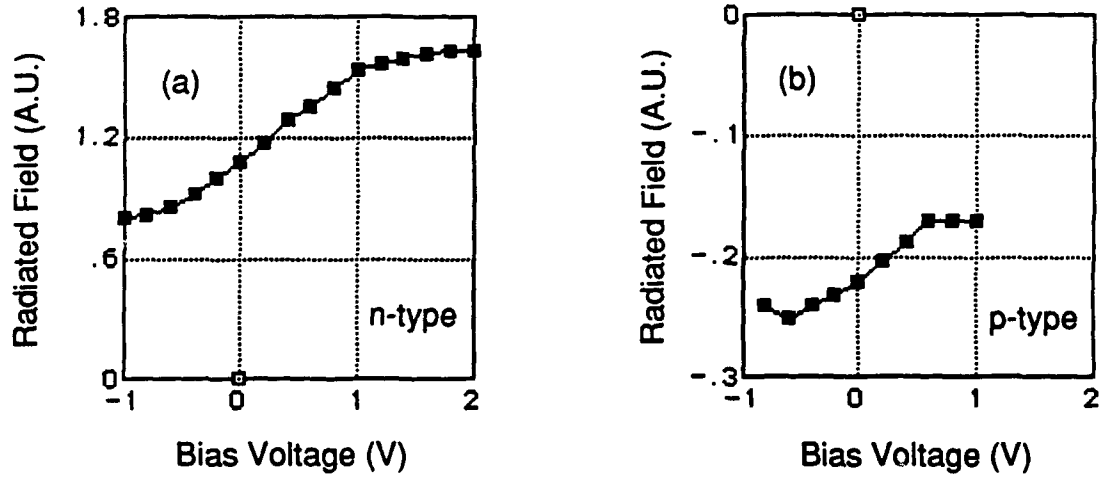

Figure 2: The amplitude of the outward radiated field vs an external bias voltage on the Schottky barrier from (a) n-type ($n=5.3\times10^{15}$; positive voltage → reverse bias) and (b) p-type ($p=6.8\times10^{16}$; positive voltage → forward bias) GaAs samples.

The transient behaviors of the hot carrier mobility $\mu(x)$ as a function of carriers position x and the bias voltage V_{bias} are complicated. However, if the mobility μ is assumed to be less sensitive with the position x than the built-in field which is linear with x, and the built-in field can be calculated from the amplitude ratio of the radiated signals at the different bias voltages. We have

estimated that the built-in field V has a value of 0.79±0.08 eV and 0.35±0.08 eV for n-type and p-type Au/GaAs Schottky samples, respectively.

We have investigated the strength and polarity of the surface fields by using several n-type and p-type GaAs samples with doping concentrations from 10^{15} /cm^3 to 10^{19} /cm^3 and semi-insulating LEC GaAs samples. The results are listed in Table 2. A higher doping concentration reduces the radiation field due to the absorption of submillimeter waves from the conducting substrate. The absorption coefficient at submillimeter wavelengths is proportional to the square root of the doping level. There are other effects of doping which have not been well characterized, such as the dependence of the transient carrier mobility on the doping level. In Table 2, the n-type samples show the opposite polarity compared with the p-type samples. This difference comes from their opposite directions of the depletion fields due to the different type of majority carrier. For the undoped GaAs (LEC), the energy level of EL2 makes it close to n-type, therefore the waveform of the radiated field of undoped GaAs has the same polarity as that of n-type GaAs. The radiated field E vs the doping concentration N can be derived as $E \propto N^{-0.5}$. In GaAs samples, as shown in Figure 3, $E \propto N^{-0.4}$ has been measured with the doping concentration N from 10^{15} /cm^3 to 10^{19}/cm^3.

Table 2

Doping Level /cm^3	LEC	n=3.5x10^{15}	p=6.7x10^{16}	n=6.3x10^{17}	n=2.0x10^{18}	p=1.6x10^{19}
Amplitude	+ 1.7	+ 2.02	- 0.47	+ 0.25	+ 0.18	- 0.08

Table 2: The amplitude of the outward radiated field from GaAs samples with different doping concentrations. The polarities of the radiated fields from n-type samples and p-type samples are opposite.

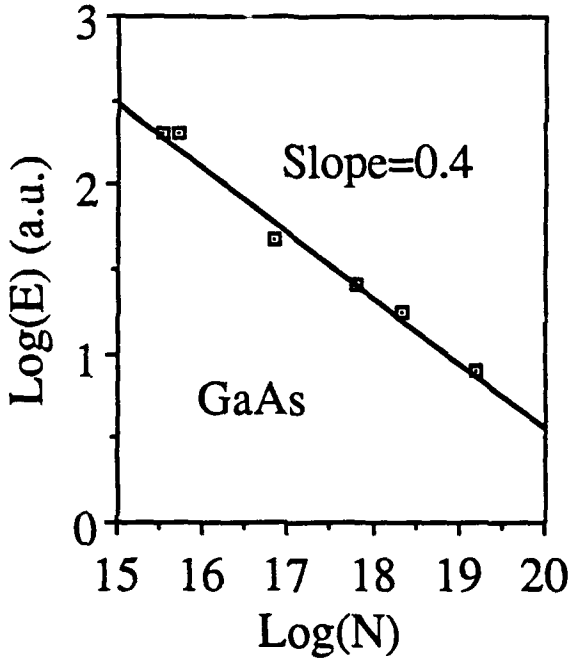

Figure 3: The amplitude of radiated field E vs the doping concentration N from GaAs samples plots in the logarithmic scale. A slope of 0.4 is measured.

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C. FUNDAMENTALS OF PROCESSING GAS/SURFACE INTERACTIONS

1. Quantum State Resolved Studies of Gas/Surface Chemical Reactions, George Flynn, Principal Investigator

Our efforts over the past year have been aimed at the detection of chlorine atoms and studies of their chemical reactions; the production and detection of hot electron/molecule collisions by a novel new technique; and a new effort to use lasers and laser photochemistry to enhance the sensitivity and selectivity of scanning tunneling microscopy. These experiments are providing data of fundamental interest for polymer etching, semiconductor surface etching and preparation, and plasma etching environments.

Chemical Dynamics of the Reaction between Chlorine Atoms and Deuterated Cyclohexane

Product energy disposal in chemical reactions has been widely studied both experimentally and theoretically.[1] Modern laser spectroscopic techniques allow the determination of both rotational and vibrational quantum states of nascent product molecules, while molecular beam experiments provide information on angular and translational energy distributions. Reactions of chlorine atoms have important applications in atmospheric chemistry,[2,3] in chemical etching of surfaces,[4] and in organic chemistry.[5] We are pursuing three different experimental efforts which involve the detection and investigation of Cl atoms and their reactions.

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[2]Molina, M. J.; Rowland, F. S. Nature 1974, 249, 810.

[3]Atkinson, R.; Aschmann, S. M. Int. J. Chem. Kinet. 1985, 17, 33.

[4]Danner, D. A.; Hess, D. W. J. Appl. Phys. 1986, 59, 940. Ritsko, J. J.; Ho, F.; Jurst, J. Appl. Phys. Lett. 1988, 53, 79.

[5]Breslow, R.; Brandl, M.; Hunger, J.; Turro, N.; Cassidy, K.; Krogh-Jespersen, K.; Westbrook, J. J. Am. Chem. Soc. 1987, 109, 1205.

The first experimental method employs an excimer laser as pump and an infrared diode laser as probe. Details have been described previously.[1,2] We have studied the reaction of Cl atoms produced by excimer laser photolysis of NOCl precursor molecules:

$$NOCl + h\nu\ (193\ nm) \rightarrow Cl + NO \qquad (1)$$

This precursor produces Cl atoms with an average translational energy estimated to be approximately 16.4 kcal/mole (0.8 eV). The chlorine atoms then react with C_6D_{12} to form DCl:

$$Cl + C_6D_{12} \rightarrow C_6D_{11} + DCl \qquad (2)$$

The rate constant for the corresponding hydrogen atom reaction is 3.1×10^{-10} cm^3-$molec^{-1}$-sec^{-1} at room temperature.[3] DCl products are probed by time-resolved infrared absorption spectroscopy with a high resolution (~0.0003 cm^{-1}) lead-salt tunable diode laser:

$$DCl\ (v,J,V) + h\nu\ (\sim 4.9\ \mu m) \rightarrow DCl\ (v \pm 1, J \pm 1, V) \qquad (3)$$

where v, J, and V are the vibrational quantum number, rotational quantum number, and translational velocity, respectively.

In earlier studies we showed that Cl atoms with only 0.4 eV of energy give cold DCl rotational distributions with hot translational energy distributions(large DCl recoil) In the present case the extra energy of the Cl atoms goes almost entirely into the translational recoil of the DCl and not into the rotational or vibrational degrees of freedom.

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[1]O'Neill, J.A.; Cai, J. Y.; Wang, C. X.; Flynn, G. W.; and Weston, R. Jr., J. Chem. Phys. 1988, 88, 6240. Hershberger, J. F.; Chou, J. Z.; Flynn, G. W.; Weston, R. E. Jr., chem. Phys. Lett. 1988, 149, 51. Hossenlopp, J. M.; Hershberger, J. F.; Flynn, G. W., submitted to J. Phys. Chem.

[2]Hershberger, J. F.; Hewitt, S. A.; Sarkar, S. K.; Flynn, G. W.; Weston, R. E. Jr., Chem. Phys., 1989, 91, 4636.

These results clearly represent nonstatistical partitioning of energy into rotationally cold, but translationally hot DCl molecules. The present results with 0.8 eV Cl atoms confirm earlier trends seen with lower energy (0.4 eV) atoms. The data strongly suggest a direct abstraction mechanism with a collinear C....D....Cl recoil geometry for the transition state. The Cl atom does not necessarily have to approach in a linear configuration; even with non-collinear approach, a very small motion of the light D atom can produce a collinear transition state which then rapidly falls apart.

The observation of such a simple mechanism for a reaction between a large gas phase molecule and an atom raises the question as to whether reactions between atoms and thin film surface polymers might also exhibit similar behavior. Efforts to answer this and other questions regarding the reactivity of Cl atoms are continuing in our laboratory.

In a second experimental effort we have developed a multiphoton ionization apparatus to study the quantum state resolved dynamics of reactions which produce HCl or DCl molecules. The initial results with this device have been very promising, and we expect to use it to detect HCl from reactions within the next few months. This technique is very sensitive and should be applicable to the study of Cl reactions with polymer films, many of which produce HCl as products, even under conditions of high vacuum.

We have also continued our efforts to directly detect Cl atoms by infrared absorption. Our initial work in this area was slowed by lack of good quality infrared diode lasers. We have just received and tested an excellent device which improves our detection capability by one or two orders of magnitude and should allow us to study the reactions of Cl atoms with surfaces even at very low pressures.

Photoproduction and Scattering of Hot Electrons

We have recently discovered a simple method for producing hot electrons and studying their collisions with molecules in the gas phase.[1] A key and novel feature of the experiments is the resolution, 0.0003 cm^{-1} or approximately $4x10^{-8}$ eV! This compares with standard electron scattering experiments which have a typical energy resolution of about 80 cm^{-1} or 10 meV. The high resolution is obtained by observing the molecular collision partner rather than the scattered electron as is normal in most electron scattering experiments. Such studies can provide fundamental insight into the mechanisms and processes which are important in plasma etching reactors. Considerable interest in this technique has been exhibited by scientists working on plasma etching diagnostics at the IBM East Fishkill facility.

In brief the method is as follows. Electrons are produced in a pulse by two photon excimer laser photoionization of I_2 molecules.

$$I_2 + h\nu\ (193nm) \rightarrow I_2\ (D) \qquad I_2\ (D) + h\nu\ (193nm) \rightarrow I_2^+ + e\ (0\text{-}3eV)$$

The electrons then collide with other species in the sample, producing vibrationally excited molecules,

$$e + M \rightarrow M\ (v,J,V) + e$$

where v denotes the level of vibrational excitation, J the level of rotational excitation, and V the velocity recoil of species M. The M(v,J,V) species are detected using infrared diode laser radiation having a frequency purity of 0.0003 cm^{-1}. A brief summary of the results obtained so far in the study of a variety of collision partners M is as follows. The electron imparts essentially no angular momentum or translational recoil to the molecule. In essence, the electron is so light that at the

[1] Hewitt, S.A., Zhu, L., and Flynn, G.W., J. Chem. Phys., 1990, 92,6974

energies available in this particular experiment (0-3 eV), it cannot impart any significant momentum to the heavy M species. Vibrational energy is quite another matter, however. We find that all vibrational modes are excited efficiently. The relatively high efficiency of exciting vibrational states is due to the strong interaction of the electron with the molecular electronic structure.

We have also constructed an apparatus to measure directly the electron "pressure" in these experiments using a simple axial magnetic field and a pick-up coil around the sample cell. When the laser photoionizes the I_2, the electrons so produced exclude magnetic flux from the center region of the sample tube. This produces a detectable electronic signal in the pick-up coil wrapped around the cell. We have measured the current induced in such a coil when photoionization occurs. The signal shows both production and cooling of the electrons and can be used to determine electron density. Such a measurement is necessary in order to obtain cross sections for electron excitation of molecules, a parameter of key interest to scientists at the IBM East Fishkill facility working on the fundamental physical processes of importance in plasma etching reactors.

Future efforts will be aimed at using other sources to produce photoelectrons in an attempt to make more monoenergetic electrons. Studies of other molecular systems of interest in plasma etching environments will be made using both I_2 as an electron precursor and other atomic or molecular precursors.

Scanning Tunneling Microscopy and Laser Photochemistry

In a collaborative effort with Dr. Phaedon Avouris at IBM Watson Research Laboratories in Yorktown Heights, NY, we have begun an investigation of the effects of laser irradiation on the spectra observed in scanning tunneling microscopy experiments. Laser light can effect the photochemistry and the electronic properties of species formed or adsorbed on the surface of most metals and semiconductors. STM probes of these photochemical changes should be possible, and enhanced sensitivity for the STM process may result from combining the optical selectivity of lasers with the high surface specificity of the STM probe. This is a new effort which we expect will yield interesting results over the next year.

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2. Photochemical and Photophysical Probes of Interfaces

Nicholas J. Turro, Principal Investigator

Introduction

Our research program has explored the use of photochemical processes which can serve as probes to characterize the structure and dynamics of reactions which occur at a variety of interfaces. Interfacial chemistry is critical to many aspects of the microelectronics industry and for the next generations of nanostructures. Accordingly, we have emphasized investigations of fundamental processes that should reveal global, fundamental principles which are most likely to have a general impact on the field.

Published research involving ONR support has appeared on (1) studies of the modification of photochemical reactivity of ketones adsorbed on the solid/air interface of zeolites;[1,2,3] (2) studies of the structure dependent photoinduced electron transfer between metal complexes adsorbed at the DNA/aqueous interface;[4] and (3) studies of the conformation of poly(acrylic acid) adsorbed on the alumina/water interface.[5]

Current research involves the investigation of photochemical reactions of novel photoresist materials in collaboration with IBM scientists at East Fishkill, New York and Almaden, California. In the way of an introduction to this research, the photochemical generation of Bronsted acids from N-hydroxy-sulfonyl esters has found valuable applications on photoresist technologies which are

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[1]V. Ramamurthy, D. R. Corbin, C. V. Kumar and N. J Turro, "Modification of Photochemical Reactivity by Zeolites: Cation Controlled Photodimerization of Acenaphthylene within Faujasites," Tetrahedron Letters 31, 47 (1990)

[2]V. Ramamurthy, D. R. Corbin, N. J. Turro and Y. Sato, "Modification of Photochemical Reactivity by Zeolites: Cation Enhanced a-Cleavage of Aryl Alkyl Ketones Included in Faujasites," Tetrahedron Letters 30, 5829 (1989).

[3]V. Ramamurthy, D. R. Corbin, D. F. Eaton and N. J. Turro, "Modification of Photochemical Reactivity by Zeolites: Role of Cations in Controlling the Behavior of Radicals Generated within Faujasites," Tetrahedron Letters 30, 5833 (1989).

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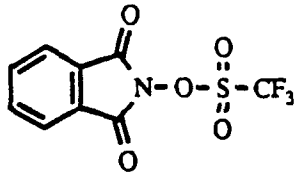
[5]K. Tjipangandjara, Y. B. Huang, P. Somasundaran and N. J. Turro, "Correlation of Alumina Flocculation with Adsorbed Polyacrylic Acid Conformation," Colloids and Surfaces 44, 229 (1990).

at the heart of the microelectronics industry. The efficiency of these compounds as photopolymerization initiators depends directly on the yields of acid generated with respect to the irradiation dose. It is important to understand the factors that determine the reactivity of the excited states and the manner in which they may be perturbed by their medium. Despite the enormous practical importance of these materials, there has been little systematic fundamental photochemical investigations of the photoreactions. A number of questions that remain unanswered relate to the actual acid generation mechanisms such as the nature of the cleavage step (homolytic vs. heterolytic) and the origin of the protons of the photochemically formed Bronsted acids. Our studies have involved the photochemistry of the N-hydroxy-imide-esters as models for photoresist systems. The compounds employed in this study are the triflic and tosyl esters of N-hydroxyphthalimide (**1** and **2**) and the triflic ester of N-hydroxy-succinimide (**3**) shown in the scheme below. The methodologies employed include: product analysis, uv-absorption and emission, flash photolysis, and chemically induced dynamic nuclear polarization (CIDNP).



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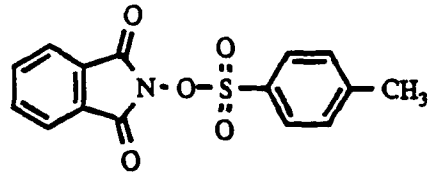

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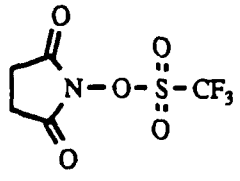

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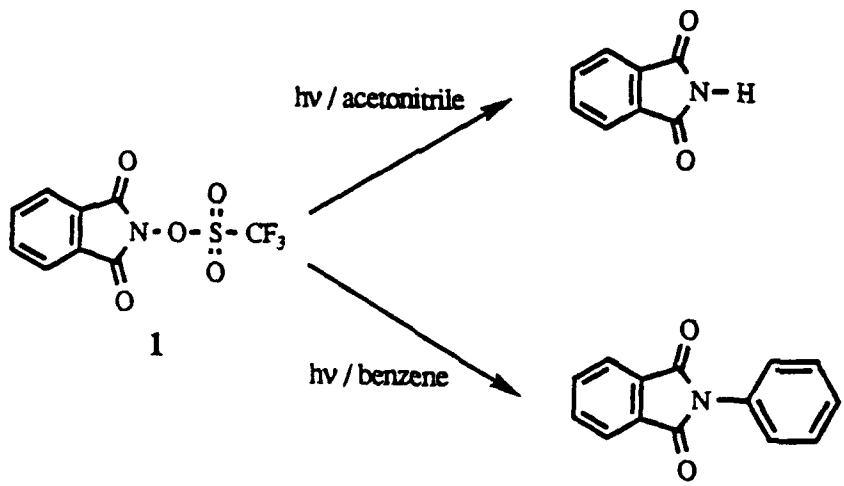
Product Analysis. The formation of sulfonic acids from the sulfonyl esters of N-hydroxy-imides can be rationalized in terms of cleavage of the N-O bond and organic products with the imide fragment to be expected. Exploratory irradiations of compounds **1**, **2** and **3** were carried out with 0.01 M benzene and acetonitrile solutions using a medium pressure Hanovia lamp with a 313 nm filter solution run through a quartz cooling jacket. The relative photoreactivity of these compounds after 1 hr. irradiation turned out to be substantially different from that of each other as judged by glc analysis. Large conversions of 80%, for instance, were observed from compound **1**, while compounds **2** and **3** gave only small amounts (>5%) and traces of detectable products, respectively. Based on these reactivity differences, and in order to carry out photoproduct isolation and identification, further studies were performed on compound **1**.

Product Identification. Photolysis of compound **1** in acetonitrile resulted in a relatively low conversion, and phthalimide was identified as the major product (65% of product mixture) by its glc retention time and by co-injection with an authentic sample. Preparative photolysis in benzene resulted in a much larger conversion (75%) with the formation of only trace amounts of phthalimide. A major product accounting for 93% of the product mixture was identified as N-phenyl-phthalimide by combined ^{1}H and ^{13}C NMR and by mass spectrometric analyses.



Irradiation of compound **1** in other aprotic solvents such as cyclohexane and ethyl acetate resulted in the formation of phthalimide along with relatively large amounts of unidentified products (Table

1). Irradiation in a polar protic solvent such as methanol gave 100% conversion and phthalimide turned out to be by far the major product (80%). The yields of phthalimide in aprotic solvents suggest that sources of hydrogens can probably arise from moisture in the solvents. Differences of about 10% in the product yields were found in all of these solvents when photolyses were carried out under oxygen saturated solutions. It should also be pointed out that formation of N-phenyl phthalimide can also be observed upon longer irradiations of the tosyl derivative **2**.

Table 1. Product analysis from N-hydroxy-phthalimide trifluoromethyl sulfonic ester 1 in several solvents. Irradiation at 313 nm for 60 min.

Solvent[a]	Conversion[b] %	Phthalimide %	Major Products
cyclohexane	10c	traces	>20
benzene	75	traces	1[d]
acetonitrile	16	10	8
ethyl acetate	100	15	4
methanol	100	80	~15

[a] Solvents were used as received with no drying treatment.

[b] Differences of about 10% found when irradiations were carried out in oxygen or nitrogen saturated solutions.

[c] Measured by glc.

[d] Product identified as N-phenyl-phthalimide.

The formation of phthalimide and phthalimide-benzene addition products clearly suggests a mechanism where cleavage of the N-O bond is involved. That the extent of reaction and yield of phthalimide in non-protic solvents should be limited by the availability of protons in the media is

suggested by comparison of the results in cyclohexand and methanol. The high yields of reaction in benzene and ethyl acetate along with the small yields of phthalimide indicate that both electrophilic and nucleophilic addition may be involved in the chemistry of the reaction intermediates. It should be pointed out that such behavior should be expected in the case of neutral radical intermediates.

It was recognized that substitution on the benzene ring should provide evidence as to the nature of the intermediates generated upon photolysis of compound **1**. The yields of product formation from photolysis of **1** in benzene, toluene, chlorobenzene and nitrobenzene would be expected to be very dependent on the nature of the intermediates. Homolytic cleavage of the N-O bond would yield a radical pair, while heterolytic cleavage would generate a phthalimidyl cation. Radical addition to substituted benzene rings is expected to be facilitated with respect to unsubstituted benzene regardless of the nature of the substituent. Large conversions would be expected for these reactions. Electrophilic addition, on the other hand, is expected to obey well known substitution patterns where chloro and nitro substituents should inhibit the reaction while toluene should increase it.

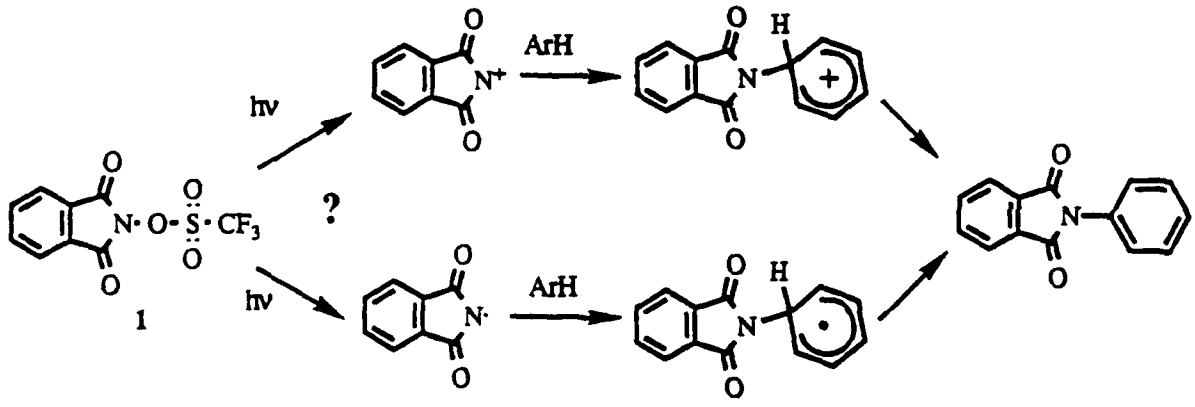


Table 2. Results from photolysis of compound **1** in substituted benzenes.

Aromatic Compound	Conversion	Major Addn Prods (%)
Benzene	45	(43)
Toluene	92	(35, 17, 23)
Chlorobenzene	83	(27, 52)

Reaction in nitrobenzene, which absorbs strongly at 313 nm, resulted in the formation of small amounts of a large number of peaks. Although it was concluded that positive reactivity could be observed, no further attempts have been made to quantify this reaction. The fact that there seems to be some reactivity with nitrobenzene, the higher yields of product formation from both electrophilic-addition activating (Me) and deactivating (Cl) substituents, and the clear formation of three products from toluene are all facts that point to a radically mediated mechanism.

Absorption Spectra. The absorption spectra of compounds **1**, **2** and **3** were obtained in benzene, acetonitrile and methanol. A significant solvent shift on the lowest transition can be observed on compounds **1** and **2** as λ_{max} changes from ~ 300 nm in benzene and acetonitrile to ~ 320 nm in methanol. A long extending shoulder unique to the methanol spectra was also observed up to ~ 370 nm. An interesting aspect of the spectrum of compound **3** relates to the fact that no absorption maxima can be observed at as low as 210 nm in any of the solvents studied. The long tail observed, however, extends to as far as ~ 300 nm.

Flash Photolysis Experiments. The possibility of observing the intermediates involved in the photoreactivity of the phthalimidyl compounds was investigated by flash photolysis experiments. Transient absorption spectra were measured by laser excitation at 308 nm in nitrogen-saturated acetonitrile solutions. With delay times of ~ 200 nsec, strong transient absorptions were observed at ~ 320 nm. These transients were then analyzed kinetically in order to

determine whether their absorption corresponds to an excited state or to a radical intermediate. The lifetime of the transients from the tosyl and triflic esters, which can be attributed to a similar intermediate (different radical pairs), were first measured and determined to be 4.6 and 3.6 μsec. The optical density from the tosyl ester turned out to be about 6 times less strong than the transient from the triflic ester, in complete agreement with the photochemical yields observed before. The effects of oxygen on the fluorescence intensity and on the lifetime of the transient were investigated to determine whether they can be assigned to the same species. Such was found not to be the case, as oxygen saturation results in an effect of 10% on the fluorescence intensity while a 16-fold decrease can be detected on the lifetime of the triflic ester (230 nsec).

The assignment of the transient observed as that of the phthalimidyl radical can be further substantiated by observing whether it can be quenched upon reaction with benzene. Such was indeed found to be the case, as addition of benzene onto the phtalimidyl-triflic esters results in a systematic decrease of its lifetime. A bimolecular reaction rate constant of $k_r = 1.37 \times 10^6$ mol^{-1} sec^{-1}, which is lower than diffusion control, can be calculated from these measurements.

CIDNP. Attempts to observe chemically induced dynamic polarization upon irradiation of compound **1** proved unsuccessful. Several deuterated solvents were explored including methanol, acetonitrile and benzene.

Summary. The studies reported here provide some information into the photochemical mechanisms of N-hydroxy-imide sulfonic esters. The evidence collected, especially in the case of the phthalimide trilfic ester, indicates a homolytic cleavage of the N-O bond to generate a phthalimidyl radical. Products arising from this fragment can apparently form through hydrogen abstraction or by addition to unsaturated electrophilic or nuclophilic sites. The mechanism for formation of triflic acid remains uncertain and pathways involving electro-reduction or radical coupling may be involved. Further investigation should be carried out, especially in light of the fact that we may have carried out the first optical detection of an imidyl radical.

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IV. PRESENTATIONS

ELECTROCHEMICAL SOCIETY MEETING, October 1989, "Characterization of n-type 3C Silicon Carbide Strain Gauges," Joseph Shor.

IBM, T. J. WATSON RESEARCH LABORATORIES, Yorktown Heights, NY, September 29, 1989, Short Course, "Laser Chemical Processing - A Tutorial Overview," Richard M. Osgood.

ISPSR Conference, Kyoto, Japan, November 14, 1989, "Laser Surface Chemistry for Microelectronics," Richard M. Osgood, Jr.

IBM, T. J. WATSON RESEARCH LAB., Yorktown Heights, NY, January 8, 1990, "Fundamental Mechanisms in UV-Assisted Surface Reactions," Richard M. Osgood, Jr.

IBM, EAST FISHKILL, NY, March 6, 1990, "Studies of Light Induced Surface Chemistry on Semiconductors," R. M. Osgood, Jr.

GORDON RESEARCH CONFERENCE, Ventura, CA, February 26 - March 2, 1990, Chemistry of Electronics Materials, "Chemical Structure of the GaAs Oxide Formed by Deep Ultraviolet-Light-Enhanced Growth," Michael Schmidt.

SURFACE ANALYSIS AND INTERFACE ANALYSIS, Albuquerque, New Mexico, April 25-27, 1990, 12th Annual Symposium on Applied Surface Analysis, "A Marker Technique to Identify Diffusing Elements During Initial Reactions Using Ion Scattering Spectroscopy," Michael Schmidt.

ELECTROCHEMICAL SOCIETY, Montreal, Canada, May 6-11, 1990, SOTAPOCS, "Etch Rate and Feature Size in the Micrometer Scale, Laser-enhanced Aqueous Etching of III-V Semiconductors," Xiaoge Zhang.

ELECTROCHEMICAL SOCIETY, Montreal, Canada, May 6-11, 1990, SOTAPOCS, "Laser Electrochemical Etching of SiC," Xiage Zhang.

KULITE, Howard University, Wahington, DC, April 11-13, 1990, 3rd International Conference on Amorphous and Crystalline SiC, "Surface Micromachining of B-SiC Using Laser Assisted Photoelectrochemical Etching," J. S. Shor.

CITY UNIVERSITY OF NEW YORK, New York, NY, September 12, 1990, "The Chemical Physics of Light-Surface Interactions," Richard M. Osgood, Jr.

AMERICAN VACUUM SOCIETY, Boston, MA, October, 1989, High Temperature Superconducting Thin Films: Processing, Characterization and Applications, "Chemistry and Resistance at Metal Contacts to YBa (2) Cu (3) O (7)," Mike Schmidt.

MATERIALS RESEARCH SOCIETY SYMPOSIUM, Boston, MA, October, 1989, "Use of Si-YBaCuO Intermixed System for Patterning of Superconducting Thin Films," Q. Y. Ma

SURFACE ANALYSIS AND INTERFACE ANALYSIS, Albuquerque, New Mexicao, April 25-27, 1990, 12th Annual Symposium on Applied Surface Analysis, "A Marker Technique to Identify Diffusing Elements During Initial Reactions Using Ion Scattering Spectroscopy," Michael Schmidt

GORDON CONFERENCE ON THE CHEMISTRY OF ELECTRONIC MATERIALS, Ventura, CA, February, 1990, "Chemical Structure of the GaAs-Oxide Formed by Deep Ultraviolet Light Enhanced Growth," Michael T. Schmidt, Zhong Lu, Dragan V. Podlesnik, and Richard M. Osgood, Jr.

ELECTROCHEMICAL SOCIETY, Montreal, Canada, May 6-11, 1990, SOTAPOCS, "Etch Rate and Feature Size in the Micrometer Scale, Laser-enhanced Aqueous Etching of III-V Semiconductors," Xiaoge Zhang

ELECTROCHEMICAL SOCIETY, Montreal, Canada, May 6-11, 1990, SOTAPOCS, "Laser Electrochemical Etching of SiC," Xiaoge Zhang

APS MEETING, Anaheim, CA, March 1990, "Studies of Thin Metal Contacts to High T_c Superconducting Films," Q. Y. Ma, M. T. Schmidt, L. S. Weinman, E. S. Yang, and Chin-An Chang

OE/AEROSPACE SENSING CONFERENCE, "Superconductivity Applications for Infrared and Microwave Devices," Symposium, Orlando, FL, April, 1990, "Patterning of High T_c Superconducting Thin Films on Si Substrates," Q. Y. Ma, C. Shu, E. S. Yang, and Chin-An Chang.

ROCKWELL SCIENCE RESEARCH CENTER, CA, March 18, 1990, "Transition Characterization of Heterostructure-Emitter Bipolar Transistor," X. Wu.

RUTGERS UNIVERSITY, DEPT. OF ELECTRICAL ENGINEERING, NJ, May 19, 1990, "Low Temperature Performance of AlGaAs/GaAs Heterostructure-Emitter Bipolar Transistor," X. Wu.

LITTON SOLID STATE ELECTRONICS, INC. CA, May 28, 1990, "Surface Chemical Passivation of AlGaAs/GaAs Heterostructure Transistor," X. Wu.

MARYLAND UNIVERSITY, CENTER FOR SUPERCONDUCTIVITY, MD, May 15, 1990, "Physical and Material Properties of HTS Thin Films," Q. Y. Ma.

MCMASTER UNIVERSITY, MATERIALS RESEARCH INSTITUTE, CANADA, June 2, 1990, "Interfacial Properties of Metal-YBCO Contacts," Q. Y. Ma.

CONDUCTUS, INC., CA, Feb. 3, 1990, "Material Characterization of Si-YBCO Intermixed Films," Q. Y. Ma.

MICROELECTRONICS AND COMPUTER TECHNOLOGY CORP., TX, June 14, 1990, "Processing, Characterization, and Device Development of HTS films," Q. Y. Ma.

STANFORD UNIVERSITY, January 1990, "Generation and Detection of Femtosecond Electromagnetic Pulses," D. Auston.

UNIVERSITY OF TEXAS, February 15, 1990, "Ultrafast Optoelectronics," D. Auston.

PRINCETON UNIVERSITY, February 22, 1990, "Ultrafast Optoelectronics," D. Auston.

NATIONAL RESEARCH COUNCIL, Ottowa, February 27, 1990, "Ultrafast Optoelectronics," D. Auston.

AMERICAN PHYSICAL SOCIETY, March 1990, "Generation of Femtosecond Electromagnetic Pulses at Semiconductor Surfaces," D. Auston.

LOS ALAMOS NATIONAL LABORATORY, March 16, 1990, "Ultrafast Optoelectronics," D. Auston.

IEEE CHAPTER, Chicago, March 1990, "Ultrafast Optoelectronics," D. Auston.

GTE LABORATORY, Boston, April 12, 1990, "Ultrafast Optoelectronics," D. Auston

GEORGIA INSTITUTE OF TECHNOLOGY, April 17, 1990, "Ultrafast Optoelectronics," D. Auston.

UNIVERSITY OF MARYLAND, May 8, 1990, "Ultrafast Optoelectronics," D. Auston.

LASERS AND ELECTRO-OPTICS CONFERENCE, Anaheim, May 1990, "Large Aperture Photoconducting Antennas," D. Auston.

OSA TOPICAL MEETING ON ULTRAFAST PHENOMENA, Montery, May 15, 1990, "Generation of Femtosecond Electromagnetic Pulses at Semiconductor Surfaces," D. Auston.

ALLIED SIGNAL CORPORATE RESEARCH LAB, Morristown, NJ, September 18, 1990, "Ultrafast Optoelectronics," D. Auston

SWISS FEDERAL INSTITUTE OF TECHNOLOGY (ETH), Zurich, September 29, 1989, "Super High Resolution Studies of Chemical and Collision Dynamics," G. W. Flynn.

NEW YORK ACADEMY OF SCIENCES, SYMPOSIUM ON SCIENCE AND TECHNOLOGY, New York, NY, April 25, 1990, "Infrared Laser Cartography: Vibrational, Rotational and Translational Energy Probes of Chemical and Collision Dynamics," G. W. Flynn.

AMERICAN CHEMICAL SOCIETY, SYMPOSIUM ON INTERMOLECULAR POTENTIALS: SPECTROSCOPIC, THEORETICAL AND DYNAMICAL PROBES, Washington, DC, August 28, 1990, "Infrared Laser Cartography: Vibrational, Rotational and Translational Energy Probes of Chemical and Collision Dynamics," G. W. Flynn.

CIBA-GEIGY RESEARCH LABORATORIES, Ardsley, NY, December 5, 1989, "Mechanisms of Photostabilization of Polymers," N. Turro.

BOWLING GREEN, BOWLING GREEN, OH, March 24, 1990, "Photochemistry in Restricted Spaces," N. Turro.

UNIVERSITY OF OKLAHOMA, May 3, 1990, "Novel Mechanisms of Photoreactivity at Interfaces," N. Turro.

ORGANIC REACTION MECHANISMS CONFERENCE, Boulder, CO, June 11, 1990, "Photochemical Reactions in Nanoscopic Reactors," N. Turro.

REACTION MECHANISMS IN SOLUTION CONFERENCE, Canterbury England, July 4, 1990, "Photochemistry and the Cage Effect," N. Turro.

UNIVERSITA DEGLI STUDI DI FIRENZE, Florence, Italy, July 12, 1990, "Photochemical Probes of Interfaces," N. Turro.

CONFERENCE ON SOLAR ENERGY CONVERSION AND STORAGE, Sicily, Italy, July 18, 1990, "Photoinduced Electron Transfer on Anionic Interfaces," N. Turro.

SYMPOSIUM ON PHOTOELECTRON TRANSFER, ASC NATIONAL MEETING, Washington, D.C., August 28, 1990, "Photoinduced Electron Transfer Between Metal Complexes Adsorbed on Micelles, Starburst Dendrimers and DNA," N. Turro.

UNILEVER RESEARCH LABORATORIES, USA, Edgewater, NJ, "Photochemical Probes for the Structure and Dynamics of Interfaces," August 24, 1990, N. Turro.

20TH INTERNATIONAL CONFERENCE ON THE PHYSICS OF SEMICONDUCTORS, Thessaloniki, Greece, August 6-10, 1990, "Optically Induced Screening of the Strain Induced Electric Fields in (111) GaSb/AlSb Quantum Wells," B.V. Shanabrook, D. Gammon, R. Beresford, W.I. Wang, and R.P. Leavitt.

SIXTH INTERNATIONAL CONFERENCE ON MOLECULAR BEAM EPITAXY, San Diego, CA., August, 1990, "Resonant Tunneling in Polytype InAs/AlSb/GaSb Heterostructures,".K.F. Longenbach, L.F. Luo, S. Xin and W.I. Wang.

48TH DEVICE RESEARCH CONFERENCE, UC Santa Barbara, CA, June 25-27, 1990, "Large Bandwidth (13KHz-1 GHz) Planar-doped 2DEG CCD with High Transfer Efficiency at Room Temperature," J.I. Song, D.V. Rossi, S. Xin, W.I. Wang, and E.R. Fossum.

IBM EAST FISHKILL FACILITY, January 16, 1990, I. Herman

STATE UNIVERSITY OF NEW YORK, STONY BROOK, NY, October 3, 1989, I. Herman.

V. PATENTS

D. H. Auston and X. C. Zhang, "Large Aperture Photoconducting Antennas," *in preparation.*

D. H. Auston and X. C. Zhang, "Noncontacting Probing of Semiconductor Surfaces with Femtosecond Optical Pulses," in preparation.

E. S. Yang and Q. Y. Ma, Patent pending, "Method of Patterning Superconducting Films in Which Superconductivity is Inhibited by Diffusion of Impurites"