JOINT SERVICES ELECTRONICS PROGRAM
FINAL REPORT

RESEARCH INVESTIGATION DIRECTED TOWARD EXTENDING
THE USEFUL RANGE OF THE ELECTROMAGNETIC SPECTRUM

for Grant DAAG55-97-1-0166
For the Period May 1, 1997 – April 30, 2001

Presented to:
THE JOINT SERVICES TECHNICAL COORDINATING COMMITTEE
Representing: THE U.S. ARMY RESEARCH OFFICE,
THE OFFICE OF NAVAL RESEARCH,
and THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Submitted by:
COLUMBIA RADIATION LABORATORY
DEPARTMENTS OF APPLIED PHYSICS, CHEMISTRY,
eLECTRICAL ENGINEERING, PHYSICS
COLUMBIA UNIVERSITY in the City of New York
NEW YORK, NEW YORK 10027

June 30, 2001

Approved for Public Release: Distribution Unlimited
MEMORANDUM OF TRANSMITTAL

October 12, 2001

U.S. Army Research Office
Attention: Sylvia Hall
AMSRL-RO-B1
4300 South Miami Boulevard
Durham, NC 27703-9142

RE: COLUMBIA UNIVERSITY'S JSEP FINAL REPORT
CONTRACT DAAG55-97-1-0166 for the period May 1, 1997 – April 30, 2001

Dear Mrs. Hall:

An extra copy of Columbia University’s Final JSEP Report is enclosed as requested by William Clark, Associate Director, Electronics Division, for Contract: DAAG55-97-1-0166 for the period May 1, 1997 – April 30, 2001. Original copies of this report were sent to ARO the last week of June 2001. An extra copy is also being sent as requested to AMSRL-RO-EL (Mr. William Clark).

Title: Research Investigation Directed Toward Extending the Useful Range of the Electromagnetic Spectrum

Thank you for your support.

Please let Columbia’s Office of Projects and Grants know if you have further questions (Veronica Murray at (212) 854-6851).

Sincerely,

Melvin Ziegel for George Flynn
JSEP Laboratory Director

bb
cc: JSEP file
Joint Services Electronics Program Final Report
for Contract DAAG55-97-1-0166
Covering the period May 1, 1997 – April 30, 2001

"Research Investigation Directed Toward Extending the Useful Range
of the Electromagnetic Spectrum"

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ABSTRACT (Standard Form 298 No. 13)

Experiments are described that have the goal of understanding the basic physics of quantum confined electronics. In the first experiment new fabrication processes for making GaSb-based quantum dots have been examined. The scientific goal of this work is to develop methods to realize damage free etching of the dots. In the second experiment stepped metal surfaces have been used to measure the scattering cross-sections of electrons at simple features, such as used in quantum corrals.

Mesoscopic science has been investigated in several areas using local probe and confocal optical methodologies: (1) The self-assembly properties of metallic and semiconductor nanocrystals, and the collective electrical and optical properties that result from self-assembly, were explored on graphite. The observed patterns show that the particles behave as phase separating 2D van der Waals particles. (2) Electric Force Microscopy was developed to detect the presence of a single charge on a single nanocrystal in a thin film at 23 C. This EFM method was also used to explore the electrostatic properties of self-assembled Trioctyl phosphine oxide layers on graphite. (3) The Raman scattering of single Rhodamine 6G molecules at junctions between large Ag particles was detected with high signal to noise ratio. This work has been extended to nanocrystal dimers coupled by rigid linker molecules. (4) Carbon nanotubes are probably the most novel electronic material system that has been discovered in the past decade. Optical methods were developed to obtain the Raman spectra of single tubes. It was observed that an interference occurs between vibrational and electronic scattering, creating a Fano lineshape in the Resonance Raman Spectra.

Current mode-locked laser technology can provide time resolution as fast as 10 fs = 10^{-14} s. These capabilities have had a major impact on many areas of science and advanced technology. Methods have been examined in which this extraordinary capability could be exploited to generate and detect electrical fields on transmission lines and in other circuit geometries with a time resolution dictated by the laser pulse duration. These efforts are motivated by both technological considerations (characterization of high-speed electronic and optoelectronic devices) and by scientific considerations (time-domain far-infrared spectroscopy and materials characterization). This work resulted in the demonstration of a new non-contact method of electric field generation involving optical rectification and in a new detection scheme suitable for Si and other centrosymmetric materials that relies on the process of optical second-harmonic generation.

A basic study of long-chain organic molecules that represent a model system for those used in organic molecular devices or in polymer thin films has been performed. The studies use STM techniques to probe and control order in thin films, specifically those formed at the liquid-solid interface. The molecular arrangement of adsorbrates at the liquid-solid interface is, furthermore, very important in the study of wetting, lubrication, adhesion, adsorption and the fabrication of future microelectronic devices. These studies have also been extended to systems incorporating chiral molecules. Determining and controlling the chirality of molecules that form monolayer films on surfaces represents an important step in the development of molecular devices. Ultimately, it should be possible to construct highly uniform films of
molecules having only a single chiral species. Such films can be of enormous importance as sensors and optical discriminators in many device applications.

The preparation and properties of porous SiC (PSC) films prepared by electrochemical anodization from 6H SiC were studied in a series of experiments that included: photoluminescence and Raman scattering of PSC, reflectance to determine the effective-medium dielectric function of PSC films, and successful SiC vapor-phase epitaxy on PSC substrates as monitored by polarized micro-Raman scattering. The structural phase transitions and ferroelectric ordering in crystalline bulk and thin film relaxor lead zinc niobate - lead titanate (PZN-PT) were studied from -190°C to 600°C using polarized micro-Raman scattering. The optical and structural properties of several large-band gap materials were studied, including ε-doped ZnSe:Te, Zn_{1-x}Be_xSe and GaN. Little evidence for interdot coupling of carriers was seen in three-dimensional arrays of organically passivated CdSe nanocrystals under hydrostatic pressure, probed by photoluminescence and absorption spectroscopies. Using FTIR ATR to study arrays of CdSe nanocrystals capped with pyridine, it was shown that only about 30% of the pyridine ligands remain after three days of drying.
SUBJECT TERMS (Standard Form 298 No. 14)

ab initio calculations
adsorbates
alcohols
alkane
amine
arrays
Atomic Force Microscopy (AFM)
Bi-FET
bromide
carbon nanotubes
CdSe
charge transfer salts
chemical assisted ion etching
chemical etching
chirality
chloride
coherence properties
coherent surface effects
copper surface
cutoff frequency
dielectric
dielectric function
disulfide
electron cyclotron resonance (ECR) etching
enhanced tunneling current
entangled photons
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femtosecond measurements
fractal exponent estimation
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high electron mobility transistor
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iodide
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nonlinear optics
one-dimensional quantum confinement
optical rectification
orientation
parametric downconversion
phonons
photoemission
photoluminescence
photonic band gap
photonic crystals
porous layers
pulse generation
quantum dots
quantum wells
Raman
Scanning Tunneling Microscopy (STM)
second-harmonic generation
self-assembly
semiconductor nanocrystal
SiC
silicon ion insulator
solid/liquid interface
stepped surface
strained layers
structure
superlattice
surface photoabsorption
thiols
Ti:Sapphire
two photon photoemission
ultrafast optoelectronics
vapor phase epitaxy
VPE
BASIC RESEARCH ON THE ELECTROMAGNETIC SPECTRUM

1. QUANTUM CONFINEMENT IN ELECTRONIC AND MAGNETIC MATERIALS

1.1 Nanoscale Fabrication For Advanced Semiconductor Devices (Mid IR Lasers and Photonic Crystals)
Richard M. Osgood, Jr., Principal Investigator
Research Area 1, Work Unit 1
(212) 854-4462

1.1A High-quality Etched Quantum Structures in GaSb-based Material

GaSb-based compound semiconductors are of increasing importance because of a wide range of emerging optoelectronic applications at mid-infrared wavelengths. For example, lasers with GaInAsSb active layers and AlGaAsSb confining layers can provide good optical and electrical confinement and are able to produce high power at low-threshold current densities [1]. Thermophotovoltaic cells with high internal quantum efficiency and high open-circuit voltage have been achieved with GaInAsSb[2]. For devices made of GaSb and its alloys, it is often desirable to replace wet chemical etching with dry etching because of the more anisotropic profile, uniformity and reproducibility of the latter. Despite the technological importance of GaSb-based ternary and quaternary materials, investigation of the dry etching of these materials has been limited. For example, electron cyclotron resonance (ECR) plasma etching, which is known to be suitable for III-V materials because of its high etch rate at low ion energy and pressure[3], has not been extensively studied for etching of GaSb-based ternary and quaternary alloys. Here, electron cyclotron resonance plasma etching with a mixture of argon and chlorine has been used to fabricate submicrometer-scale GaInAsSb/AlGaAsSb multiple-quantum-well (MQW) structures.

In our study, the gas-composition dependence and temperature dependence of the etch rate was determined. As shown in the inset of Fig.1, smooth surfaces with vertical sidewalls were obtained at chlorine concentrations between 15% and 28% and a substrate temperature of 150°C. To characterize any MQW damage for the etching conditions, the etched features were examined with photoluminescence spectroscopy with the 647 nm line of a Kr+ ion laser. The data obtained from the luminescence study were analyzed with a mathematical model[4] that assumes that the nonradiative damaged surface layer is thin compared to the bulk volume of the material. The results suggest that our ECR etching conditions introduce little, if any, bulk and near-surface damage; see Fig.1. This work was done in close collaboration with George Turner and his group at MIT-Lincoln Laboratory.
1.1B  **Fundamental Physics of Electron Motion at Interfaces: Observation of One-Dimensional Physics on Nanotextured Surfaces**
(X. J. Shen, H. Kwak, D. Mocuta, A. M. Radijevic, S. Smadici, R. M. Osgood, Jr.)

We have used high-resolution, angle-resolved two-photon photoemission to observe a new one-dimensional surface state, 0.27 eV below the Fermi level, on a stepped model surface. This new surface state was observed on the periodic 14Å x 2Å steps on Cu(775). The surface was investigated to determine if any evidence of reduced dimensionality is present in its electronic structure. The experiments used high-resolution, angle-resolved, two-photon photoemission (ARPPE) in conjunction with a high-repetition-rate femtosecond optical source to examine the dispersion and energy distribution curves of this surface state on the stepped surface. Comparative dispersion measurements along and perpendicular to the step edges showed that one of these surface states was occupied and had a one-dimensional character; this state apparently results from step-potential confinement. The surface of the single-crystal sample was probed under a variety of surface conditions. While this state is quenched at large values of oxygen exposure, the state appears to be enhanced by a small coverage of O₂. Further studies such as systematic time-resolved measurements on the newly observed state, STM observations of clean and oxygen exposed Cu(775) surface, step decoration with model adsorbates such as Xe, and, finally, polarization-dependence experiments may lead to new insights into the localization physics. The experiments on this system have been discussed in more detail in the Physical Review article cited in the publications.
Fig. 2. Dispersion of the newly observed occupied band perpendicular and parallel to the step. Monochromatic 2PPE at 3.1 eV is used. The inset provides one typical electron distribution curve, taken at θ=9 degrees which shows the co-existence of both the localized state and the n=0 surface state.

References:
JSEP PUBLICATIONS AND PRESENTATIONS of Professor Richard Osgood


2. Papers published in non-peer-reviewed journals or in conference proceedings:

None

(c) Papers presented at meetings, but not published in conference proceedings


(d) Manuscripts submitted, but not published:

(c) JSEP Technical Reports submitted (1997-2000)

INVENTIONS
None
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Mocuta, D., Postdoc (IBM)
Moryl, J., Research Scientist (Seton Hall)
Nagy, G., Postdoc (Intel)
Osgood, Jr., R. M., Professor, Principal Investigator
Radojevic, A. M., GRA PhD
Rao, H., GRA PhD
Scarmozzino, R., Research Scientist (Chief Technical Officer, RSoft)
Shen, X. J., GRA Ph.D (Computer Systems)
Smadici, S., GRA Ph.D.
1.2 ORDERED QUANTUM DOT THIN FILMS AND MATERIALS
Louis E. Brus, Principal Investigator
Research Area 1, Work Unit 2
(212) 854-4041

1.2A Self-Assembly of Nanocrystals

We explored the self-assembly properties of metallic and semiconductor nanocrystals, and the collective electrical and optical properties that result from self-assembly. We investigated 2D self-assembly on graphite surfaces, in order to explore fundamental questions of nanocrystal-solvent phase diagrams, and the interaction potential between two solvated nanocrystals. The observed bicontinuous patterns, as a function of surface coverage and drying time, imply that aggregation occurs by fluid-fluid spinodal nucleation and subsequent coarsening. Theoretically we investigated the nature of the van der Waals forces between mesoscopic objects. We also explored the mechanism of surface diffusion on graphite.

1.2B New Experimental Methods

We also developed new experimental methods for observation of single nanocrystals and nanotubes. We developed Electric Force Microscopy in order to detect the presence of a single charge on a single nanocrystal in a thin film at 23 C. Using an AFM modified to operate as a capacitor in non-contact mode, we detect the electric field gradient of one charge as a downshift in AFM cantilever resonant frequency. We have demonstrated that a single charge, either intrinsic or due to photoionization, can be observed with signal to noise of about five. This EFM method was also used to explore the electrostatic properties of self-assembled Trioctyl phosphine oxide layers on graphite.

1.2C Raman Scattering from Silver Nanocrystals

We have also carefully explored the Raman scattering of single Rhodamine 6G molecules on large Ag particles. While it has been known for 2 decades that there is an apparent local field Raman enhancement for molecules near Ag particles, we find that the Raman cross section is about 200 square Angstroms for Rhodamine molecules adsorbed in special sites. This is far larger than expected, and we believe it indicates the molecule is coupled to the transition dipole of the Ag particle by direct electron exchange. We are exploring a mechanism involving the interaction of ballistic electrons in the Ag with chemisorbed molecules at the junctions of two 50 nm particles. This work has been extended to nanocrystal dimers coupled by rigid linker molecules.

1.2D Raman Scattering from Single Carbon Nanotubes

Carbon nanotubes are probably the most novel physical system that has been discovered in the past decade. These tubes are the object of intense and accelerating study in the microelectronics community, as a possible physical system for "molecular electronics" in future decades into the coming century. Synthetic methods make a broad mixture of tubes, of varying diameter and helicity. We carefully explored the Raman spectra of single nanotubes. We discovered that interference between the electronic and vibrational Raman scattering creates a Fano lineshape in the Resonance Raman Spectra. Via analysis of this scattering we should be able to understand the position of the Fermi level in metallic tubes, as a function of adsorbed surface molecules. We also were able to make structural assignments by analysis of the Stokes to anti-Stokes intensity ratio of the nanotube breathing mode, by use of a simple Resonance Raman model.

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JSEP PUBLICATIONS AND PRESENTATIONS of Professor Louis Brus

(b) Papers published in non-peer-reviewed journals or in conference proceedings:
Bosang Kim, Mohammad A. Islam, Louis E. Brus, and Irving P. Herman, "Pressure-Induced interdot interactions in CdSe nanocrystal arrays," Abstracts of the MRS 1999 Fall meeting in Boston, MA, Presentation H2.3, p. 152.

(c) Papers presented at meetings, but not published in conference proceedings:
Major presentations "Physics and Chemistry of Mesoscopic Particles" with partial JSEP support:
Colloquium, Chemistry Dept., University of Maryland, 2/4/98.
Colloquium, Physics Dept., City College of New York, 2/11/98.
Invited Talk, ACS National Meeting, Dallas, Texas, 3/30/98.
Colloquium, Physics Department, Columbia University, New York, NY, 4/24/98.
Physical and Materials Science Colloquium, Research Division, Bell Laboratories, NJ, 6/2/98.
Colloquium, Physics Department, University of Ohio, Toledo, Ohio, 9/2/98.
Colloquium, JILA, University of Colorado, Feb. 12, 1999.
Harold Nation Lecture, Georgia Institute of Technology, Nov. 19, 1999.
Chemistry Division, Brookhaven National Laboratory, Feb. 16, 2000.
NSF sponsored Materials Research Science and Engineering Center Director's Meeting, University of Chicago, April 7, 2000.
Chemistry Department, Long Island University, Feb. 13, 2001.

(d) Manuscripts submitted, but not published:

(e) JSEP Technical Reports Submitted (1997-2000)
INVENTIONS
None

SCIENTIFIC PERSONNEL in Research Group of Professor Louis Brus
Personnel with full or partial JSEP support:
Postdoc Todd Krauss, now Assistant Professor at the University of Rochester
Postdoc Manoj Nirmal, now with the 3M Company
Amy Michaels, PhD (August 2000)
Zhonghua Yu, PhD (August 2000)
PhD Student Guanglu Ge
PhD student Jiang Jiang
PhD student Jing Tang
Undergrad student Zack Weinberg, now a PhD student at Stanford
2. ULTRAHIGH SPEED ELECTRONICS: NEW DEVICES AND PROBING TECHNIQUES

2.1 ULTRAFAST STUDIES OF ELECTRONIC MATERIALS AND DEVICES

Tony F. Heinz, Principal Investigator
Research Area 2, Work Unit 2

(212) 854-6545

2.1A Generation of Ultrafast Electrical Pulses by Optical Rectification

The established approach for producing electrical transients using femtosecond optical excitation of photoconductors exhibits a fundamental limitation in response time, in the range of 0.5 ps, related to the transient dynamics of the photoexcited carriers. In addition, the photoconductive switch must be designed into the transmission line in advance and requires specialized processing steps or growth processes to achieve reduced carrier lifetimes that may be incompatible with other required fabrication steps. In investigations supported by the JSEP program, we have demonstrated a new approach to the production of ultrafast electrical signals on transmission lines that is flexible, non-invasive, and has the potential to produce electrical pulses whose duration is constrained only by that of the optical pulses. The new scheme that we have introduced involves the optical rectification process, an effect also mediated by the electro-optic response of the material. In this case, a short optical pulse passing through the nonlinear medium generates a polarization that follows the intensity envelope of the optical pulse. We have demonstrated that the transient polarization induced by an ultrafast optical pulse can be effectively coupled to a transmission line structure to produce an ultrafast electrical transient.

In our experiment, the generation process occurs in a LiTaO₃ nonlinear crystal bonded to a coplanar transmission line in a sliding contact geometry; phase coherent detection of the resulting electrical pulses on the transmission line is accomplished with a gated photoconductive switch integrated into the device. A bipolar temporal waveform with a width of 0.9 ps is measured after a propagation distance of a fraction of a mm. This pulselength is limited by the response time of the radiation damaged Si-on-sapphire-based photoconductive sampler. We observe both broadening and amplitude reduction in the temporal waveform due to propagation. A substantial improvement in both the bandwidth and amplitude is expected for a phase-matched geometry wherein both the optical and electrical pulses co-propagate along the transmission line. The present generation scheme may be used to inject electrical pulses at arbitrary points in a device or circuit. The combination of this approach with electro-optic sampling to reduce the detection response time will permit a compact all-optical spectroscopy system with extremely high bandwidths to be developed for transmission line measurements. The approach should also facilitate new measurements in circuit and device characterization.

2.1B Detection of the Vector Character of the Electromagnetic Field by Second-Harmonic Generation

A promising new optical technique for probing transient electric fields is that of optical second-harmonic generation (SHG). SHG has been employed to detect electrical pulses [1] and microwave signals in transmission line structure [2], as well as freely-propagating terahertz radiation [3]. The method, which utilizes the nonresonant material response of the sample, provides exceptional time resolution. The approach of field-induced SHG complements the powerful and well-established laser-based techniques of photoconductive sampling and the method of electro-optic sampling. The attractiveness of the SHG scheme lies in its simplicity and flexibility. For centrosymmetric materials, SHG permits direct optical probing of the field present in the sample without the introduction of external
crystals or special device structures. This property arises from the fact that the SHG process is forbidden (within the dipole approximation) in centrosymmetric materials, but becomes allowed in the presence of an electric field. Thus, in contrast to the linear optical response, the second-order nonlinear response of a centrosymmetric material is strongly influenced by the presence of relatively weak electric fields and measurements may be made in a simple reflection geometry.

Here we describe two recent advances that we have made in this method for probing electric fields: (i) A scheme for linearizing the relationship between the electric field and SHG intensity; and (ii) an approach for determining the vector nature of the electric field. Measurements have been carried out in silicon samples to illustrate these improvements in the technique experimentally. In our application of the method, we have also demonstrated the possibility of obtaining detailed spatially resolved 2-dimensional maps of the vector electric field distributions.

In order to understand the features of the EFISH technique, consider the behavior of the SH response observed for a static electric bias applied across the electrodes of Fig. 1. These data indicate the expected lack of a background signal in the absence of any bias field. Under application of a bias field, the relationship between the measured SH signal and the applied electric field \( E^0 \) is seen to be quadratic: \( I_{2\omega} \propto (E^0)^2 \). This expression reflects the linear relationship between the applied electric field \( E^0 \) and the nonlinear polarization, together with the quadratic relation between the SH intensity and the strength of the nonlinear polarization. Such a quadratic relation is clearly inconvenient, since it is more difficult to calibrate than a linear relationship. It also implies that information on the sign of \( E^0 \) is lost.

![Fig. 1. Quadratic dependence of SH intensity with the applied bias voltage.](image)

To characterize fully the applied electric field \( E^0 \) and linearize the relationship between the measured SH intensity and \( E^0 \), we take advantage of interference techniques. In the present work we have applied a homodyne detection scheme [4]. In this approach, a reference SH field, \( E_{\text{ref}} \), is introduced that interferes with the SH field \( E_{\text{sig}} \) arising from the field-induced SH radiation. The total SH intensity then becomes

\[
I_{2\omega} \propto \left| E_{\text{sig}} + E_{\text{ref}} \right|^2 = E_{\text{sig}}^2 + E_{\text{ref}}^2 + 2E_{\text{sig}}E_{\text{ref}} \cos \phi
\]

where \( \phi \) is the relative phase between the two SH fields. In the limit of a strong reference field \( (E_{\text{ref}} \gg E_{\text{sig}}) \), the measured SHG is linear in \( E_{\text{sig}} \), which is in turn proportional to \( E^0 \), i.e.,

\[
I_{2\omega} \propto E_{\text{ref}}^2 + 2E_{\text{sig}}E_{\text{ref}} \cos \phi.
\]

In our experiment, the reference field, \( E_{\text{ref}} \), was provided by SHG from a \( z \)-cut quartz plate positioned before the sample.
Figure 2 shows the behavior of the total SH intensity over a large range of the bias voltage when the phase difference between $E_{pl}$ and $E_{ap}$ was arranged to yield $\phi = 0$. The inset in the figure illustrates the case when $E_{ref} \gg E_{ap}$, which clearly demonstrates the expected highly linear dependence of the SHG signal on the bias voltage or applied electric field $E_a$. In addition, we can establish the sensitivity of this technique to be $\sim 100 \text{ V/cm/Fz}^{1/2}$, which should be amenable to further optimization through improvements in laser and material parameters.

![Graph showing SH intensity versus bias voltage](image)

**Fig. 2.** Total SH intensity versus applied voltage for the case of $\phi = 0$ over a wide range of bias voltage and for the case where the applied voltage is small.

We now wish to discuss the second improvement in the EFISH technique for probing electric fields and transients. This concerns measuring the vector character of the electric field. While previous studies have illustrated the sensitivity and time resolution of the method for probing the strength of the electric field, the potential for determination of the vector character of the electric field has not been examined. We have recently developed a scheme for such vector electric field measurements [5]. We illustrate the method by mapping the spatial distribution of the in-plane electric field in a silicon sample. By analyzing the tensor properties of the relevant nonlinear optical process in EFISH, we were able to develop a protocol for measuring the orthogonal components that compose the applied electric field. This could be accomplished simply by measuring the two orthogonal components of the field-induced SHG signal for normal incidence excitation. The approach was combined with the homodyne detection scheme described above to yield a linearized response.

Figure 3 shows experimental data for the electric field of a silicon-on-sapphire substrate patterned with aluminum lines. The electrode geometry consisted of $750 \times 750 \mu\text{m}^2$ rectangular pads that are separated by 80 $\mu\text{m}$. For purposes of illustration, a bias voltage of 360 V, corresponding to an average electric field strength of approximately 45 kV/cm, was applied across the electrodes. The electric field components were sampled by scanning along the $x$-axis for each $y$-position at 10 $\mu\text{m}$ increments in a square grid. The optical SHG measurements were made with a modelocked Ti:sapphire laser.

In the resulting vector field map note that in the area between the electrodes, the electric field is relatively uniform and aligned along the $x$-direction. We attribute the weak irregularities in the electric
field direction seen in certain spatial regions to local imperfections and inhomogeneities in the substrate and electrode structure. In the region beyond the end of the electrodes, we observe the expected fringing pattern. The electric field in this region has both $x$ and $y$ components, which can be comparable, especially near the corners of the electrodes. Because of the finite spatial resolution of the SHG probe, the inferred amplitude of the electric field at grid points adjacent to the electrodes is reduced and, conversely, finite values for the electric field are found for grid points just inside the electrodes. Well inside the electrodes, no electric field was detected within experimental uncertainty.

It is anticipated that this approach will find application in analysis of high-speed electronic and optoelectronic devices.

Fig. 3. Experimental results from field-induced SHG measurement: vector map of the electric field distribution at the end of a pair of metal electrodes deposited on a silicon-on-sapphire substrate.

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3. MATERIALS PROCESSING AND DIAGNOSTICS FOR ADVANCED ELECTRONIC MATERIALS

3.1 ELECTRONIC AND STRUCTURAL PROPERTIES OF SURFACES AND SURFACE ADSORBATES USING SCANNING TUNNELING MICROSCOPY (Controlling Chirality of Interfacial Films)

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3.1A Packing of Br(CH₂)ₙCOOH and Br(CH₃)₁₀COOH on Graphite: An Odd-Even Length Effect Observed by Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) is a powerful tool for studying molecular ordering at the liquid-solid interface. Early STM studies of singly substituted long chain alkane molecules at the solution-substrate interface have shown that different functional groups can have important effects on molecular ordering. For example, n-alkanes form lamellar structures on graphite with their molecular axis perpendicular to the lamellar boundary; 1-alcohols have a 60° angle between their molecular axes and the lamellar direction; 1-carboxylic acid molecules assume an interdigitating structure; and 1-bromo- and chloro-alkanes take the same surface arrangement as the n-alkanes. Thus, the end groups of these molecules play a pivotal role in their packing pattern.

STM has been used to investigate doubly substituted 11-bromoundecanoic acid, Br(CH₂)₁₀COOH, and 12-bromododecanoic acid, Br(CH₃)₁₁COOH, where it was observed that chain length, in particular even and odd numbers of carbon atoms, can have a significant impact on thin film, interfacial ordering. The absolute conformations of these molecules have been determined unambiguously. Both molecules adopt structures different from their monosubstituted counterparts. The packing structure of these molecules on the surface has been found to be significantly affected by whether the hydrocarbon chain has an odd or even number of carbon atoms. A simple geometric effect and molecular model have been used to explain the source of this difference.

3.1B Direct Determination of The Chirality of Organic Molecules Adsorbed At Liquid-Solid Interfaces Determined By Scanning Tunneling Microscopy

In some cases, STM has achieved atomic resolution allowing the relative position of individual atoms in a molecule to be clearly observed. Given this sensitivity, SPM seems to be a promising method for determining the absolute configuration of chiral molecules. Indeed some progress has been made in this direction. By using atomic force microscopy (AFM), a few chiral symmetry breaking phenomena in Langmuir-Blodgett films have been observed. R and S enantiomers of chiral biphenylbenzoates have been found by STM to give different 2-D chiral images; however, the molecular resolution obtained in these studies did not allow the direct assignment of the absolute configuration of the individual enantiomers. Recently, there has been a beautiful demonstration of the principles of chiral HPLC using chemical force microscopy. In our study atomically resolved STM images of 2-bromohexadecanoic acid adsorbed on a graphite surface provide a direct assignment of single molecules as having R or S chiral centers through the use of STM “marker” chemical groups and atoms. The chiral molecules, (R)/(S)-2-
bromohexadecanoic acid, adsorbed on the graphite surface have been imaged by STM with atomic resolution. These two enantiomers segregate on the graphite surface and form different, pure R or S domains. The two enantiomers give mirror image packing patterns on the graphite surface. The absolute configuration of these molecules can be directly observed in the STM images.

3.1C Controlling Chirality of Interfacial Films

The chirality of individual molecules has been determined and investigated using scanning probe methodologies in the studies of 2-bromohexadecanoic acid and the asymmetric induction of alkenes on a silicon surface. It is now appropriate to ask how the self-assembly of chiral molecules is affected by the presence of other non-chiral species. De Feyter et al. have studied monolayers of enantiomerically pure isophthalic acid derivatives coadsorbed with the achiral solvent 1-heptanol onto a graphite surface. The effect of a third element (a coadsorbate in the form of another solute), however, has not been previously studied. Such achiral coadsorbates show promise as powerful tools to segregate chiral molecules and control self-assembled monolayers.

The self-assembly of a mixture of achiral hexadecanoic acid with racemic 2-Br-hexadecanoic acid has been investigated in our laboratory using scanning tunneling microscopy. Hexadecanoic acid has the ability to control the two-dimensional structure formed at the interface by creating a template that sets the angle between the molecular and lamellar axes in the mixed monolayer. Further, inherently achiral hexadecanoic acid self-assembles on the graphite surface into two distinct, although almost indistinguishable domains that exhibit mirror image morphology, similar to that observed for other even-numbered fatty acids. This property leads to resolution of (R)/(S)-2-Br-hexadecanoic acid into enantiomerically pure (R and S) domains when physisorbed onto a graphite surface from the mixture. Achiral molecules such as hexadecanoic acid are, thus, shown to have remarkable potential as tools to manipulate self-assembly and more specifically, to induce enantiomeric resolution of racemic mixtures like 2-bromohexadecanoic acid.

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3.2 NEW OPTICAL MATERIALS, SOURCES, AND METHODS
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3.2A Processing, Physics and Applications of Porous SiC

The preparation and properties of porous SiC were studied in a series of experiments. The optical transmission, temperature-dependence of the photoluminescence (PL), and Raman scattering of porous SiC prepared from p-type 6H-SiC were compared with those from bulk p-type 6H-SiC. While the transmission spectrum of bulk SiC at room temperature revealed a relatively sharp edge corresponding to its band gap at 3.03 eV, the transmission edge of porous SiC (PSC) is too wide to determine its band gap. It is believed that this wide edge might be due to surface states in PSC. At room temperature, the PL from PSC is 20 times stronger than that from bulk SiC. The PL PSC spectrum is essentially independent of temperature. The relative intensities of the Raman scattering peaks from PSC are largely independent of the polarization configuration, in contrast to those from bulk SiC, which suggests that the local order is fairly random.[1]

The reflectance of PSC thin films on SiC substrates was measured in the infrared reststrahl region by Fourier transform infrared reflectance spectroscopy and compared to simulated spectra based on phenomenological and Bergman statistical effective-medium dielectric functions. The phenomenological models evaluated include the Bruggeman, cavity- and sphere-Maxwell-Garnett (C-MG and S-MG), Landau-Lifshitz/Looyenga (LLL), and Monecke models. In addition, modifications to the Bruggeman and C-MG models with variable particle shapes and surface layers were examined. Hybrid versions of the C-MG and LLL models were also considered, alternatively by using a phenomenological mixing approach, which gives a direct physical interpretation of the topology, and by directly mixing the statistical spectral density functions of the C-MG and LLL effective dielectric functions. This latter statistical hybrid model gave the best (and quite good) agreement with experiments (Fig. 1). The differences in the hybrid models can be understood by comparing their spectral density functions. The dip (or splitting) in the PSC film reststrahlen band is attributed to a wide spectrum of surface optical phonon modes.[2]

The infrared reflectance from PSC prepared in n-type SiC, both as-anodized and passivated, was also studied. The passivation of PSC was accomplished using a short thermal oxidation. Fourier transform infrared (FTIR) reflectance spectroscopy was employed ex situ after different stages of the thermal oxidation process. The characteristics of the reststrahlen band normally observed in bulk SiC are altered by anodization; further changes in the reflectance spectra occurred following oxidation for different periods of time. An effective medium theory model that includes air, SiC and SiO2 as component materials was shown to characterize the observed changes in the reflectance spectra after different stages of PSC oxidation.[3]

SiC vapor-phase epitaxy on PSC substrates formed by electrochemical anodization was demonstrated. Polarized micro-Raman scattering indicated that the polytype of the optically smooth SiC grown on PSC formed in both p-type and n-type 6H-SiC substrates is 6H. The Raman scattering selection rules in these films are the same as those observed in the bulk substrate and epilayers grown on bulk, indicating high crystalline quality (Fig. 2). The formation of epitaxial 6H-SiC on porous 6H-SiC may open up new possibilities for dielectric device isolation, fabrication, and epitaxial lift-off.[4]
Fig. 1. Modeled reflectance from PSC films on SiC substrates using the Bergman statistical hybrid model with $\alpha = 0.5$ (dashed lines) for the three PSC films; the measured reflectance is denoted by the solid lines. For comparison, model fits for $\alpha = 0.3$ and 0.7 are also shown for PSC3.
Fig. 2. Cross-section polarized Raman spectra of SiC on porous (a) sample P1, and (b) sample N2. The solid, dashed, and dotted lines denote the $y(x,z)\parallel$, $y(x,z)\parallel$ and $y(x,x)\parallel$ configurations, respectively. The spectra have been taken near the top surface in (a1) and (b1), near the center of the regrown layer in (a2) and (b2), and within the underlying bulk substrate in (a3) and (b3).
3.2B Properties and Processing of Oxide and Large Band-Gap Semiconductor Films

In a collaboration with Prof. Osgood's group, a novel process to form thin films of lead zinc niobate - lead titanate (PZN-PT) from a bulk crystal for microelectronic and microelectromechanical device applications was studied. The structural phase transitions and ferroelectric ordering in unpoled crystalline bulk and thin film relaxor PZN-PT were studied from -190°C to 600°C using polarized micro-Raman scattering. The structural phase transitions in this material were observed by distinct changes in the polarization selectivity (Fig. 3). The results for the thin film and the bulk crystal were found to be in good agreement for a wide range of the temperatures studied, indicating that the thin-film PZN-PT retains much, if not all, of the structural and ferroelectric properties of the original bulk substrate.[5]

In a collaboration with Prof. Neumark's group, the optical and structural properties of the δ-doped ZnSe:Te system were studied using photoluminescence (PL), x-ray and polarized Raman scattering. The Herman group did the Raman studies in this work. All of these samples are of reasonable crystalline quality and have the symmetry of the host ZnSe lattice as determined by x-ray diffraction and Raman scattering.[6] As part of this collaboration, evidence of isoelectronic traps were found in MBE grown Zn1-xBe_xSe, using photoluminescence (PL). Studies of the PL as a function of pressure in a diamond anvil cell confirmed that this state is linked to the band transition.[7] In several samples of GaN films, highly unusual and reversible decay and enhancement of PL was also studied.[8]

3.2C Properties of Arrays of CdSe Nanoparticles

Three-dimensional arrays of organically passivated CdSe nanocrystals were investigated under hydrostatic pressure using photoluminescence (PL) and absorption spectroscopies. Interdot separations were varied coarsely by varying the organic ligand on the nanocrystal and finely by applying hydrostatic pressure. The PL and absorption spectra of solutions and arrays of CdSe nanocrystals capped by either tri-n-octylphosphine oxide (TOPO) or tri-n-butylphosphine oxide (TBPO) are the same up to 60 kbar, which suggests that they exhibit no interdot coupling since the interdot separation in the solutions (~50 nm) are much greater than those in the arrays (~1 nm). While the variation with pressure is roughly that expected from the increase in band gap energy of bulk CdSe with pressure and the increase in confinement energies of electrons and holes with increased pressure, there is still a significant difference in the energy of the PL peak and the first exciton in absorption (the Stokes shift) for both these solutions and arrays that increases with pressure (Figs. 4 and 5). This is attributed mostly to increased vibrational relaxation due to the movement of nuclei in the excited state. In contrast, there is a distinct difference between the pressure dependence of CdSe/pyridine dots in solution and arrays; the increase of the energy of the first exciton peak in absorption with pressure becomes markedly slower above about 30 kbar in CdSe/pyridine arrays, and is lower than that in the corresponding solution by ~ 50 meV at 50 kbar and ~70 meV at 60 kbar (Fig. 6). Experiments with CdSe/shell/pyridine dots, with large electron and hole barriers, cast doubt on the mechanism of interdot electron and/or hole tunneling leading to a decrease in electron and/or hole confinement energy. Also, interdot tunneling of single carriers may be inhibited by the charge separation energy. The differences in the dielectric medium surrounding each dot in the solution and array explain their different absorption exciton energies at ambient pressure, but not the changes at elevated pressure.[9]

The observed loss of much of the pyridine ligands during array drying could be very significant, and contact between pyridine-capped dots at elevated pressure may be important. Using FTIR ATR, it was shown that only about 30% of the pyridine ligands remain after three days of drying (Figs. 7 and 8).[10]
Fig. 3. (a) Raman scattering intensities of the \( \sim 780 \text{ cm}^{-1} \) line for the bulk sample for the \( z(x',y')z \), \( z(x,y)z \), \( z(x',x')z \), and \( z(x',y')z \) configurations, and (b) the polarization ratios \( p \) (solid squares) and \( p' \) (open diamonds) plotted as functions of temperature. The intensities are offset for clarity, and the polarization ratios are on a log scale.
Fig. 4. (a) PL and (b) absorption spectra of CdSe/CdS/TBPO nanocrystal arrays as a function of pressure; for clarity only selected spectra at intermediate pressures are shown. These spectra are fairly typical for CdSe nanoparticles capped by TOPO or TBPO in dilute solution or in an array. Note the structural phase transition from wurtzite to rock salt above 65 kbar.
Fig. 5. (a) Peak energy of PL and (b) the first excitonic peak energy of the absorption spectra vs. pressure for solutions and arrays of CdSe nanocrystals capped by either TOPO or TBPO. Each plot in each figure has been shifted vertically by up to ~10 meV so that each overlaps at 1 bar. The solid curve is a least-squares fit to the data in each part. The expected band gap energy of isolated CdSe nanocrystals vs. P is plotted in both parts, which accounts for changes in the bulk band gap and confinement energies.
Fig. 6. The first excitonic peak energies in absorption spectra for several CdSe/pyridine runs. Note the significant difference between the solution and the array runs. Each plot has been shifted by up to \(-10\) meV so that each overlaps at 1 bar. The solid line is the fit to the exciton absorption data in (and also plotted in) Fig. 5-(b).
Fig. 7. ATR spectra of CdSe/pyridine arrays formed with pyridine solvent 2, 15, and 60 min. into self-assembly, along with those of pure TOPO and a CdSe/TOPO array formed with hexane solution. The inset shows spectra of CdSe/pyridine arrays after 20 min. and neat pyridine.

Fig. 8. Heights of 1445 cm⁻¹ peaks in the ATR spectra of (a), (b), and (c) CdSe/pyridine arrays from pyridine solution and (d) CdSe/TOPO arrays from pyridine solution as a function of drying time, normalized to unity at the maximum of each trace. The inset shows this (unnormalized) on a finer time scale at 1445 cm⁻¹ (bound pyridine) and also at 1436 cm⁻¹ (neat pyridine).
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