

Physical and Chemical Sciences Center

Research Briefs

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Message from the Director

The Physical and Chemical Sciences Center provides new scientific knowledge in support of Sandia's missions for the Department of Energy. One area of emphasis for our research is to support predictive reliability in existing and emerging technologies. With the demise of underground nuclear testing and the requirement for longer life of the stockpile, the science underlying the viability of the stockpile is critical in understanding and quantifying aging effects. This knowledge provides a foundation for stockpile certification. At the same time, our investments in fundamental science lead to new material systems, processes, theoretical understandings and technologies that improve the safety, security and reliability of nuclear weapons; provide the means to monitor and assure nonproliferation objectives; and support DOE initiatives in energy and environmental needs.



While our research investments span the longer term (more fundamental) to nearer term (more applied) spectrum, this Research Briefs specifically highlights our recent accomplishments supporting application needs. We emphasize neutron generator devices and advanced weapons components. Neutron generators are limited life components which initiate a nuclear device. Miniature lasers will provide high voltage switching and explosives initiation in the future, important functions where replacing electrical by optical approaches gives enhanced safety. Microdevices, based on micro-electromechanical technologies, will help pave the way for a new generation of surety devices, providing increased security and safety at reduced cost and size.

In addition to these focus areas, we illustrate some of the exciting developments in our laser, optical, and semiconductor science investments for monitoring and sensing science, which will provide new techniques, and approaches for nonproliferation and materials control. Equally exciting, many of the nanoscale techniques and scientifically tailored materials principles being developed are also broadly applicable to energy or environmental issues.

The activities of the Physical and Chemical Sciences Center are supported by a diverse set of funding sources (see page 75), and are managed to assure integration and synergy between projects. The research described in this Research Briefs provides examples that illustrate the importance of a strong science base in physics and chemistry to the success of DOE's Stockpile Stewardship mission. This work also provides insights into the connections between science and the wide range of DOE technologies. In essentially all the research described, our partnerships with colleagues in program areas across the Labs have been critical and we acknowledge with gratitude their collaboration.

S. Tom Picraux Director

"Exceptional Service in the National Interest"

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Plasma Evolution in Neutron Tubes

by P. A. Miller, G. A. Hebner, J. R. Woodworth, B. P. Aragon and T. W. Hamilton

M otivation—Sandia has prime responsibility for the design and production of neutron generators, at the heart of which is the neutron Within the neutron tube, plasma is tube. generated by an electrical discharge in deuterium. The plasma expands and flows to a grid from which ions are accelerated towards a tritiated target. Upon impact, a burst of neutrons is produced. The expansion and flow of plasma to the grid affect the intensity, pulse shape, and spatial distribution of the ion beam. The evolution of the plasma and the ion beam are being modeled in the ASCI program. These models must be validated against experimental measurements in order to develop confidence in the models. Our experimental work will provide We also will test novel validation data. approaches to improve the plasma flow for better utilization of plasma in order to reduce power requirements for the plasma source.

A ccomplishment—An experimental test facility has been developed for diagnosing plasmas generated by neutron-tube sources. The facility includes a vacuum system for holding demountable plasma sources, an electrical pulseforming line to excite the sources, and a variety of diagnostics.

To facilitate diagnostic development, initial work has been performed using ersatz plasma sources consisting of surface arcs between electrodes made of various materials. These sources generate many different ion species but have total ion and electron densities similar to those from the real sources used in neutron tubes. However, in contrast to the real sources, these ersatz sources are very inexpensive and have extremely long lifetimes, which are valuable attributes for diagnostic development. Initial source characterization was performed using an array of Langmuir probes biased to collect ion saturation current. Figure 1 shows the linear array of eight probes and sample pulse data from an ersatz plasma source. The currentdensity values are similar to data taken in other experiments several years ago using plasma sources from neutron tubes. However, the ion output from ersatz sources frequently has large spikes. Analysis of the axial dependence of data such as these indicates that the plasma is expanding spherically with constant velocity. This type of data from real sources will be compared directly with model predictions.

Several optical diagnostics are also being developed. Figure 2 shows a series of framing photographs of the expansion of the plasma plume. The oscilloscope trace shows the total time-dependent optical emission from the copper-electrode source. The time integrated spectrum shows the dominance of copper emission lines and the presence of hydrogen impurities in this source. Such optical emission data will be used to determine if the demountable plasma sources operate in the test facility in the same way that they do in real neutron tubes. Other optical diagnostics that have been tested successfully include of neutral-atom density measurement by refractive bending of a laser beam.

S ignificance—The testbed and experimental diagnostics are now ready for tests with neutron-tube plasma sources. The first set of sources have just been obtained and await testing. The demonstrated capability of the diagnostics indicates that validation data will be obtained rapidly.

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Figure 1. Ion saturation current density and integrated charge vs. transverse position. Variation with axial location (not shown) indicates constant-velocity spherical expansion of plasma from the ersatz plasma sources.



Figure 2. Optical data from ersatz plasma source using copper electrodes. Framing photographs show side view of plasma plumes expanding to the left, emanating from the anode (A) and cathode (K) of the surface arc

Emission and Absorption of Deuterium in Neutron Tube Ion Sources

by W. R. Wampler

M otivation—A neutron tube operates by extracting deuterium ions from a pulsed vacuum arc plasma. The plasma is fueled by deuterium emitted from a metal deuteride thin film which is heated by the arc. Deuterium emission from the film involves bulk diffusion to the surface and molecular recombination and desorption at the surface, these are thermally activated processes. The neutron output during a shot and the number of shots to end-of-life are critical tube parameters which depend on repeated emission of deuterium from the film. In addition, the ion source lifetime may be extended by absorption of deuterium back into the film after a shot. Realistic modeling of D emission and absorption is required for reliable prediction of neutron output during a shot and of changes in output from shot to shot.

A ccomplishment—A computer simulation was developed to model deuterium emission during operation of a neutron tube ion source. In addition, experiments have been initiated to obtain data needed to validate the modeling. These experiments consist of measurements of the deuterium concentration versus depth in the film by ion-beam analysis (IBA), and measurement of the areal distribution of broadband visible (Fig. 1) and H α light emission during ion source operation. The initial composition was dideuteride throughout the entire thickness of the film. Similar measurements after partial depletion of the reservoir will reveal the evolution of the D depth distribution with number of shots.

The model numerically solves diffusion equations to determine the temperature and deuterium concentration in the film as a function of depth and time. Figure 2 shows the surface temperature versus time from previous IR radiance measurements $(symbols)^{\dagger}$ and from the simulation. The surface temperature rises very rapidly initially but then levels off at longer times. Figure 2 shows calculated surface temperatures when the heat flux to the surface is constant (dashed curve) and when the heat flux to the surface decreases as the deuterium flux from the surface increases (solid curve). The corresponding deuterium flux from the surface is shown by the dotted curve. The simulations show that a feedback mechanism exists which regulates the surface temperature by reducing the heat flux to the surface as the deuterium flux from the surface increases. Cooling effects of vaporization, dissociation and ionization of deuterium are too small to produce the observed temperature regulation. The model predicts that the emitted deuterium leaves a depleted region near the surface after a shot which may fill in slowly by diffusion between shots. This suggests that the time delay between shots may affect ion source performance. This prediction can also be tested by IBA experiments.

S ignificance—Sandia has responsibility for production of neutron generators. Nuclear decay of tritium makes neutron tubes a limitedlife component requiring periodic replacement. Reliable production of tubes with predictable performance therefore essential is for maintenance of a functioning nuclear stockpile. A detailed understanding of the physical mechanisms involved in the operation of neutron tubes can help identify critical processing parameters in their production and may point to improved tube designs. The work described here improves understanding of the role of deuterium emission in the operation of the ion-source.

† D. A. Benson, Sandia Report, SAND81-0116.

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Figure 1. Broadband visible emission during ion source operation.



Figure 2. Source surface temperature (experiment: circles, model: solid line) and deuterium emission (dotted line) as a function of time.

Dynamic Electromechanical Response of Ferroelectric Ceramics

by R. E. Setchell, L. C. Chhabildas, M. D. Furnish, and S. T. Montgomery

M otivation—Shock-induced depoling of the ferroelectric ceramic PZT 95/5 has been utilized in pulsed power applications for many years. Recently, new design and certification requirements have generated a strong interest in numerically simulating the operation of pulsed power devices. The poled ceramic has a complex behavior, however, with nonlinear coupling between mechanical and electrical variables. Because few relevant studies have been performed during the past twenty years, we have initiated an extensive experimental study to provide insight and well-characterized data for the development of improved material models to be used in the numerical simulations.

A ccomplishment—The first phase of this study has addressed the mechanical behavior of unpoled PZT 95/5. Using planar impact techniques, samples from 2 to 4 mm thick have been subjected to shock compression and subsequent release over the range of axial stresses of interest (0.5 to 5.0 GPa). The rear surface of each sample is bonded to either a fused silica or sapphire window with a diffusively reflecting surface at the interface. Laser velocity interferometry (VISAR) is used to obtain particle velocity histories at this interface. Figure 1 shows transmitted wave profiles recorded in three experiments with identical target and projectile assemblies but different impact velocities. A small ramp at the start of each profile represents the behavior of the PZT 95/5 in its ambient ferroelectric (FE) phase. The ramping behavior corresponds to compressibility increasing with increasing pressure. The front of this feature propagates at the longitudinal acoustic speed. The lowamplitude ramp is followed by a fairly steep rise reflecting a transition to an antiferroelectric (AFE) phase. This shock-driven phase transition is the process by which depoling occurs in power supply elements. The final wave feature during shock compression represents relatively slow pore-compaction processes in this material (9% porosity by volume).

An approximate method to determine stressstrain paths during loading has been used to estimate end states achieved in each experiment, and these states can be compared to the Hugoniot and end-state data found in previous studies of unpoled PZT 95/5. Such a comparison is shown in Fig. 2, along with a polynomial fit to the combined data.

S ignificance—The present work represents only the first phase of extensive experimental characterizations of the dynamic electromechanical response of the ferroelectric ceramic PZT 95/5. The current results confirm the material behavior described in previous studies and provide a continuous characterization of this behavior from 0.5 to 5.0 GPa. Numerical simulations performed to date with current material models fail to reproduce accurately both the wave structure corresponding to the FE to AFE phase transition and the structure corresponding to dynamic pore compaction seen in the current study. This confirms that the present work and subsequent studies with poled PZT 95/5 will be essential for the model development necessary to achieve a simulation capability.

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Figure 1. Transmitted wave profiles at the sample/window interface.



Figure 2. PZT 95/5 Hugoniot measurements and end states calculated from transmitted wave profiles.

Dielectric Properties of and Relaxations Effects in Neutron Generator Encapsulants

by G. A. Samara and L. V. Hansen

M otivation—The dielectric constant, \in' , and dielectric loss, tand, of the encapsulant (ALOX) and their dependences on stress, temperature and frequency are important properties needed to understand the operation of neutron generators power supplies and to allow accurate modeling and simulations. The purpose of this study is to determine and understand these properties. Hydrostatic pressure was employed in this initial phase of the work. Shock wave experiments are planned.

A ccomplishment—We have investigated the effects of temperature (77-500K), hydrostatic pressure (0-20 kbar) and frequency $(10^2 - 10^6 \text{ Hz})$ on ϵ' and tand of ALOX. The response at 1 bar is found to be dominated by a molecular relaxation process at low temperatures and by the glass transition at higher temperatures - phenomena that can be expected to influence the dynamic mechanical response as well. Figure 1 shows the temperature dependence of \in' at 1 bar. The Sshaped response and the frequency dispersion are signatures of a dipolar relaxation process. The frequency-dependent loss peak shown affirms this conclusion. Measurement on the encapsulant without the Al_2O_3 filler revealed identical dispersion characteristics indicating that this relaxation is associated solely with the (The Al_2O_3 particles polymeric component. mainly enhance the magnitude of ϵ'). The characteristics of this relaxation process are common to many polymers, and the process is the so-called b relaxation which is attributed to micro-Brownian motions of dipolar molecular segments in the amorphous phase. Pressure hinders this motion, and consequently we find that this relaxation shifts to higher temperatures at a rate of a ~10K/kbar.

The glass transition is manifested by broad peaks in \in' , as shown in the 1 bar (~0 kbar) response in Fig. 2, as well as in tand (not shown). These peaks shift rapidly to higher temperatures with increasing pressure and become smeared as can be seen in the 5-kbar data. The glass transition is also a relaxational process, and the dielectric properties in its vicinity exhibit strong frequency dispersion. As a consequence of the anomalous and dispersive dielectric responses associated with the b relaxation and glass transition, \in' can either increase or decrease with increasing pressure temperature, pressure and depending on Far enough away from these frequency. relaxations ∈′ increases with pressure. Analysis of the results shows that whereas the bulk polarizability of ALOX decreases with decreasing volume, this effect is more than counterbalanced by the increase in density leading to the observed increase in \in' .

S ignificance—This work has provided results for understanding and modeling the operation of neutron generator power supplies. The occurrence of both the b relaxation and the glass transition within the operating range of this device is significant in that the relatively large changes in both dielectric and mechanical properties associated with these phenomena have to be taken into consideration for this application. A finding not discussed above is the observation of irreversible effects in the dielectric properties at the high temperature end of our measurements. These effects were determined to be due to the fact that the standard cure process for ALOX does not lead to full cure of the resin and hardner (828/Z), a fact that has to be taken into account during component processing and storage.

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Figure 1. Temperature dependence of the real (ϵ') and loss (tand) parts of the dielectric function of ALOX showing the dispersion and anomalies associated with the b relaxation process.



Figure 2. Temperature dependence of ϵ' of ALOX measured at 10⁴ Hz and different pressures. The broad peak associated with the glass transition is seen in the 0 kbar isobar. It shifts rapidly to higher temperatures and broadens further with increasing pressure.

Loading- and Release-Wave Behavior of the Neutron Generator Encapsulant ALOX

by G. T. Holman⁺, S. T. Montgomery, and R. A. Graham*

Motivation—Proper functioning of explosively driven neutron generators is critically dependent on details of the stress pulse transmitted from the high explosive, through thin aluminum plates and the ALOX encapsulant into the active ceramic. Historically, component design was based on large numbers of tests balancing numerous effects to arrive at a design configuration. In the future we will rely increasingly on numerical simulation with computer codes such as SUBWAY for troubleshooting and for design changes. Validation of numerical simulation results requires that the mechanical properties under shock-loading of all materials be determined and understood, and realistic materials models be developed. In the case of ALOX, the loading wave is strongly attenuating as it propagates through the ALOX. The relatively long propagation path in the ALOX makes its release behavior critical in the system design. Such release-wave behaviors of materials in general are poorly understood, and for ALOX there is essentially no detailed knowledge of the behavior of the release-waves.

A ccomplishment—We have initiated a study of the shock and release behavior of ALOX. Accomplishments to date include: development of a precise shock- and releaseexperimental configuration loading wave including selection of loading-pulse durations, exploratory investigation of wave-attenuation and detailed release-wave measurements from 11 to 41 kbar. Figure 1 depicts the principal characteristics of the experiment as carried out in Organization 1152's Precision Impact Laboratory. With the use of single crystal sapphire impactors of various thicknesses an unusually well-defined release loading is achieved due to sapphire's fully elastic behavior. The typical loading pulse shown in Figure 1 consists of well-defined "steps" as the release wave reverberates in the impactor. Typical propagated wave data, also shown in the figure, reveal a strongly dispersed responses, on both the loading and release profiles. Such behaviors clearly show that materials response models must incorporate strongly rate-dependent behavior.

Figure 2 shows wave speeds, both loading and release. As the waves are dispersed, it must be recognized that such a characterization of the pulses is overly simplified. It is necessary to consider the entire pulse characteristics. We have determined the release wave profiles from various loading states up to 41 kbar and having wave-front rise times ranging from 50 to 500 nsec. These are the first such ALOX response data available. They provide direct information from which release behavior and attenuation can be defined. These profiles are strongly dependent on loading stress.

S ignificance—Although few data are available to date, the experiments have successfully defined attenuation and release behavior sufficient to refine modeling and to continue to obtain ALOX response data over ranges of sample thicknesses, loading duration and stress. The data are of high quality and unique as to the stress-rate behavior and releaseloading characteristics, and they make it clear that models based solely on hydrodynamic equilibrium (Hugoniot) models are entirely Strongly unsatisfactory. rate-dependent materials models are required for both the loading and release.

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Figure 1. Precision shock compression and controlled pressure release experiments carried out with piezoelectric polymer PVDF gauges show pressure profile and stress-rate measurement results. Times for discrete incremental releases in pressure are controlled by thicknesses of the sapphire crystal impactors. Note change of scale of the ordinate for the input and propagated profiles. Stress is in kbar and current in amp.



Wave Speed and Release Wave Speed vs Stress

Figure 2. Arrival times of loading and release waves can be characterized by release wave speeds which are found to be extraordinarily fast with increasing wave speed with pressure. The wave profiles in both loading and release are poorly approximated by shocks; rather, relaxational processes dominate the loading and release.

Dielectric Breakdown in Field-Structured Encapsulants

by J. E. Martin, C. P. Tigges, R. A. Anderson

M otivation—Filled polymeric resins are widely used to encapsulate devices, including These encapsulants are neutron generators. sometimes used merely to protect the device from shock or moisture, but in the case of neutron generators the encapsulant serves to propagate a shock wave from the explosive to the ferroelectric PZT power supply. At the high pressures produced by the shock wave the PZT de-poles and a large voltage is delivered to the neutron tube. The device can fail if dielectric breakdown through the filled encapsulant diverts the current to the base plate of the generator, or between the dual PZT elements. Thus a filled encapsulant with a high breakdown strength would increase device reliability.

A ccomplishment—The filled encapsulants used in neutron generators consist of epoxy resin which is dispersed Al_2O_3 particles. into Normally the encapsulant is an isotropic material, but we have been investigating encapsulants that have the particles organized into chains by electric or magnetic fields. These materials exhibit large anisotropies in the dielectric constant, thermal and electrical conductivity, optical transmittance, etc. Studies of the conductivity anisotropy led us to suspect that these materials might have a significant anisoptropy in their dielectric breakdown strength. We prepared samples of 40% BaTiO₃ particles in an epoxy resin and structured these with an electric field during cure. The dielectric breakdown strength parallel to the ordering field was found to be about 5-10% below that of the control sample, but perpendicular to the ordering field the breakdown strength is ~40% larger -a significant increase. To understand these effects we applied a simple model, Fig. 1.

We assume that current conduction will occur through the particulate phase, because of the large electric fields that exist in the gaps between the high permittivity particles, and that the resistivity is dominated by the gap resistance. A voltage is then applied to the opposite sides of the simulation volume and when the current passing through a resistive gap exceeds a threshold value, the gap shorts, Fig. 2. The minimum field required to form a breakdown path is the breakdown field. Striking differences occur when this algorithm is applied parallel and perpendicular to the ordering field. First, the breakdown field is significantly larger perpendicular to the ordering field, Fig. 3, in agreement with experiment. Second, the failure is catastrophic parallel to the ordering axis (each successive short occurs at a lower field), but perpendicular to the ordering field there is a domain of negative feedback that presages catastrophic failure.

S ignificance—These studies demonstrate that field structuring filled composites can improve the dielectric breakdown strength perpendicular to the ordering field, with a small decrease parallel to the ordering field. Applying this to the neutron generators would not be difficult; a ferromagnetic particulate phase could be structured by placing the device in a solenoid during cure. This would chain the particles along the direction of shock wave propagation, and breakdown across the power supply would be perpendicular to the ordering field. As an added benefit, acoustical measurements show a 10% increase in the sound velocity parallel to the ordering field, and a higher shock wave velocity would be beneficial in better matching the velocity in the power supply.

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Figure 1. A simulated field structured material consisting of 10,000 particles, viewed along the uniaxial ordering field.



Figure 2. A visualization during breakdown: the red and green balls are at the electrode potentials, and the blue particles are sized by their currents. Most currents emerge through the unstable tip.



Figure 3. The computed dielectric breakdown field parallel and perpendicular to the structuring field as a function of the particle volume fraction ϕ .

Neutron Generator Standoff Studies

by M. U. Anderson, H. D. Radloff, L. E. Voelker, E. S. Hertel, M. E. Kipp

M otivation—Neutron generators are a critical component of nuclear weapon systems. They must be isolated from effects of the high explosive detonation until a pre-determined function time. This isolation time from detonation effects is termed standoff time. Standoff time is measured experimentally during functioning of an inert nuclear weapon system by detonating the high explosives and then measuring the arrival time of destructive shock waves at the neutron generator region during the hydrodynamic implosion of the weapon system. These measured arrival times at the generators are then compared to the weapon designer's specifications to determine if the neutron generators have sufficient standoff time in order to function before being destroyed.

Traditional methods of measuring standoff include self-powered piezoelectric crystals and remotely-powered shorting switches. Piezoelectric crystals provide accurate measurements of shock wave arrival time and amplitude at the expense of disturbing shock wave propagation beyond the crystal. The shorting switches provide a less accurate arrival time without information about shock amplitude.

A ccomplishment—We have used piezoelectric polymer (PVDF) shock gauges in recent hydrodynamic weapon tests yielding previously unattainable experimental data. These thin (25 micron), non-intrusive gauges provided data on shock wave amplitudes and arrival times at key locations within the weapon system without disturbing the shock wave propagation. The measured data are crucial for assessing adequate standoff and functioning of vital components as well as for improving and validating numerical simulations. These recent tests were conducted at flash X-ray facilities at Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL). They were designed and performed in collaboration with SNL/CA, LANL and LLNL researchers. The gauges which employ the piezoelectric polymer film polyvinylidene fluoride (PVDF) as the active, time-resolved sensing element were developed by Organization 1152 and represent a unique diagnostic capability for shock wave phenomena.

The experimental results have been analyzed and compared to numerical simulations of shock propagation through the experimental structure. The simulations, performed at SNL, were done in 2-D and 3-D geometries as part of the Strategic Computing Initiative Advanced Some differences between (ASCI). the simulations and the experimental measurements are providing a basis for improving the simulation capabilities in the complex geometry involved.

S ignificance—The availability of the thin self-powered non-intrusive. film. **PVDF** piezoelectric shock gauges is providing a needed new capability for diagnosing the performance of weapon components and systems. For the present standoff application, these gauges in combination with traditional piezoelectric crystal gauges and shorting switches have provided a critical set of data on shock amplitudes and arrival times which are challenging and improving our predictive capabilities.

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Figure 1. The thin film PVDF piezoelectric gauge (shown standing against the large quartz crystal to the left) represents an advance in piezoelectric shockwave gauges over earlier designs which employed thick single crystals cut from large quartz or lithium niobate (boule on the right) crystals



Figure 2. Typical stress-time-profiles from adjacent PVDF gauges showing shock wave structure at two locations in the neutron generator region.

Ferroelectric Copolymers for Time-Resolved Shock Wave Diagnostics

by G. A. Samara and L. V. Hansen

M otivation—In collaboration with the French-German Research Institute at St. Louis. France (ISL), we have been developing a family of non-intrusive, thin-film shock wave gauges based on the ferroelectric polymer polyvinylidene fluoride (PVDF) which are now being used in studies supporting neutron generator development. Recently, ISL succeeded in developing a reproducible poling process for copolymers of PVDF and trifluoroethylene (TrFE) which are believed to have advantages for gauges over PVDF in terms of longer recording time (related to ease of poling of thick films) and higher temperature capability. We are studying the influence of pressure on the properties and phase diagram of a copolymer with 77 mole % PVDF and 23 mole % TrFE - a necessary first step in assessing its potential for an improved time-resolved shock gauge.

A ccomplishment—The phase diagram for $P(VDF_{0.77}TrFE_{0.23})$ was determined from measurements dielectric spectroscopy as functions of temperature, hydrostatic pressure and frequency. The important features in phase space for PVDF and its copolymers are (with increasing temperature) a prominent molecular relaxation process centered around $T_{a} \cong 270 K$ (the \dot{a} relaxation which is associated with micro Brownian dipolar motion in the amorphous regions) and the melting transition (T_m) . In addition the copolymer exhibits a ferroelectric transition (T_c) below T_m . All of these transitions have strong influences on the electrical and mechanical responses of these polymers. The transitions T_{a} , T_{c} and T_{m} are well-defined features in the real (\in') and imaginary (\in'') parts of the dielectric response. With increasing

temperature there is a frequency-dependent shoulder in $\in'(T)$ and a sharp peak in $\in''(T)$ associated with the *á*-relaxation process; this is followed by frequency-independent peak in $\in'(T)$ at T and a sharp minimum in $\in'(T)$ at T (Fig. 1). All features shift to higher temperatures with increasing pressure - results that can be understood in terms of the reorientation and motion of various molecular groups. The low pressure region of the phase diagram is shown in Fig. 2. The initial slopes of the phase boundaries dT_x/dP for $T_{\dot{a}}$, T_c and T_m are 11 \tilde{n} 1 (independent of frequency), 24 ñ 1, and 41 ñ 1 K/kbar, respectively. The slope dT_{a}/dP is the same as that we observed earlier for PVDF and thus appears to be independent of composition. The slope dT_m/dP , on the other hand, exhibits strong dependence on composition and is only 29 ñ 2 K/kbar for PVDF.

S ignificance—The results contain much information relevant to the application of the copolymer as shock gauges. Specifically, it is clear that pressure strongly stabilizes the ferroelectric phase (i.e., the phase below T_c in Fig. 2). This fact, represented by the large $T_c(P)$ slope, along with the very large coercive field for poling make it certain that the electrical output of the gauge would be determined solely and favorably by the piezoelectric response, i.e., there is essentially no domain switching. Additionally, the much larger $T_m(P)$ slope for the copolymer compared to PVDF suggests that the copolymer should have advantages over PVDF for high pressure (100 kbar) applications. Finally, the $T_{a}(P)$ results give guidance as to the location of the \dot{a} relaxation in the P-T plane. Shock experiments should be designed to avoid or take account of this strong relaxation.

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Figure 1. Real part of the dielectric constant vs temperature showing the large influence of pressure on the ferroelectric (T_c) and melting (T_m) transitions in the copolymer.



Figure 2. The Temperature-Pressure phase diagram for P(VDF_{0.77}TrFE_{0.23}).

Miniature Laser Development for Weapon Systems Applications

by R. L. Schmitt, W. J. Alford, and T. D. Raymond

M otivation—Advanced weapon architectures increasingly rely on optical transmission of both signals and power to improve safety and reliability. By eliminating electrical connections between key firing set components, one minimizes the risk that spurious electrical signals (generated by lightning, for example) may cause a malfunction.

We are developing miniature laser technology for weapon systems applications, including direct optical ignition (DOI) of explosives and optical triggering of high-voltage vacuum switches used in firing sets. Our goal is to miniaturize the pulsed laser head to allow its use in spaceconstrained applications and to provide a new level of electrical isolation that will enhance the overall safety of the weapon system.

A ccomplishment—We have designed a fiber-coupled, laser-diode-pumped solid-state laser that will serve as a developmental prototype laser for advanced firing set applications. The laser system, shown in Figure 1, consists of a high-power diode laser (called the pump laser) coupled to a Q-switched solidstate laser head via an optical fiber. The optical fiber provides electrical isolation between the pump laser (which requires electrical power) and the Q-switched laser head (which needs only optical power to operate). In addition to electrical isolation, this architecture allows physical separation between the components and allows extreme miniaturization of the Oswitched laser head.

The pulsed laser head, shown in Figure 2, consists of a solid-state laser material (Nd-doped GSGG), a saturable absorber Q-switch

material (Cr⁴⁺-doped YAG), and mirrors to form a laser cavity. The prototype laser has discrete components so that the laser system may be easily reconfigured to optimize the length of the gain medium, transmission of the Q-switch, and mirror reflectivities. For the eventual end-use application, the mirror coatings would be applied directly to the ends of the crystals and the two crystals would be bonded together to form a rugged, monolithic device.

Our modeling indicates that we can produce ~ 1 mJ of output energy in a several-nsec-long pulse from an active volume of only 10⁻² cm⁻³ with 10 mJ of pump energy from an off-the-shelf diode laser. The laser output energy can be scaled up or down by scaling the pump power and the active mode volume appropriately. We estimate that 1 mJ may be enough energy to trigger existing vacuum switches (which use a carbon film on the cathode to trigger). We anticipate that electrode coatings optimized for optical triggering (a parallel effort in our Organization) may reduce trigger energy requirements to 10's of µJ, thereby allowing further miniaturization of the laser system.

S ignificance—Development of solid-state lasers will offer new capabilities and enhanced safety for advanced firing sets by providing increased electrical isolation between key components and miniature lasers that can be used in space-constrained applications. In addition, these miniature lasers could be optimized for repetitive pulse operation and be used in the future for remote sensing applications.

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Figure 1. Miniature Q-switched solid-state lasers may provide new capabilities for advanced firing sets. The Q-switched laser head is optically pumped by a high-power diode laser through a fiber optic, thus providing electrical isolation between firing set subsystems. The miniature laser stores energy from the pump laser until it emits the energy as a short pulse of laser light which may be used to trigger a switch tube or operate some other system function.



Figure 2. Schematic of the fiber-coupled Q-switched solid-state laser system. The input power to the trigger laser is transmitted through a fiber optic, eliminating any direct electrical connections to the trigger. Ultimately, the components of the laser will be bonded together to form a rugged, monolithic device.

Novel Laser-to-Fiber Injection Optics for Direct Optical Firing Systems

by R. E. Setchell, W. C. Sweatt, and M. E. Warren

M otivation—Optical firing systems have been under development at Sandia for nearly a decade. This "wireless" technology provides a means for initiating high explosives with inherent safety against unintended electrical signals. To meet weapon requirements, an optical firing system must generate strong shock waves in detonator explosives very rapidly. This is accomplished by transmitting the Q-switched output of a compact, solid-state laser to optical detonators using fiber optics. Operating margins are currently limited by laser-induced damage in the fiber optics, where intensities are on the order of 10^9 W/cm². A critical element for achieving high damage thresholds is the method used for injecting the laser beam into the fiber. After several preliminary iterations, we have now designed, fabricated, and tested an injection technique based on diffractive optics that inhibits fiber damage significantly better than any of our previous methods.

A ccomplishment—Current firing system lasers produce a highly multimode beam 5-6 mm in diameter, with significant "hot spots" possible within the profile. This beam is injected through air into step-index, multimode fibers whose core diameter is 400 µm or smaller. To avoid laser-induced damage, the ratio of peak to average fluences at the fiber entrance face must be minimized, the initial mode power distribution produced in the fiber must be as broad as possible, and the injected light must not refocus within the fiber core. The injection method we have developed combines a short focal length lens with a unique diffractive optic, shown in Fig. 1. This optic consists of many individual segments arranged within

concentric rings. Within each segment is a binary phase structure that diffracts incident light into four separate spots in the focal plane of the lens. The diffraction structure is perpendicular to a radial axis from the optic center, consequently the path leading to each spot in the focal plane has a skew angle that prevents normal focusing on the symmetry axis of the lens. The diffraction angles and the fraction of light diffracted into each order are design variables. In practice, the fiber entrance face is positioned at the focal plane of the lens, and the design variables are chosen to produce a fairly uniform fluence distribution across most of the fiber core diameter. "Hot spots" in the beam are mitigated by the fact that the portion of the beam hitting each segment is divided into four separate areas on the fiber entrance face. The numerical aperture of the fiber is nearly filled (hence a broad mode power distribution is achieved) by choosing a lens with an appropriate focal length. The skew angles introduced by the individual segments prevent the beam from refocusing within the fiber core. A beam profile recorded at the focal plane of a 15-mm focal-length lens is shown in Fig. 2.

S ignificance—The prototype optics tested to date have achieved good efficiencies (80%), and ratios of peak to average fluence at the fiber entrance face (2.2-2.3) are significantly lower than any previous injection method. These numbers represent a substantial improvement in operating margins for optical firing systems with essentially no penalty in system volume and weight. The design variables can be easily scaled to address the requirements of fiber delivery systems desired for Q-switched lasers currently used in biomedical applications.

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Figure 1. Diffractive optic used for laser-to-fiber injection. Total diameter is 6 mm.



Figure 2. Beam profile produced in the focal plane of a 15-mm focal length lens. The profile diameter is $350 \,\mu\text{m}$.

Superior Tribological Properties of Diamond-like Carbon on MEMS Alloys *

by D.M. Follstaedt, J.A. Knapp, T.A. Friedmann, J. Sullivan, M.T. Dugger and T. Christenson

M otivation—Micro-electromechanical systems (MEMS) are being developed for potential use as safing devices in weapons. An important class of devices are made by electro-depositing nickel alloy in precision molds to make miniature components (~1 mm) with sub-micrometer tolerances (German process acronym: LIGA). However, adhesion between metal components during sliding contact results in a high coefficient of friction (> 1.0) that varies erratically, and produces significant wear of the components as material is torn from the surfaces. To assure proper operation over extended usage, a treatment is needed for nickel surfaces that provides a constant, low coefficient of friction and greatly reduced wear.

A ccomplishment—We have evaluated diamond-like carbon (DLC) layers as potential tribological coatings for LIGA components and found that they exhibit minimal adhesion to a sliding counterpart, giving a very low coefficient of friction ($\mu \sim 0.2$; see Figs. 1 & 2) and almost negligible wear. Moreover, the benefits with DLC deposited on nickel persist for 1000 cycles at contact stresses needed for operating MEMS devices.

This material, DLC, is hydrogen-free amorphous carbon with a high fraction of sp³ bonds that give high hardness just as in crystalline diamond. We evaluated layers synthesized with two techniques. First, we examined DLC deposited at LBNL by vacuumarc deposition. The depositions initially use a 2 kV bias to produce energetic carbon ions that intermix with the nickel substrate to form an adherent interface with the deposited layers. The bias for subsequent material is adjusted to control the hardness and stress of the layer. This approach produces layers with hardness of 27 or 68 GPa that give extended low friction when deposited on Ni (Fig. 1). The second type of material was formed by pulsed laser deposition (PLD) at Sandia. Using methods described previously we showed that this DLC has an exceptional hardness of 88 GPa, second only to diamond (100 GPa). The PLD material gives similar low friction and wear (Fig. 2). Future work will examine the wear-life of thin layers (~60 nm), identify the optimum hardness for best performance, and examine methods to reduce layer stress.

S ignificance—The extended low friction and wear found with DLC layers on Ni provide the tribological performance needed for safing devices, and several aspects of this treatment are favorable for LIGA components. DLC can be deposited at room temperature so that the strength and precise tolerances are not thermally degraded. Furthermore, thin (~20 nm) DLC layers are in wide commercial use as protective coatings for computer disk drives to prevent damage when the head contacts the spinning The coatings must also prevent platter. "stiction" of the heads to the platter after periods of non-use, which is important for strong-link switches as well. In addition, DLC layers are smooth and pin-hole free at thicknesses of ~10 nm, and their chemical inertness is expected to provide corrosion protection. Deposition onto flat areas such as the sides of gears and magnetic actuators appears straight forward, and treatment of gear teeth may also be possible.

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Figure 1. Friction coefficient traces for a steel pin sliding on 0.5 μ m-thick layers of vacuum-arc deposited DLC on Ni, versus number of cycles of the reciprocating tester with a contact stress of 500 MPa (for 2 kV bias) and 600 MPa (0.1 kV bias). Material was deposited at LBNL.



Figure 2. Friction coefficient traces for a steel pin sliding on 0.17 μ m-thick layer of pulsed-laser deposited DLC on Si, versus number of cycles with a contact stress of 600 MPa. The coefficient of friction appears to decrease with continued wear, which may reflect a conversion of the contact surface to graphitic carbon. Material was deposited at Sandia.

Hardening and Tribological Improvement of MEMS Ni Alloys by Ion Implantation by S. M. Myers, J. A. Knapp, D. M. Follstaedt, M. T. Dugger, and T. A. Christenson

M otivation—The performance and lifetime of micro-electromechanical systems (MEMS) constructed from electroformed nickel alloys would be greatly enhanced by surface hardening and reductions in unlubricated friction and wear. Processing to achieve these benefits must minimize dimensional changes and heating, and must avoid the introduction of surfaces layers susceptible to debris-forming exfoliation or aging degradation. Ion implantation satisfies these constraints, and the technique has been shown at Sandia to allow controlled modification of near-surface composition and microstructure leading to strengthening and reduced friction and wear. We are therefore exploring the use of ion implantation to harden the surfaces and reduce the friction and wear of Ni-based alloys used in MEMS. A scientific objective is to understand and quantify the relationship of mechanical properties implantation-modified to microstructure.

A ccomplishment--We demonstrated that dual ion implantation of titanium and carbon produces an amorphous layer with superior mechanical properties in annealed bulk Ni and in the electroformed Ni and Ni₇₅Fe₂₅ of MEMS. A representative microstructure is seen in the cross-section micrograph of Fig. 1, taken from annealed bulk Ni after implantations of Ti and C. Concentrations of 16 at.% Ti and 22 at.% C stabilized the fully amorphous, featureless zone labeled II, which was subsequently extended to the surface by additional C injection at lower energy. Amorphization is demonstrated by the diffuse electron diffraction pattern in Fig. 1. The intrinsic yield strength of the amorphous Fe-Ti-C layer was determined from nanoindentation and finite-element modeling to

be 5 GPa. This exceeds by a factor of two the strength of maximally hardened martensitic bearing steel, as seen in Fig. 2, and it is also about twice the strength of conventional, metalloid-stabilized amorphous Ni-Fe alloys. Such exceptional resistance to plastic flow is ascribed to the absence of dislocation glide combined with strong atomic-pairing reactions between Ti and C. Implantation of electroformed Ni and Ni75Fe25 again produced amorphous layers with strengths near 5 GPa, well above the already high, ~1.5-GPa strengths of the untreated electroformed materials due to small grain size. The near-surface strengthening resulting from implantation is found to suppress the destructive adhesion-and-fracture wear characteristic of untreated Ni surfaces in sliding contact. This beneficial effect is demonstrated in Fig. 2 for annealed bulk Ni, where implantation is seen to eliminate the jagged wear track and the large excursions in frictional force that are indicative of the destructive wear mode. There is also a drop in average friction coefficient. Initial results indicate that the friction reduction caused by Ti+C implantation is greater and more persistent for the harder, electroformed Ni, where a post-treatment friction coefficient near 0.3 is measured.

S ignificance—The large strengthening of Nialloy surfaces by Ti+C implantation, with the associated improvement tribological in properties, is expected to enhance the lifetime performance Ni-based and of MEMS. Scientifically, the present investigation is the first to quantify and mechanistically account for the properties mechanical intrinsic of an implantation-amorphized alloy.

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Figure 1. Cross-section transmission electron micrograph and diffuse electron diffraction pattern from Ni implanted with Ti and C. The amorphous Ni-Ti-C layer appears as the featureless zone II.



Figure 2. Near-surface yield strength, wear-track topography, and friction trace of implanted Ni compared with untreated material.

Microdomain Laboratories to Measure Stiction, Adhesion and Mechanical Properties of Micromachined Devices

by Maarten de Boer and Terry Michalske

Notivation—Micro-electromechanical systems (MEMS) are allowing rapid development of integrated, miniaturized components that can provide sensing and actuation for a wide range of micro-scale chemical inertial. optical. and devices. Currently, our ability to model and predict the performance of MEMS devices is limited by a lack of direct materials measurements. At the micro-scale, mechanical interaction forces are dominated by surface energy and adhesive forces. In addition, the mechanical properties of micromechanical structures can not be reliably extrapolated from macro-scale test specimens. We are developing a suite of miniaturized test devices that can directly measure micro-scale MEMS properties on structures. These Microdomain Laboratories can also be used to routinely monitor changes in materials character that may influence long-term device performance.

Accomplishment—We have recently developed a set of Microdomain Laboratory test structures that can be used to measure surface roughness, interfacial adhesion, and residual stress in surface micromachined polysilicon structures. The test devices are based on singly and doubly supported beams that have been physically released from the underlying silicon wafer. Figure 1 is a schematic showing a singly supported beam that can be actuated (pulled down) by applying an electrical potential. Using an interferometric probe station (Fig. 2), we accurately measure the deformation in actuated beams. Comparing the measured deformation with elastic models allows us to extract, with nanometer resolution, the physical gap between the substrate and beam due to inherent surface roughness. Measurements made

in this way agree well with surface profiles measured by scanning probe microscopy. Measurement of the interfacial energy is made by using the electrostatic actuation to first pull the beam into contact with he substrate surface. After the voltage is released, elastic energy stored in the beam acts to peel the beam and substrate apart. The distance over which the beam is peeled away from the substrate is used to directly measure the adhesive energy. We have used this measurement technique to evaluate various surface treatments intended to reduce adhesion of as-fabricated MEMS devices. Results of these measurements show that the apparent surface energies for these materials are orders of magnitude lower than simple predicted by adhesion models. Measurements of surface roughness are being used to understand these unusually low adhesion energies. Finally, deformations in electrostatically-actuated, doubly-supported beams provide a sensitive measure of residual stress produced in manufacture.

Significance—Accurate measurements of properties materials for micromachined structures are needed to develop reliable miniaturized devices. Since the Microdomain Laboratory test structures are fabricated by the same processes as the micromachined devices themselves. is assured that one the measurements are directly applicable. Currently, we use an optical probe station to analyze our test results. However, once the response of the test structure has been verified, onboard electrical measurements can be used to extract the test results. This will allow future integration of our test structures for real-time performance diagnosis.

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Figure 1. Schematic diagram showing micromachined polysilicon test structure. Singly supported beam is electrostatically actuated and measured deformations are used to determine properties such as surface energy, surface roughness and residual stress.



Figure 2. Probe station with optical interference microscope allows Microdomain Laboratory test structures to be operated in a range of environmental conditions. Detailed measurements of elastic deformation are extracted from interferograms and used to determine a wide range of micromachined materials properties.

Control of Optical Performance from Optical-Amplifier Materials Synthesized Using an ECR Plasma

by J. C. Barbour, B. G. Potter, D. M. Follstaedt, J. A. Knapp, M. B. Sinclair and C. H. Seager

M otivation—ECR plasma deposition of Erdoped alumina offers a method which is scalable to large area production capabilities. A comprehensive understanding of the materials and optical properties which can be formed using this deposition technique were determined. This is the first step toward making photonic circuits which can be monolithically integrated with the compound semiconductor source of light.

A ccomplishment—Fundamental studies of the synthesis of alumina (Al₂O₃) and erbiumdoped alumina using electron cyclotron resonance plasmas have yielded advances which extend and mechanistically illuminate the properties of optical ceramics. First, the mechanism governing the formation of the crystalline gamma phase of Al₂O₃ at low temperatures was determined. Normally, physical vapor deposition techniques form the amorphous phase at temperatures below 850°C. However, if during the deposition process, lowenergy oxygen ions are extracted from a plasma with sufficient energy to cause displacement of aluminum atoms in the surface of the Al_2O_3 , then the gamma phase forms at temperatures as low as 400°C (Fig. 1). Second, a method was developed for simultaneous incorporation of optically active, rare-earth elements such as erbium (Er) into optical ceramic waveguide materials: Al_2O_3 and La_2O_3 . This low temperature, plasma-assisted deposition technique enables the direct integration of optical amplifiers into compoundsemiconductor photonic integrated circuits. Previously, direct integration of the optical amplifier on compound semiconductors was

unattainable because the technology utilized ion implantation to incorporate Er into the optical ceramic, followed by a high temperature annealing treatment to reduce implantation This damage causes a decrease in damage. optical quality as seen by a decreased radiative lifetime, and high temperature annealing treatments are incompatible with compound semiconductor devices. Furthermore, bv controlling the phase of the material, the local environment of the Er was manipulated in order to understand and enhance the optical activity of this ceramic system (Fig. 2). The local environment of Er in amorphous Al₂O₃ is more like that environment in gamma Al₂O₃ than in alpha Al_2O_3 (sapphire). Erbium in the gamma phase has a significantly longer radiative lifetime than Er in sapphire, and therefore this plasmasynthesis process provides a method to form high quality optical devices.

S ignificance—Ceramic materials can be used across a broad spectrum of applications requiring optical signals and data transfer. Applications range from amplification of signals in long-distance communication to use in high voltage locations where electrical isolation is essential, e.g., safeguarding weapons from inadvertent electrical shock. Improvement in the optical quality and luminescence efficiency will enable these applications and future optical device technologies. The technology learned in these investigations is the first step to creating a monolithic photonic integrated circuit in which the light generation source (generally a compound semiconductor light source) is closecoupled to the amplification, waveguide, and other optical-ceramic components.

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Figure 1. Cross-sectional transmission electron micrograph of ECR deposited alumina demonstrates the ability to vary the phase and density of the layer in depth as a function of the deposition parameters.



Figure 2. Photoluminescence (PL) spectra reveal the control over the optical lifetime (τ) by changing the local Er environment from Er-doped γ -phase to α -phase to amorphous alumina.

Controlled Stress Relaxation of Amorphous Diamond Films for Future Component Applications

by J. P. Sullivan and T. A. Friedmann

M otivation—Amorphous diamond (a-D) is a hydrogen-free form of carbon deposited at room temperature with chemical, mechanical, and tribological properties near that of diamond yet with unique electronic properties. These combined properties make the material especially suitable for reducing wear and friction in mechanical components and for enabling vacuum microelectronic devices based on cold cathode electron emission. Despite these promising film properties there has been a major obstacle for the effective utilization of this material: the deposition process leads to films with high levels of compressive stress, and this limits the maximum film thickness and, hence, potential applications for this material.

A ccomplishment—We have discovered a new type of stress relaxation behavior that is operative in a-D and have developed a process to fully relieve the film stress. Furthermore, we have combined stress relaxation measurements with electrical measurements leading to a novel procedure for identifying the electronic transport mechanism. Stress relaxation in a-D occurs by thermally activated transformation of 4-fold coordinated carbon atoms into 3-fold coordinated atoms. Due to differences in bond symmetry and average bond length between 4fold and 3-fold atoms, the high in-plane compressive stress of the film is reduced when newly transformed 3-fold atoms are created with a preferential orientation that reduces the strain energy of the film. A simple first order kinetic model has been developed to explain this unique stress relaxation behavior. Figure 1 shows the experimentally measured time-temperature stress relaxation behavior of a-D films deposited by pulsed-laser deposition. Fits to the data using our stress relaxation model are also shown (solid lines). An anneal at 600° C for several minutes is sufficient to reduce the compressive stress in the film to zero (± 50 MPa). The reduction in compressive stress afforded by this procedure enables a-D films of arbitrary thickness to be synthesized (see inset of Figure 1), overcoming one of the major obstacles for utilization of these films.

By modeling the stress relaxation behavior, we can determine the increase in 3-fold atoms as a function of time and temperature. Coincident with stress relaxation, thermal annealing induces permanent changes in the electrical conductivity of the films. Combining stress relaxation and electronic transport measurements. the dependence of electrical conductivity on 3-fold content of the films may be determined, as shown in Figure 2. The normalized electrical conductivity is found to be exponentially proportional the increase in 3-fold to concentration. This relationship results from a heterogeneous conduction process in which thermally-activated hopping conduction occurs along linkages of 3-fold atoms in a matrix of 4fold atoms.

S ignificance—The ability to stress relieve a-D films and the new understanding of the electronic transport mechanism enable advanced applications of this material. In particular, stress relieved a-D films can now be integrated with micro-electromechanical systems (MEMS) to create thick tribological or structural layers or to create advanced micro-sensors. Knowledge of the electronic transport mechanism is important for identifying the mechanism of electron emission from this material.

Internal partners/customers: J. J. Sniegowski (1325), and K. W. Schubert (1315) Sponsors for various phases of this work include: LDRD, TPP, DP Research Foundations

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Figure 1. Time-temperature dependence of stress relaxation in a-D films. Fits to the data using the stress relaxation model are shown as solid lines. The inset shows the theoretical maximum thickness for deposition of a-D films on Si substrates as a function of the a-D film stress.



Figure 2. Normalized electrical conductivity of a-D films as a function of the increase in 3-fold carbon content as determined from combined stress relaxation and electronic transport measurements. The indicated temperatures are the anneal temperatures at which the data was obtained.
First Principles Calculations for Cu Sulfidation Aging

by J. S. Nelson, A. F. Wright, P. A. Schultz, and T. A. Michalske

M otivation—In this project, first-principles atomic-level models for surface adsorption. interdiffusion and chemical reaction will be coupled with continuum-scale finite element and finite difference codes to provide a capability for predicting the nucleation and rate of corrosion layer formation on metal materials in weapon component applications. The corrosion of aluminum and copper components that are used in electrical interconnects and fuses pose a serious risk to the readiness and safety of aging weapons systems. This project will take advantage of pioneering work done at Sandia in the development of massively parallel (MP) electronic structure code. The calculations now possible with the MP code QUEST (QUantum Electronic STructure) will allow us to directly model the atomic-level processes controlling metals corrosion. The quantitative results for these atomic-level events will provide direct input for our finite element and finite difference codes that have been developed at Sandia to model chemical vapor deposition processes. The SOLID CHEMKIN code and the MP code SALSA will be developed to provide a predictive capability for metal surface corrosion.

A ccomplishment—Currently, first-principles calculations are being used to determine activation energies (formation and migration

energies) for the diffusion of copper vacancies through bulk and oxide (Cu₂O) layers; solid state transport of copper atoms to the growing sulfide (Fig. 1) layers is thought to be an important limiting mechanism. In Fig. 2 the lattice parameter and density of states of bulk Cu₂O calculated from first-principles planewave calculations is depicted. The calculations are in good agreement with the experimental value of the lattice parameter as well as peaks in the density of states. To evaluate diffusion parameters, large supercells (~50-100 atoms) of bulk copper and Cu₂O are necessary to describe the energetics of isolated vacancy defects. The bulk calculations can be performed on workstations, while the supercell calculations will rely heavily on massively parallel TeraFlop computing. The current ASCI TeraFlop platform has 9000 Pentium-Pro processors (200 MHz) and 0.6 Terabytes of random access memory (RAM) to perform large scale weapons simulations.

S ignificance—The development of predictive multi-scale (atomistic to continuum) models for corrosion, as well as other applications involving chemically reacting heterogeneous materials, represents a significant step forward in our ability to realistically simulate complex materials and phenomena.

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Figure 1. Illustration of the cubic Cu_2S crystal structure. The sulfur atoms are in yellow.



Figure 2. Calculated cubic Cu₂O lattice parameter and density of states.

Si Dimer Binding Near Defects and Its Influence on Surface Diffusion Rates

by **B. S. Swartzentruber**

Motivation—Because small differences in reaction energetics can profoundly effect reaction rates, the overall reactivity of surfaces at relevant temperatures may be dominated by a relatively small density of active sites. Additionally, subtle changes in the atomic configuration of surface structures, such as defects, can alter the local energetics thereby enhancing or suppressing the local reactivity. In order to understand the long-term stability of materials surfaces we need the capability to accurately measure kinetic processes at the reaction-site length scale and determine the factors that govern the underlying energetics.

A ccomplishment—We extracted the binding free energy of adsorbed silicon dimers as surface а function of location from measurements of the position and hop statistics of the dimers as they migrate over the Si(001) surface in the thermodynamic limit. This type of measurement introduces the idea of the "atom as a probe." In this context, the adsorbed dimers themselves are used to probe the surface potential energy, while the instrument continually monitors their positions.

We acquired these measurements using atomtracking – a technique in which the probe tip of a scanning tunneling microscope (STM) is locked onto a selected dimer using two-dimensional lateral feedback. Once locked, the feedback electronics maintain the tip over the dimer as it diffuses over the substrate tracking its coordinates. The time response of the atom tracker is fast enough to record every hop of the dimer. When every diffusion event can be captured, the statistics of the diffusion process can be analyzed directly, without the assumptions implicit in a classical random-walk analysis. Furthermore, the high spatial resolution allows us to extract the details of the dimer binding and diffusion energies at every lattice site. As an example, Figure 1 shows three images of a diffusing dimer trapped between various surface defects. The dimer is confined to migrate only among the lattice sites located between the defects which act as hard-wall The relative binding free repulsive barriers. energy as a function of location is shown in Figure 2. We find that an adsorbed dimer is bound to the edge of an island or step with ~30-50 meV and that the binding falls off over several lattice sites. In addition, other types of surface defects can have a slightly repulsive interaction with the diffusing dimer. The dimers spend less time in the repulsive regions and more time in the attractive regions of the sample.

S ignificance—Adopting the viewpoint of the "atom as a probe" opens up many new areas of investigation into materials surface processes. From observations of atom diffusion over heterogeneous surfaces, for example, it should be possible to obtain a map of the surface composition on materials where there is no contrast mechanism in conventional STM techniques. It should also enhance our ability to investigate the atomic-scale details of surfactantmediated growth, such as understanding diffusion surfactant-atom and ultimate incorporation in surfaces, and the energetics between surfactant and substrate atoms.

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Sponsors for various phases of this work include: BES, LDRD, DP Research Foundations

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Figure 1. Empty-state STM images of adsorbed Si dimers trapped in wells between hard-wall repulsive defects. The wells contain (a) 10, (b) 12, and (c)14 sites. The scale of the images is ~10 nm.



Figure 2. Plot of the relative binding free energy as a function of distance from the left wall of the wells in Figure 1. The circles, squares, and diamonds are from the wells shown in (a), (b), and (c) respectively.

Radiation Effects Microscopy for Rad-Hard Microelectonics Validation

by B. L. Doyle, D. S. Walsh, F. W. Sexton and P. E. Dodd

M otivation—Circuit malfunctions caused by strikes of individual high-energy nuclear particles are referred to as single-event effects (SEE). A low sensitivity to SEE is a continuing radiation requirement for integrated circuits (ICs) in weapon systems. Two expensive W88 joint-testassembly (JTA) failures in the early 1990s were attributed to SEE in commercial ICs due to high-energy protons in the South Atlantic SEE is becoming increasingly Anomaly. important for unhardened terrestrial systems using sub-quarter-micrometer circuit technologies, and one can only imagine how much more sensitive circuits would be should they be located next to a nuclear package, encounter the radiation environment of space, or have to survive on the nuclear battlefield. Both and circuit design mitigation technology techniques must be developed from a firstunderstanding principles to reduce this increasing microelectronics vulnerability for stockpile applications.

A ccomplishment—Research at Sandia has already (see Feb. 97 Research Brief) led to the perfection and now routine application of two forms of very-high-resolution Radiation Effects Microscopy: Single-Event Upset (SEU) Imaging Ion-Beam-Induced and Charge Collection (IBICC). SEU Imaging pinpoints where upsets occur by producing frequency maps of IC malfunctions caused by scanned MeV heavy ions, while IBICC images the charge generated and collected by each individual ion. Comparisons to this data have been made with 3-D radiation-response simulations of transistor and circuit behavior using the DAVINCI code. Figure 1 schematically shows the theoretical and experimental elements involved in this program.

During the current reporting period, a new and even more powerful technique, Time-Resolved, Ion-Beam-Induced Charge Collection or TRIBICC has been demonstrated. TRIBICC extends the IBICC data by recording the individual current transient caused by the passage of a single ion through an IC with extremely high lateral and time resolution. A TRIBICC 4-D spectrum (current vs. x, y, t) of a CMOS6 FET drain is shown in figure 2

S ignificance—The early results of this Radiation Effects Microscopy project are very encouraging. These new tools are starting to benchmark computer models of SEU tolerance of ICs manufactured in the MDL. SEU-Imaging was also recently used to locate and identify a single rad-weak component in a very complicated part being commercially developed for a DoD agency. The future routine application of these tools should result in a superior method of predicting the reliability of replacement electronics in nuclear weapons. This program is therefore a stepping stone toward the goal of providing model-based calculations of SEE-reliability at the component (transistor), IC, circuit, sub-system and, system Beyond underwriting the surety of level. stockpile micro-electronics, this capability will save DOE money by reducing the number of process iterations during the development of future radiation-hardened integrated-circuits.

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Figure 1. Schematic of the experimental and theoretical program to understand and model Single Event Effects in Sandia's rad-hard integrated circuits



Figure 2. The first Time Resolved Ion Beam Induced Charge Collection data. The TRIBICC image on the left shows laterally resolved current transients resulting when 12 MeV C ions strike a CMOS6 n-channel transistor fabricated in the MDL. The plot on the right shows two transients recorded at the center and edge of the n-drain, and clearly demonstrates a difference in the time dependence of this singe ion-induced current.

Atomistic First Principles Modeling of Metal-Ceramic Bonding

by D. R. Jennison, C. Verdozzi, P. A. Schultz, and M. P. Sears

M otivation—Oxide layers bound to metallic surfaces provide critical thermal, corrosion, and electrical barriers, and are used in a wide variety of devices, sensors, and seals. For the predictive modeling of performance and aging it is thus important to understand on an atomic scale the fundamental nature of metal-ceramic bonding, and the effect of impurities and defects thereon. Few theoretical first-principles studies have been performed, especially on the more complex but technologically relevant systems such aluminum oxide, Al_2O_3 . Recent advances in code development and massively parallel computing at Sandia now permit the large scale calculations required for these systems, so the nature and strength of the bonding and the interfacial geometries can be found.

A ccomplishment—We have used thick (up to eighteen oxygen-layer) slabs to model the surface of sapphire, or \dot{a} -Al₂O₂, also known as corundum. We used the accurate local density approximation (LDA) method and computed forces to allow geometry relaxation. We found that a very large surface relaxation extends deeper than the slab thickness used in all previous first-principles studies (i.e., three oxygen-layers); thus, thick slabs are а prerequisite for an accurate description of metal-oxide binding. We found both silver and platinum overlayers to be bound electrostatically, with little electron transfer between the metal and the oxide surface. Both metals prefer the atop-aluminum sites, as opposed to atopoxygen or a hollow, and this preference is strong: the ratio of binding energy is 1:1/2:1/4, respectively. However, platinum is bound by almost 2 eV per atom, much stronger than silver at 0.4 eV. Although the LDA method generally overestimates bond strengths, this is not true for electrostatic bonds, and we thus believe these numbers to be accurate. The calculations also found additional large relaxations of the oxide surface induced by both metal overlayers.

S ignificance—These studies are the first accurate calculations of metal overlayers on alumina, the first to use sufficiently thick slabs to include the full surface relaxations, and the first to determine the metal-atom binding sites. The latter can be predicted from simple electrostatic models, after one is aware of the basic nature of the binding. Our results differ from several previous works in the literature, which attempted to understand the interface using small cluster models or thin slabs. Recent experimental advances, in measuring heats of adsorption and in growing thin oxide layers on metallic substrates, have increased activity in this area of research, and promise calibrations of LDA accuracy. The basic understanding of the interfaces obtained perfect from these calculations enable us to now investigate changes produced by surface defects such as oxygen vacancies, and by impurities such as sulfur (known to weaken the interface) or reactive metals (known to strengthen it).

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Figure 1. The (0001) surface of sapphire. The oxygen ions are large, the aluminum ions are small, and the shading shows the varying depth of the first three aluminum layers. The oxygen ions are drawn smaller than the ionic radius to permit viewing deeper ions; in reality, they would be touching. The preferred binding site for both silver and platinum overlayers is above each visible aluminum ion.

The Role of Interfacial Hydrogen on Aluminum Thin Film Nucleation

by T. M. Mayer, D. P. Adams, B. S. Swartzentruber

M otivation—Impurity adsorbates, intentional or unintentional, at the interface of a growing film may alter kinetic processes such as surface diffusion, precursor reaction, etc., leading to changes in nucleus density, structure, or orientation, and growth mode of a thin film. This may be beneficial, as in the use of surfactants to control surface morphology, or detrimental, as in impurity incorporation during CVD growth. We examine the effects of H adsorbed on Si surfaces on nucleus formation during Al thin film growth, for the purpose of predicting and controlling the microstructure of Al films in CVD and Al evaporation.

A ccomplishment—Atomic hydrogen is a decomposition product of amine alane precursors for Al CVD. At the decomposition temperature of most precursors, H₂ will desorb from the Al surface, but not from a Si surface. Therefore we expect that nucleation of Al films on Si will be affected by the coadsorption of H during the initial decomposition of the precursor. Occupation of a large number of Si dangling bond sites by H may alter Al adatom mobility, precursor reaction probability, formation of Al nuclei, and evolution of nuclei structure, and the resulting thin film.

We observed formation of Al nuclei on Si(001) surfaces in the scanning tunneling microscope, by thermal decomposition of trimethyl amine alane. Many small Al nuclei and coadsorbed H were observed on the surface, confirming the expectation that H would remain at the interface and play a role in nucleus formation.

Because of the difficulty of quantitatively interpreting the STM images in the CVD experiment, we carried out a series of control experiments, in which Al was evaporated onto Si surfaces predosed with controlled amounts of H. Figure 1 shows the morphology and density and Al islands formed at submonolayer coverage by Al evaporation onto a clean surface and one covered with 0.15 monolayer of H. The dramatic difference in size, density, and configuration of nuclei can be ascribed to the effect of H on the mobility of Al adatoms on the surface. Site blocking by H restricts the diffusion of Al and lessens the probability of formation of larger, well-ordered Al islands, which are observed on the clean surface.

We have also examined the dramatic effects on Al film growth caused by complete passivation of the surface by H. In Figure 2, we compare the structure and morphology of Al films formed on clean and fully H-terminated Si (001). On the clean surface. classic Stranski-Kranstanov growth results, in which an ordered 2x2 overlayer of Al atoms forms, followed by growth of three dimensional Al islands. In contrast, on H-terminated Si, no ordered monolayer forms, dimensional three Al islands form and immediately on the H-terminated Si surface. This three dimensional growth mode is indicative of an altered interaction energy of Al adatoms with the Si substrate.

S ignificance—We have demonstrated that the presence of H at the interface of a growing Al film has marked effects on the size, density and structure of nuclei, as well as the growth mode of the film. This leads to the possibility of controlling the orientation, texture, and microstructure of thin films by interfacial chemical control. We are currently examining the effects of interfacial chemistry on bulk film properties.

Sponsors for various phases of this work include: BES, LDRD

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Figure 1. Submonolayer Al nuclei formed by evaporation of Al onto (a) clean, and (b) 0.15 monolayer H-terminated Si(001) surfaces.



Figure 2. Nucleation of Al films on (a) clean, and (b) monolayer H-terminated Si(001) surfaces. The 2x2 Al layer on the clean substrate is visible between Al islands in (a), while the 2x1 H-terminated reconstruction of the Si substrate is visible between the islands in (b).

The Influence of Atomic-Scale Defects on Surface Deformations

by J. A. Kiely, R. Q. Hwang, J. E. Houston and T. A. Michalske

M otivation— Understanding the origins of cystal plasticity is needed to accurately model the initial stages of mechanical damage in conventional engineering structures as well as predicting properties of new micromachined electromechanical devices. In this work we use Interfacial Force Microscope the as nanometer-scale contact probe to study the mechanical response of materials subjected to highly localized loads. This new approach allows us to investigate the intrinsic damagability of materials and the role of defects in altering damage thresholds.

A ccomplishment—We have shown in previous mechanical-probe measurements on single crystals that shear stresses near the theoretical limit (G/10, where G is the shear modulus) are required to produce plastic These results suggested that indentation. deformation on the nano-scale is controlled by the homogeneous nucleation of dislocations and not the motion of pre-existing dislocation structures. In this study, we expand on our earlier work and apply Interfacial Force Microscopy (IFM) to explore the effect of surface steps on the nanomechanical response of single-crystal Au surfaces. Using a controlled with mechanical probe а radius of approximately 250 nm, we explore the critical conditions for initiating local plasticity on singlecrystal Au(111) surfaces.

In Fig. 1, we show the constant repulsive-force image of a Au(111) surface containing a double and several single steps. Figure 2 illustrate the loading curve (probe force vs. probe displacement) with the probe tip located astride

the double step in the center of the image ofFig. 1. The initial rise of the force after contact follows the Hertzian relationship and can be used to obtain the local elastic modulus of the material., while the point where the curve deviates from Hertzian identifies the plastic threshold. The hysteresis loop width quantifies the depth of the plastic indentation. Figure 3 shows a series of indentations at various distances from the step edges. Typically the indentations are about 30 nm wide and about 6 nm deep indicating the displacement of only a few thousand Au atoms.

Table I indicates the quantitative results of these studies tabulating the distance of the indentation from the step edges and the calculated maximum shear stress at the plastic threshold. Clearly, probing in the vacinity of the step edge has a significant effect on the initiation of plasticity.

S ignificance— These results illustrate the unique mechanical properties of materials that are localized at the nanometer level and show how atomic-scale defects can greatly influence those properties. The ability to directly observe damage processes at the nanometer level provides an important means to validate materials models needed for Science-Based Stockpile Stewardship and will contribute strongly to the development of nanostructured and nano-phase materials. This understanding is especially important for materials which are dominated by the presence of interfaces, such as fiber reinforced, matrix and nano-precipitate hardened materials.

Internal partners/customers: K. D. Meeks (2167), R. J. Salzbrenner (1805), and J. C. Hamilton (8717)

Sponsors for various phases of this work include: BES, LDRD, DP Research Foundations

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Figure 3. Additional dents with the tip located at various distances from the step edges.

Figure 1. A repulsive-force image of a carefully prepared, thiol covered Au(111) surface. Single and double steps can be seen intersecting along crystallographic axes. As a reference, we have marked a contaminant particle with the symbol c.

Figure 2. The loading curve for a 2500 Å probe deforming a Au(111) surface. After contact, the curve follows the Hertzian relationship, indicating an elastic deformation. Deviation from this relationship signals the threshold of plasticity. The width of the hysteresis loop is a measure of the indentation depth.

Table I. Summary of the results investigating the effect of steps on the nanomechanical properties of a single-crystal Au(111) surface.

Distance from Step Edge Å	Threshold Shear Stress Gpa
3400	5.7
1300	5.4
570	4.8
0	3.6

Surface Segregation Induced Morphology Changes on Si(100) Surfaces

by J. B. Hannon, N. C. Bartelt, B. S. Swartzentruber, and G. L. Kellogg

M otivation—Understanding the basic physics that controls the evolution of surface morphology at the sub-micron scale is required for the development of predictive models of semiconductor surface stability. Low energy electron microscope (LEEM) and scanning tunneling microscope (STM) investigations show that heavily boron-doped Si(100) surfaces exhibit an unusual step faceting transition during cooling from high temperatures. Single-atom high steps first break up into triangles and subsequently form long stripes that span across the single-crystal terraces (Figure 1). This transition is not observed in lightly doped Si samples. The motivation for this investigation is to identify the fundamental interactions leading to formation of this striking "striped" surface morphology, and determine the relative importance of step energetics vs. surface stress driving the transition.

A ccomplishment—Our LEEM measurements and modeling studies show that the formation of triangular facets and striped morphology on heavily boron-doped Si(100) surfaces is a direct consequence of a vanishing free energy of formation of the "A" steps. The equilibrium structure of the "normal" Si(100) surface is a periodic array of two-atom-wide rows (dimer rows). The direction of the dimer rows rotates by 90 degrees when crossing Those steps that are atomic-height steps. parallel to the upper terrace dimer rows are called "A" steps and those perpendicular are called "B" steps. We have made three independent LEEM measurements showing that, in the case of heavily boron-doped samples, the B-step energy is relatively constant as a function of temperature, but that the A-step energy

vanishes as the temperature is lowered from 1000 to 900 C. The measurements include the temperature dependence of: (1) the A- and Bstep stiffnesses (the energy per unit length required to bend a step); (2) the apex angle of the triangular facets; and (3) the aspect ratio of elliptical-shaped islands. The step stiffnesses are determined from a detailed analysis of step fluctuations observed in the LEEM images and are directly related to the step-formation energies. Step energies are derived from the facet apex angles and equilibrium island shapes through the use of the Wulff construction. All three measurements, which span overlapping temperature regimes, show a consistent decrease A-step energy with decreasing in the (Figure temperature 2). From these measurements, we conclude that increasing amounts of boron segregate to the surface as the temperature is lowered and cause the A-step formation energy to decrease and eventually vanish. The finding that the A and B step stiffnesses vary differently with temperature and the lack of a terrace-width dependence suggest that models involving boron-induced changes in the surface stress are incorrect.

S ignificance—These results provide a clear indication of how small changes in step energetics can lead to dramatic changes in surface morphology. The conclusion that step energetics drive the transition is counter to the conventional picture that the evolution of surface morphology on semiconductors is due entirely to surface stress effects. By manipulating step energies through the use of chemical additives, the findings suggest that one should be able to tailor surface morphology and self-organization specific even induce processes.

Sponsors for various phases of this work include: BES, DP Research Foundations, LDRD

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Figure 1. Low energy electron microscope (LEEM) images showing the step faceting transition and striped phase formation on Si(100).



Figure 2. A-step free energy of formation as a function of temperature as determined by measurements of step fluctuations, equilibrium island shapes, and facet apex angles

Time-Delayed Ultraviolet Fluorescence Spectra of Microorganisms

by P. J. Hargis, Jr.

Motivation—Advances in sensor technologies, including miniaturized ultraviolet (UV) laser sources, high-speed single-board computers, and multichannel photodetectors, are now permitting electro-optic sensing techniques address needs that were previously to impractical due to cost and complexity issues. Sensors that can detect the proliferation of chemical and biological weapons and their use in terrorist acts is one such need which has received national attention because of recent worldwide terrorist activities. Another such need requires sensors that can detect and identify microorganisms such as the bacteria E. coli O157:H7 which is responsible for recent food poisoning incidents. As a first step in addressing these needs, time-delayed UV fluorescence measurements have been made to determine whether or not UV fluorescence spectra of microorganisms are sufficiently unique to identify the microorganisms.

A ccomplishment—Time-delayed UV fluorescence spectra of the tryptophan UV fluorescence bands of three different bacteria suspended in phosphate buffered saline (PBS) solutions were measured with a unique broadly-tunable allsolid-state pulsed UV laser developed by Sandia and Aculight Corp. for remote sensing measurements (see Fig. 1). The fluorescence measurements show that bacteria fluorescence lifetimes have two components, a short component with a lifetime of about 0.15 nsec and a longer component with a lifetime of about 13 nsec. We have taken advantage of the 13fluorescence lifetime nsec to measure tryptophan fluorescence spectra at a time delay of 6 nsec from the peak of the laser excitation

pulse. Under our measurement conditions, bacteria fluorescence spectra were almost totally free of the interfering effects of scattered light from the bacteria and Raman scattered light from the PBS solution. These anomalies have distorted bacteria fluorescence spectra measured by other research groups, making it difficult to ascertain similarities or differences between bacteria fluorescence spectra. Our time-delayed measurements, shown in Fig. 2, illustrate the surprising similarity of fluorescence spectra of bacteria when interfering effects are eliminated. Only two minor anomalies are present in the spectra shown in Fig. 2: (i) a fluorescence signal from the quartz cell used to hold the suspended bacteria and (ii) a decrease in the fluorescence signal intensity at a wavelength of about 355 nm due to a decrease in the response of the detector that occurred between measurements. UV fluorescence spectra of the three bacteria in Fig. 2 are also identical at other laser excitation wavelengths between 250 nm and 380 nm.

S ignificance—Time-delayed fluorescence measurements have allowed us for the first time to measure bacteria fluorescence spectra which are not affected by scattered light artifacts. The measurements show a high degree of similarity which makes it difficult to develop sensors that can identify specific bacteria but does make it possible to develop sensors that can detect and monitor the presence of broad classes of microorganisms in the presence of interfering backgrounds. Biological sensors that can detect broad classes of microorganisms in near realtime are expected to have applications in both proliferation detection and food safety.

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Sponsors for various phases of this work include: DOE NN20

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Figure 1. Photograph of the Ultrasource used to measure ultraviolet fluorescence spectra of bacteria (R.D. Mead, D.D. Lowenthal, T.D. Raymond, W.J. Alford, and A.V. Smith, "Optical Parametric Oscillator-Based Laser Source Continuously Tunable from 350 to 400 nm," in *OSA Proceedings on Advanced State Lasers, 1994, Vol. 20*, T.Y. Fan and B.H.T. Chai, eds., Optical Society of America, 1994, p. 381).



Figure 2. Time-delayed measurements made with a short-pulse broadly tunable UV laser show that the tryptophan UV fluorescence bands of three different bacteria (one of which was grown in two different growth media) are virtually identical. Fluorescence spectra were measured at a time delay of 6 nsec from the peak of the laser excitation pulse.

Optimal Selection of Array Sensors for Chem-Lab-on-a-Chip Microsystems

by G. C. Osbourn and J. W. Bartholomew

M otivation—There is strong interest in using small, portable sensing systems to carry out chemical analyses for applications ranging from characterization of hazardous chemicals in the environment to the detection of chemical warfare agents. These miniature "chem-lab-ona-chip" sensing systems will consist of arrays of chemical microsensors combined with intelligent analysis algorithms to interpret the distinctive signatures of array responses associated with various chemicals of interest. Such systems will be designed to include those microsensor combinations that provide the most distinctive response patterns from the chemicals of interest, so that the intelligent computer algorithms can provide the best evaluations of the measured chemical environment. A key issue for such systems is how to select this suite of sensors, i.e. how many sensors and which ones are most effective as inputs to the data analysis.

A ccomplishment—We have carried out studies to determine how to select the optimal set of chemical sensors for a particular sensing We have used laboratory data application. obtained for volatile organic compounds from a set of thirteen candidate sensors developed by the Microsensor Department at Sandia. Two versions of the data were examined. One contained responses from the "fresh" new sensors, and the other set included the modeled effects of aging on the sensor sensitivities. We used the SNL VERI pattern recognition algorithm to directly compute and compare the effectiveness of the (over 8000) alternative array combinations that can be selected from the thirteen available sensors. This novel approach is computationally feasible only because our VERI pattern recognition algorithm requires no user-adjustments or training calculations (e.g., as needed for neural net techniques). This selection approach is superior to the popular principal components (PCA) technique because we are guaranteed to find the optimal sensor combinations.

Figure 1 shows the chemical recognition errors found for the best and worst possible array, using new sensors, as a function of the number of sensors in the array. The results show that arrays of any size can be found which essentially distinguish all of the chemicals. The results also show that the array performance for the smaller arrays can be quite poor if the wrong sensor combinations are selected. Figure 1 also shows the chemical recognition errors obtained from the best arrays that have up to 50% model losses in the sensitivities of the individual sensors. Comparing the results from the best new and degraded arrays shows that larger arrays are more sensitive to aging effects than smaller arrays. This work shows that the smaller arrays are the most robust choices, and that these arrays must be chosen carefully. We have also examined the performance of sensor combinations computed using the popular PCA method, and we find that the PCA-selected array vields significantly reduced chemical recognition performance compared to the optimal selections we have discovered.

S ignificance—We have developed a powerful new method for designing the best possible chemical sensor array selections which also provide the most robust performance during sensor aging.

Internal partners/customers: G. C. Frye (1315), and (A. J. Ricco) 1315 Sponsors for various phases of this work include: DP Research Foundations, LDRD

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Figure 1. Results of optimization computations used to select optimal chemical sensor combinations for detecting volatile organics. The results show the best and worst possible performance, extracted from comparisons of over 8000 arrays, for arrays with different numbers of sensors.

The Synthesis of Infrared Emitters for Use in Chemical Sensors

by R. M. Biefeld, A. A. Allerman, and S. R. Kurtz

M otivation—We are investigating the synthesis of InAsSb materials by metal-organic chemical vapor deposition (MOCVD) for use in infrared optoelectronic devices. Mid-infrared (3-6 μ m) lasers and LEDs are of interest for use in chemical sensor systems to monitor the decomposition of high explosives by measuring the concentrations of gases such as CO, CO₂ NO_x, and H₂O. These devices could also be used in other more general chemical sensing applications such as process monitoring as well as in infrared countermeasures. We have used MOCVD, the growth technique preferred by industry for manufacturing, to synthesize the structures used in these devices.

A ccomplishment—We have used MOCVD to synthesize AlAs_{1,x}Sb_x cladding layers and InAsSb/InAs multiple quantum well (MQW) and InAsSb/InAsP strained-layer superlattice (SLS) active regions for use in mid-infrared emitters. The AlAs_{1,x}Sb_x cladding layers were successfully doped p- or n-type using diethylzinc or tetraethyltin, respectively. By changing the layer thickness and composition of SLSs and MQWs, we have prepared structures with low temperature (<20K) photoluminescence wavelengths ranging from 3.2 to 6.0 µm. We have made gain-guided, injection lasers using undoped, p-type AlAs_{0.16}Sb_{0.84} for optical confinement and both strained InAsSb/InAs MQW and InAsSb/InAsP SLS active regions. The lasers and LEDs utilize the semi-metal properties of a p-GaAsSb/n-InAs heterojunction as a source for electrons injected into active regions. We have successfully prepared a multiple-stage LED utilizing this

semi-metal injection scheme. Gain-guided, injected lasers with a strained InAsSb/InAs MQW active region operated up to 210 K in pulsed mode with an emission wavelength of 3.8-3.9 µm and a characteristic temperature of 29-40 K. The maximum operating temperature of an optically pumped 3.9 µm SLS laser with an InAsSb/InAsP SLS active region was 240 K. An electrically injected structure with a similar SLS active region achieved a peak power of 100 mW at 80K with a maximum operating temperature of 180K. An SLS LED emitted at 4.0 µm with 80 µW of power and a MQW LED at 5.0 µm with 100 µW power at 300 K. We have used these LEDs to sense CO₂ to a level of about 10 ppm in a first generation LED absorption sensor with a PbSe detector. The response of the sensor system to CO₂ is illustrated in Figure 1.

S ignificance—We have prepared and evaluated InAsSb/InAsP SLSs and InAsSb/InAs MQWs as active regions for MOCVD-grown, mid-infrared lasers and LEDs. Excellent, stateof-the-art performance was observed for these SLS and MQW LEDs and lasers. We have assembled a chemical sensor system using these LEDs and actively determined the concentration With nominal improvements in of CO₂. materials and processing and the further development of multi-stage active regions, MOCVD-grown InAsSb devices should be able to more completely satisfy the system requirements for use in chemical sensor and infrared countermeasure technologies in the near future.

Internal partners/customers: J. G. Harlan (1152)

Sponsors for various phases of this work include: DP Research Foundations, LDRD, EE

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Figure 1. This graph shows the absorption by CO_2 of the infrared signal generated by an InAsSb/InAsP room temperature LED operating at 4.2 μ m. The sensitivity in this first embodiement of the gas sensor is about 10 ppm.

GaN MOCVD development for Chemical Sensing

by J. Han, R. M. Biefeld, and M. H. Crawford

M otivation—The unique physical properties associated with wide bandgap group III-nitride semiconductors (AlN, GaN, and InN) have made them attractive for a broad range of applications including short-wavelength light emitters (from green to ultraviolet, see Figure 1(a)), solar-blind UV detectors, and high temperature or high power electronic devices. Short wavelength laser diodes (LDs), though still at an embryonic stage, will play a key role in next-generation information storage devices. Compact UV detectors and sensors are expected to find use in biomedical, chemical sensing, and environmental monitoring as well as national security applications such as nonproliferation, missile defense and nuclear stockpile monitoring (see Figure (b)). The state of III-nitride material and device research resembles what GaAs technology was at approximately twenty-five years ago. The recognition of and subsequent investment into that materials system with versatile functionality eventually brought society notable rewards, such as opto-electronic and mobile communications.

A ccomplishment—So far the majority of the nitride-based devices were grown on sapphire substrates by metal-organic chemical vapor deposition (MOCVD) where *in-situ* diagnostics (process monitoring *while* the material is being synthesized) was traditionally lacking. The deposited nitride epilayers evolve from a heavily-disordered thin film (near the epilayer/substrate interface) with multiple phases and domains into essentially a coherent crystalline material through mechanisms (grain growth, surface recrystallization, and orientation selection, for example) not typically present in

the epitaxy of conventional semiconductors. The optimization of synthesis processes is normally carried semi-empirically until an acceptable recipe is found. With the use of a vertical rotating disc CVD reactor with in-situ optical reflectometer, we could monitor the evolution of growth morphology. The in-situ optical probe provides simple yet instant feedback on the crucial information of the surface morphological transients. We were able to quickly explore the MOCVD parameter space and correlate it with growth evolution and We have obtained GaN material quality. epilayers with electrical properties (mobility > 500 $\text{cm}^2/\text{V-sec}$), optical properties (free exciton emission with a line width of 3 meV), surface morphology (a surface roughness of 0.1 nm from AFM) and structural quality (total dislocation density in the high 10^8 cm^{-2}) comparable to the best reported to date.

S ignificance—The establishment of a GaN base-line growth process enables us to move into AlGaN-based UV emitters and detectors. The incorporation of *in-situ* diagnostics into the MOCVD growth of III-nitrides has proven to be critical in both enabling the preparation and optimization of device quality GaN materials, as well as providing insight into issues of great interests to material research. In situ diagnostics would also facilitate the transition from an R&D effort to a manufacturing environment. Advancement in GaN material synthesis and device fabrication technology, currently being pursued on a worldwide scale, is expected to push the use of GaN-based UV optoelectronic devices into commercial realization before the end of this decade.

Internal partners/customers: J. Vitko, Jr. (8102), and M. W. Scott (1307)

Sponsors for various phases of this work include: DP Research Foundations, BES, LDRD, Chem-Lab-On-Chip

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Figure 1. (a) Lattice constant versus band gap for III-nitride compounds; the visible spectrum is also included as a reference, and (b) Green luminescence from a UO_2^{2+} -containing material irradiated by a AlGaInN-based blue LED.

Modeling Laser Gain in GaInAlN Materials for Short Wavelength Sensing Applications

by W. W. Chow and A. F. Wright

Motivation—Group-III nitride lasers and light emitting diodes are interesting because they can potentially operate at visible and ultraviolet wavelengths. Potential applications include the fluorescence of chemicals for local or remote Light emitting diodes based on sensing. InGaN/AlGaN heterostructures are now commercially available, and room-temperature continuous-wave operation has been demonstrated in current injected InGaN/AlGaN quantum well lasers. Since these devices are still in the early stage of development, the physical mechanisms governing gain medium behavior are under active investigation. For nitride compounds, many-body Coulomb interactions play an important role. Furthermore, optical properties are affected by inhomogeneous broadening due to spatial variations in quantum well width or composition in the experimental structures. Our work involves the development of a theory that provides a consistent treatment of these factors.

A ccomplishment—We have developed a theory for the optical properties in group-III nitride quantum well structures. The approach is based on the semiconductor Bloch equations with carrier correlation effects treated at the level of quantum kinetic theory in the Markovian limit. A model for inhomogeneous broadening due to quantum well width or

composition variations is also incorporated into the theory. Figure 1 shows the computed spectra for an InGaN/AlGaN quantum well structure and different carrier densities. The low density spectra show an exciton resonance. The existence of excitons at the high temperature and carrier density of T=300K and N= 10^{12} cm⁻² is evidence of strong Coulomb attraction between electrons and holes. At high densities the exciton resonance vanishes and gain appears (see inset). Recently, there is considerable interest concerning the energy of optical emission, in particular, the observed red shift in the laser emission wavelength relative to the estimated unexcited quantum well band gap energy. The gain spectra in Fig. 1 clearly show a red shift.

S ignificance—The present theory provides a consistent description of optical gain for the strongly interacting electron-hole plasma found in group-III nitride quantum well lasers. Manybody Coulomb effects are included systematically in the Hamiltonian, which ensures a consistent treatment of the transition from low electron and hole densities, where excitons are important, to high carrier densities, where an interacting Coulomb correlated electron-hole plasma determines the gain medium properties.

Internal partners/customers: J. Vitko, Jr. (8102) and M. W. Scott (1307)

Sponsors for various phases of this work include: LDRD, Chem-Lab-On-Chip, DP Research Foundations

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Figure 1. Calculated TE gain spectra for a 4nm $In_{0.1}G_{0.9}N/Al_{0.2}Ga_{0.8}N$ at T = 300K and densities N = 0.1, 0.5, 1.0, 2.0, 4.0, and $6.0x10^{12}cm^{-2}$ (solid line corresponds to $6x10^{12}cm^{-2}$). We assumed an inhomogeneous broadening due to indium concentration variations of $\sigma = 0.01$. The inset shows the gain portion of the spectra for N = 2, 4, 5 and $6x10^{12}cm^{-2}$.

Composition Modulation in Compound Semiconductors for Advanced Photovoltaic Concepts by E. D. Jones, D. M. Follstaedt, S. R. Lee, J. Mirecki Millunchick, J. L. Reno, and R. D. Twesten

M otivation—Self-assembled quantum dots wires that result in quantum-size and configurations during growth can lead to many optoelectronic new and novel device applications. Recently, we have observed spontaneous lateral composition modulation resulting from the deposition of monolayer-thick short period superlattices of group III-V binary compounds. These compositionally modulated structures are of particular interest due to their possible use as a new class of advanced photovoltaic materials with increased light conversion efficiency. In order to obtain an understanding of the growth parameters for composition modulation, we characterized these structures with several techniques such as magneto-photoluminescence, photomodulated reflectance spectroscopy, x-ray reciprocal space analysis, and transmission electron microscopy. With the knowledge gained from these kinds of studies, practical designs for lateral composition modulation solar cells, polarizing mirror stacks for vertical cavity surface emitting lasers, and polarized photo-detectors could result.

A ccomplishment—Short period superlattices consisting of alternating layers of approximately 2-monolayer-thick AlAs and InAs were deposited on InP (001) oriented substrates by molecular beam epitaxy. The resulting spontaneous lateral composition modulation phenomena was studied by low temperature photoluminescence, cross-sectional transmission electron microscopy and x-ray reciprocal space mapping. A bright field crosssectional transmission electron microscopy micrograph of an InAs/AlAs short period superlattice structure is shown in Fig. 1. The individual superlattice layers (horizontal lines) are clearly visible. The composition modulation wavelength is about 130 Å. Analyses of the dark field image indicate that the lighter regions are aluminum-rich while the dark narrow regions are indium-rich. The modulation appears to form a cusp in the indium-rich regions, implying that the morphology of the front may be correlated with growth composition modulation. The varying indium concentration in the direction of the composition modulation was measured by scanning transmission electron microscopy and this result is shown in Fig. 2. The indium concentration was calibrated using the lattice matched InAlAs-buffer layer as a reference. The maximum and minimum indium concentrations are 78% and 38% respectively! The bandgap energy for the 78% indium-rich was confirmed by 1.4-K photoluminescence measurements. Other transmission electron microscopy data show that in contrast with the quantum wire formation found in InAs/GaAs composition modulation structures, the AlAs/GaAs system appears to form quantum dashes or boxes.

S ignificance—Self assembled quantum-size structures offer new opportunities for advanced optoelectronic devices. If the origins of composition modulation can be understood and controlled, it should be possible to develop novel optoelectronic and photvoltaic devices based on this phenomenum. For example, composition induced bandgap modulation on a microscopic scale could lead to spatial carrier separation and more efficient collection for very high efficiency photo-voltaic devices.

Partners/Customers: G. A. Samara (1152), and NREL

Sponsors for various phases of this work include: BES, BES Center of Excellence for Synthesis and Processing

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Figure 1. Bright field cross-sectional transmission electron microscopy image of an InAs/AlAs short period superlattice structure on InP.



Figure 2. Indium concentration variation along the composition modulation direction in a InAs/AlAs short-period superlattice measured by scanning transmission electron microscopy. The resolution is about 1 nm.

Advances in Unconventional Solids for Anomalously High Thermoelectric Efficiencies

by T. L. Aselage, D. Emin, and S. S. McCready

M otivation—Boron carbides are refractory solids whose unconventional structures and bonding give rise to unusual transport properties. These exceptional transport properties make boron carbides promising hightemperature thermoelectric materials. The surprisingly high thermoelectric efficiencies occur in part because the Seebeck coefficients (thermoelectric powers) of these materials are several orders of magnitude larger than would be expected for conventional solids with boron carbides' high carrier densities. Our goal has been to determine the origin of these anomalously large Seebeck coefficients. Such understanding may allow us to better optimize these materials or to identify new classes of materials with anomalously high thermoelectric efficiencies.

A ccomplishment—Measurements of the Seebeck coefficients of boron carbides now cover both an exceptionally wide temperature range, from 10 to 900 K, and the complete single-phase composition region, from 9 to 19 atomic percent carbon. Figure 1 shows the Seebeck coefficient of a boron carbide whose carbon concentration, 13 atomic percent, bestows a high carrier density of about one charge carrier per unit cell. Unlike the Seebeck coefficients of conventional semiconductors with high carriers densities (< 20 μ V/K), boron carbides' Seebeck coefficients are quite large. shows Futhermore Fig. 1 а distinctive temperature dependence: the Seebeck coefficient rises to a peak and then falls to a large, nearly temperature-independent value. All boron carbides show this general behavior despite fractionally small variations with carrier density (controlled by carbon concentration).

We have determined that this unusual temperature dependence would result if charge carriers significantly soften the lattice in their vicinity. Then the Seebeck coefficient contains a vibrational contribution that rises with temperature to asymptotically approach a constant value. In addition, with hopping-type transport as observed in boron carbides, carrierinduced softening contributes a transport term that peaks near a phonon temperature. When summed the temperature dependences of these two contributions, shown in Fig. 2, resemble the temperature dependence of Fig. 1.

Our prior measurements have shown that charge carriers pair as singlets on boron carbides' twelve-atom icosahedra. Our recent studies focus on how such charge carriers can soften their surroundings. The electronic energies of singlet states on a boron polyhedron are plotted against a deformation parameter x in Fig. 3. The solid curve has significant downward curvature, indicative of strong carrier-induced softening. This curvature, which arises from hybridization of a low-energy singlet and a high-energy singlet (upper-most dashed curve), is missing from standard ad hoc models. With sufficient deformation, the singlet represented by the solid curve is stabilized relative to the lowest triplet state (not shown in Fig. 3).

S ignificance—As evidenced by boron carbides, large Seebeck coefficients can arise from a previously unknown mechanism. Knowing the cause of the very large Seebeck coefficients in boron carbides can systematically guide us to other materials that may also be unexpectedly efficient thermoelectrics.

Internal partners/ customers: P. J. Green (5725)

Sponsors for various phases of this work include: BES, LDRD, DP Research Foundations

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Figure 1. Seebeck coefficient of a boron carbide sample with 13.3 atomic percent carbon. Different symbols represent measurements using different apparatus.



Figure 2. Vibrational and transport contributions to the Seebeck coefficient, in units of k/q (the Boltzman constant divided by a carrier's charge), are plotted against temperature divided by the phonon temperature, Θ .



Figure 3. The electronic energies, W, of singlet states on a boron polyedron are plotted against a deformation parameter, x, where U_0 is the Coulomb repulsion between two holes on a common orbital and A is the electron-lattice coupling strength. The singlet state shown as a solid line falls quadratically to become the stable state as the polyhedron is deformed.

Photooxidation Using Semiconducting Nanoclusters for Organic Waste Destruction

by J. P. Wilcoxon and T. R. Thurston

M otivation—Solar photodetoxification is a process wherein sunlight is captured by semiconductor particles in suspension to create electrons and holes that then diffuse to the particulate surface to effect the oxidation and reduction of toxic pollutants. Using solar energy to oxidize organic chemicals to carbon dioxide and dilute mineral acids would be very energy efficient compared to other methods such as incineration. Finding an efficient particulate has thus been a focus of research, which has had only limited success, the fundamental problem being that materials that efficiently absorb in the visible portion of the solar spectrum also photocorrode. Our work is focused on development of chemically stable nanosize semicondutor materials as photocatalysts.

A ccomplishment—We have demonstrated electron and hole transfer from nanosize MoS₂ using visible light. In order to oxidize organic impurities using visible light we needed to add an agent, e.g. bypyridine, which could accept an electron and be reduced. When not reduced bypridine binds strongly to nanosize MoS, and acts like an electron transfer relay to effect charge separation. The hole left behind on MoS₂ is then used to oxidize the organic In its reduced form bypridine impurities. complexes to the oxidized organic impurity and precipitates out of solution. We studied the chemistry of this process by high pressure liquid chromatography which separates each of the chemicals in the solution from the MoS₂ photocatalyst. The results of this experiment are shown in figure 1. The initially present organic impurity peak at t~5.2 minutes is destroyed as more bpyridine is added until it cannot be detected. However, the amount of nanosize

MoS₂ remains unchanged. Another, broader, organic peak observed in this figure at ~t=4.7 minutes also is destroyed by the MoS₂ as additional bpy is added, and, at higher levels of bpy (not shown) is completely oxidized and precipitates out of solution as well. A white precipitate forms which can be removed from the solvent. Studying the spectral properties of the MoS₂ before and after the reaction shows it has not changed in size or photoproperties. The structured absorbance spectrum of the MoS₂ photocatalyst is shown in figure 2. Remarkably, the above photoredox reaction occurs rapidly (e.g <1 minute) under ordinary room light (laboratory illumination) using these 3 nm nanoclusters which begin aborbing light at ~450 nm. For larger, 4.5 nm MoS₂ with a narrower band gap which begin absorbing light near 550 nm, the reaction is significantly slower and less complete under room illumination. We attribute this to the narrower bandgap and correspondingly lower reduction potential of these larger nanoclusters which provides less of driving force for the electron transfer to bpy. For these larger clusters which absorb more visible light, a stronger lamp source may be required to achieve complete photooxidation.

S ignificance—This work is the first demonstration of photoredox reactions to completely oxidize and precipitate organics from solution using nanosize semiconductors and only weak visible light as the initiator. Furthermore, using chromatography we have been able to follow the course of the photochemistry and demonstrate that the nanosize MoS_2 used is unaltered by the reaction - it functions as a true photocatalyst.

Internal partners/customers: J. K. Rice (6600), and G. A. Samara (1152)

Sponsors for various phases of this work include: ER/EM Joint Program, BES

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Figure 1. Optical absorbance at 250 nm (a measure of the organic concentration) vs. elution time for impurity chemicals and MoS_2 nanoclusters. The organic impurities shown were photooxidized by the MoS_2 nanoclusters which have bypyridine (bpy) added to them. A new complex of the reduced bypyridine and oxidized organics is formed (see new elution peak at the upper trace) and due to its limited solubility it precipitates and is removed from the solution.



Figure 2. Optical absorbance vs. wavelength for nanosize MoS_2 before and after photo-oxidation and precipitation of organic contaminants. No changes in either size or structure of the MoS_2 was observed. (The dashed curve has been shifted vertically for clarity).

Broadband Emission in Quantum-Tailored Semiconductor Heterostructures for High Efficiency Light Sources by P. L. Gourley, M. H. Crawford, M. B. Sinclair

M otivation—Illumination sources are vitally important to human society. Each day, about 10 kilowatt-hours per person are dissipated to illuminate homes, offices, shops, schools and vehicles. Only a small fraction of this power is useful. Tungsten bulbs produce 99.5% heat and 0.5% light, are inexpensive, but last only 2 years. Fluorescent tubes are more efficient (few percent), but they have the complication needing heavy of ballast transformers operating high voltages. at Modern semiconductor photonics can overcome many of these limitations and can play important role in future illumination technology. With efficiencies up to 50 percent, semicondutor devices can operate for decades and can be disposed without harming the environment. Even a one percent increase in lighting efficiency would save the energy equivalent of 1,000,000,000 barrels of oil per year in U.S. energy consumption. Multi-alloy structures like the one reported here have the potential to be developed into efficient, broadband light sources.

A ccomplishment—We have recently designed and tested a novel Aluminum-Gallium-Indium-Phosphide semiconductor structure for spectrally broadband light emission. Figure 1a conceptually illustrates our successful new semiconductor design. It shows corrugated surfaces corresponding to electronic quantum wells in a layered semiconductor heterostructure. Electrons (solid lines) are shown streaming above the quantum wells and selectively falling, by phonon coupling, into higher energy wells. The recombination of electrons and holes from these and lower energy wells gives rise to photon emission at red, yellow, and green wavelengths.

Figure 1b shows the experimentally measured photoluminescence spectrum from the semiconductor heterostructure. It includes spectra recorded at low, intermediate, and high At the highest level, the injection levels. spectrum is quite broad across the visible wavelength region, including light of green, vellow, orange and red color. The lower righthand figure (Figure 1c) shows a photomicrograph of the actual wafer (defined by the bright edges) and emitted light that has been dispersed into spectral orders by a diffraction grating.

S ignificance—The spectra measured for the new heterostructure have an energy bandwidth of 150 millielectronvolts, about six times the average thermal energy of an electron at room temperature. This result demonstrates that the distribution of electrons can energy be substantially modified by two-dimensional layering of alloys into heterostructures. At the same time, the overall heterostructure thickness is the order of one hundred nanometers making it suitable for an electrically injected device. With proper design, electrically injected devices could meet the goal of high efficiency, spectrally broadband light emission at room temperature.

Internal partners/customers: M. B. Sinclair (1812), and M. J. Hafich (1314) Sponsors for various phases of this work include: Advanced Energy Projects, BES

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Figure 1a. Schematic representation of a new AlGaInP layered semiconductor heterostructure that has been designed for broadband light emission. Electrons (solid circles) and holes (open circles) are captured into quantum wells that have a range of transition energies (designated by solid vertical arrows). Figure 1b. Room temperature photoluminescence spectra from the new AlGaInP semiconductor heterostructure under low (Io), medium (10*Io) and high excitation (100*Io). Figure 1c. Photomicrograph of optically excited semiconductor wafer with emitted light dispersed through a diffraction grating.

Spectroscopic Light Scattering Used to Monitor Surface Islanding and Self-Organization

by Eric Chason, Jerry Floro and Michael Sinclair

M otivation—Control of semiconductor microstructures can lead to new opporunities for advanced device performance as discussed in the preceding Brief in the area of photovoltaics. Further. smaller device dimensions and complicated multilayer designs in advanced optoelectronic and microelectronic devices require precise control of the film morphology. We have developed an *in situ* spectroscopic light scattering technique that enables us to monitor the evolution of surface structure during the growth of thin films. This technique is especially growth useful for monitoring the of heteroepitaxial films where film stress can greatly alter the growth morphology. Improved understanding of the process of island formation and self-organization in heteroepitaxial layers will enable us to produce periodic arrays of semiconductor clusters with novel electronic and optical properties.

A ccomplishment—Arrays of islands form during heteroepitaxial growth of strained layers to relieve misfit stress. An example of the island morphology produced during the growth of SiGe on Si (001) is shown in figure 1. These islands act like a diffraction grating and scatter light. We have developed a spectroscopic light scattering technique to monitor the evolution of surface morphology during heteroepitaxy. By using spectroscopic detection, the scattering pattern can be obtained without rotating the sample which makes the technique ideal for *in situ* monitoring.

The technique is highly sensitive, enabling us to identify the onset of islanding after less than 3 nm of growth. Because the technique is in situ and real time, the kinetics of island formation can be easily studied. Simultaneous measurement of the film stress using our multibeam optical stress sensor enables us to study the interaction between the driving force of stress relaxation and island formation. In addition, annealing studies have been performed to study the process of island coarsening. The evolution of the mean island spacing during growth of $Si_{80}Ge_{20}$ at 760 C is shown in figure 2. Previously, measurements of these growth kinetics would have required multiple growth runs and time consuming analysis.

S ignificance—Many advanced device concepts depend on more complex device structures which requires increasingly precise control of the growth process. The real time information provided by this new technique allows us to efficiently and rapidly optimize process parameters to obtain the best films. In addition, the growth kinetics give us unique into the fundamental processes insight controlling the morphology of the surface. Better understanding of these processes will enable us to create sharper interfaces for improved opto-electronic devices and more uniform arrays of quantum dots or other microstructures with novel properties for light sensing, detection or collection..

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Figure 1. Periodic array of islands produced during the growth of $Si_{80}Ge_{20}$ on Si(001) at 760 °C. The film thickness is 10.4 nm.



Figure 2. Results of spectroscopic light scattering measurement of mean island spacing.

Efficient Growth of Tl-Ba-Ca-Cu-O Superconducting Films

by M. P. Siegal, D. L. Overmyer and F. Dominguez

M otivation—High Temperature superconductivity has received widespread attention because of its future potential impact on electronics, energy, transportation, medical and military applications. Developments include improved radar, advanced navigation aids, and improved cellular telephone and satellite communications systems. TlBaCaCuO hightemperature superconducting (Tl-HTS) thin films have the best properties for many of these applications. While several major TI-HTS material phases co-exist, optimized properties require the use of single-phase, epitaxial thin films. However, because of the volatility of TIO_x at TI-HTS growth temperatures, single-phase growth is difficult to achieve.

A ccomplishment—We have developed a new method for the synthesis of high-quality Tl-HTS films that provides high yield, high throughput, and greatly reduced safety risks. The most commonly used thin film growth technique referred to as the crucible process, is based on previous Sandia research, and has two serious drawbacks: (1) throughput is low, and (2) safety requirements make costs high due to handling of hazardous Tl-oxide. A second method using a two-zone furnace promised a more scientific approach to the growth process, while at the same time increasing throughput and decreasing the handling of hazardous materials, both combining to greatly reduce manufacturing costs. Unfortunately, the two-zone process is difficult to scale, largely due to the inability to control Tl₂O partial pressure throughout the entire Tl-HTS growth process. The importance of this control is shown by the variation in morphology (Fig. 1) for two TlBa₂CaCu₂O₇ films grown under slightly different thallination conditions. Our new process, shown in Fig. 2, is a hybrid of the crucible and two-zone processes and solves all issues of thermodynamic control, resulting in:

- 1) Reproducible film properties, demonstrated for 19 consecutive runs with phase-pure epitaxial Tl₂Ba₂CaCu₂O₈ 600 nm thick films. Each film has smooth morphology, $T_c = 102$ K and J_c(T=5K) ~ 10⁷ A/cm², matching the properties of the best reported Tl-2212 crucible-grown films.
- 2) No handling of hazardous Tl-oxide powders for the duration of these runs.

S ignificance—The development of efficient, cost-effective technologies that enable safe production of reproducible, high-quality Tl-HTS materials is of great importance. The DOE has invested heavily in superconductivity for use in both electronics and bulk wire applications. For surface resistance example. the low of superconducting films, an area where TI-HTS materials excel, enables substantial reductions in both the size and weight of microwave components for defense and civilian applications, providing an unequaled combination of size and performance compared to any competing technology. In addition, the extremely short caxis coherence length and the anisotropic superconducting parameters of Tl-HTS can combine to provide an intrinsic stack of Josephson junctions, potentially leading to the development of a truly portable voltage standard. Finally, the ability to run a thallination furnace continuously without adjusting for Tloxide partial pressure will allow for continuousfeed use in Tl-HTS tape production with unsurpassed properties.

Partners/customers: NREL, DuPont, and University of Kansas

Sponsors for various phases of this work include: BES

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Figure 1. Films grown under slightly different thallination conditions by previous method: (a) morphology of an optimized 600 nm thick Tl-1212 film and (b) of a Tl-deficient region from a non-optimized 600 nm thick Tl-1212 film.



Figure 2. Schematic of the new hybrid crucible / two zone furnace process.
Scanning Cathodoluminescence Techniques for the study of Low-Voltage Phosphors

by C. H. Seager, and N. A. Missert

M otivation—Phosphors for use in emerging field emission displays must operate efficiently at low electron energies. Most phosphors used in conventional CRTs have greatly reduced efficiencies at electron energies less than 4 keV due to non-radiative surface energy losses. A technique is needed to identify the microscopic origins of such losses in order to implement processing pathways which might improve these Conventional cathodoluminescence materials. (CL) measurements generate images whose brightness cannot be quantitatively transformed into microscopic maps of local phosphor efficiency. By combining state-of-the-art digital image manipulation with a sensitive light collection system in a high quality SEM, new insights have been gained in the analysis of phosphor efficiency at low beam voltages.

A ccomplishment—Prior difficulties in the interpretation of luminescence images produced by a scanned electron beam arise from the nature of light propagation and scattering in an array of small particles. When a scanned focused electron beam excites a phosphor particle and subsequently leaves the electronhole (e-h) creation/diffusion volume, it is reflected and refracted within the phosphor crystallite, and, if other phosphor particles are present, it may scatter off these as well. Thus the fraction of excitation luminescence which actually reaches a detector depends in a complicated way on the grain morphology, grain environment, and details of the light collection system. This means that a 1:1 mapping of the image brightness of a given phosphor grain with its absolute CL efficiency is generally not possible.

However, the use of digital image processing capabilities open up new avenues for obtaining

quantitative information from this technique. When the e-h excitation volume is small compared to phosphor grain dimensions, then the light scattering and collection factors can be factored out of scanning CL images by digital techniques. The remaining image information can be directly related to local area phosphor efficiency. In practice this deconvolution is done by ratioing the brightness of scanned-beam images obtained at high and low electron energies, yielding an image which is a direct mapping of surface recombination. Typical results are shown in Figures 1 and 2. Figure 1 is an unprocessed image of the cathodoluminescence of the blue phosphor silver-doped zinc sulphide. Most of the image contrast is due to light collection artifacts unrelated to local light conversion efficiency. In Figure 2, an image is shown which is the ratio of the image in Fig.1 and an image obtained at 1.7 keV, where surface non-radiative losses are large. This ratio image is almost featureless, showing that the nonradiative losses are extremely uniform (and deleterious) in this material. Ratio images of other phosphors show more variation and reveal links between surface losses and microscopic features like grain size. This improved technique has also been used to image variations cathodoluminescence in other materials like thin films of pseudo-epitaxial gallium nitride.

S ignificance—This is the first technique which directly maps surface non-radiative losses on a microscopic scale. By correlating images such as these with specific microscopic properties it should be possible to improve processing of these important display materials.

Partners/customers: Motorola, and PTCOE

Sponsors for various phases of this work include: DARPA, AMMPEC

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Figure 1. Scanning cathodoluminescence image of silver doped zinc sulphide phosphor particles at an electron beam energy of 4 keV.



Figure 2. Image formed by ratioing (dividing individual pixel brightnesses) a 1.7 keV scanning cathodoluminescence image with the 4 keV image shown in Fig. 1. The refraction/collection artifacts are removed revealing extremely uniform surface non-radiative energy losses.

Resources and Capabilities Physical and Chemical Sciences Center

— Diagnostics and Characterization —

Materials Characterization

Our capabilities in this area include optical microscopy, scanning, electron microscopy, analytical transmission electron microscopy, double crystal x-ray diffraction, ion beam analysis of materials (RBS, channeling, ERD, PIXE, NRA), Hall measurements, photoluminescence, light scattering, electronic transport, deep level spectroscopy, magnetization, and dielectric and magnetic susceptibilities.

Surface and Interface Spectroscopies

We maintain strong capabilities in Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), thermal desorption spectroscopy (TDS), infrared reflectance-absorption spectroscopy (IRAS), and quantum state resolved laser surface probes.

Sandia Tandem Van de Graaff Ion Accelerator Nuclear Microprobe

This 6 MV EN accelerator provides ion species from hydrogen to bismuth for both radiation effects research and quantitative ion beam analysis of materials containing light elements (hydrogen to fluorine) using elastic recoil detection (ERD) and heavy elements using Rutherford backscattering spectrometry (RBS). An eXternal Micro Ion Beam Analysis (X-MIBA) capability enables analysis or irradiation of samples which are vacuum incompatible or extraordinarily large. The Sandia Nuclear Microprobe with micrometer size high energy ion beams is used to analyze materials and radiation hardness of microelectronic devices using Single-Event-Upset Imaging, Ion-Beam-Induced-Charge-Collection Imaging (IBICC) and time-resolved IBICC.

Vision Science Laboratory

We have developed a vision science laboratory with state-of-the-art hardware and software capabilities for carrying out video inspection, multi-spectral image analysis, and sensor-based pattern recognition. These capabilities can be applied to applications ranging from microsensorbased chemical detection and recognition to automated video/SEM inspection of semiconductor materials and circuits.

Low-Temperature Plasma Analysis

We have state-of-the-art capabilities for the analysis of low-temperature plasmas as found in neutron generators and commercial processing reactors. These include emission spectroscopy, electrical characterization, laser and microwave-based measurements of species concentrations, *in situ* electric field measurements and two dimensional time-resolved spatial imaging techniques.

Chemical Vapor Deposition (CVD)

We have a wide range of experimental tools for investigating CVD which include optical probes for gas-phase and surface processes, a range of surface analytic techniques, molecular beam methods for gas/surface kinetics, and flow visualization techniques. Carefully chosen experiments provide the critical information on chemical species, gas temperatures, and flows necessary for model development and validation.

Growth Science Laboratory

We have unique capabilities for in situ characterization of materials during thin film deposition, molecular beam epitaxial growth, and low energy ion beam simulated growth, using intensity profile sensitive reflection high energy electron diffraction (RHEED) for surface structure, energy dispersive x-ray reflectometry for in situ surface and interface structure, multibeam wafer curvature for strain, and Auger electron spectroscopy for surface composition.

KMAP X-Ray Diffractometer

Based on double crystal x-ray diffractometry in combination with position sensitive x-ray detection our KMAP x-ray diffraction analysis is used to determine the lattice constant, strain relaxation, composition, layer orientation, and mosaic spread of a large variety of advanced epitaxial semiconductor materials.

Atomic-Level Imaging and Spectroscopy

We have developed unique capabilities in scanning tunneling microscopy (STM), field ion microscopy (FIM), atom probe microscopy (APM), low energy electron microscopy (LEEM), and interfacial force microscopy (IFM). Selected analysis is possible in both high temperature and ultra-high vacuum.

Nanoelectronics Laboratory

We have capabilities for characterizing nanoelectronic structures (also fabricated at Sandia by e-beam lithography) through electrical transport measurements at low temperatures and high magnetic fields.

Lasers and Optics

We have extensive capabilities in characterizing and advancing the understanding in the area of solid-state lasers and non-linear optics, especially as coherent sources of broadly tunable light in rugged, compact geometries. We have established expertise in long-term and transient radiation effects characterization of optical materials.

Laser and Optical Spectroscopies

We have extensive capabilities for characterizing semiconductor materials by photoluminescence and magnetoluminescence down to low temperatures by optical laser imaging and laser microscopy, by laser excitation spectroscopy, and by time-resolved measurements of optical emission. We also have developed a high lateral resolution near-field scanning optical microscopy (NSOM) capability with time and frequency resolution.

- Synthesis and Processing -

Nanocluster Laboratory

We have developed and patented a process based on the use of inverse micelles for the synthesis of large quantities of monodisperse clusters of metals, semiconductors, and oxides.

Electron Cyclotron Resonance (ECR)

This plasma facility has been built for studying fundamental processes governing the growth of oxide and nitride dielectric films used in optoelectronics and used as hard coatings.

400 kV and 180 keV Ion Implanters

These systems are equipped with a variety of sources (gas, sputter, and metal vapor). This facility provides ion species from hydrogen to bismuth which can be used for studying fundamental irradiation mechanisms and selective chemical doping in semiconductors, metals, ferroelectrics, and superconductors.

Molecular Beam Epitaxy

We have state-of-the-art commercial semiconductor growth laboratories for MBE growth of III-V materials. In addition, we have research systems for Group IV semiconductor growth, including conventional and beam-enhanced epitaxial growth.

Metal-Organic Chemical Vapor Deposition (MOCVD)

We maintain state-of-the-art materials growth and characterization facilities with unique capabilities in MOCVD of compound semiconductor materials. Our facilities include commercial production MOCVD reactors as well as research reactors designed specifically for studies of CVD chemistry and for the development of advanced in situ diagnostics.

High Pressure and Shock Wave Physics and Chemistry Laboratories

Our capabilities in this area include large volume static high pressure apparatus which can be operated at temperatures ranging from 2° to 700° K and in magnetic fields, as well as gas gun and explosive loading facilities with state-of the-art, time-resolved diagnostics. Recovery fixtures have been developed for use with the gas gun and explosive shock loading facilities which allow unique material synthesis over broad ranges of shock pressures and temperatures.

Crystal and Thin Film Growth

Capabilities in this area include a pulsed laser deposition chamber, a thin film oxide deposition chamber, a diamond-like carbon deposition chamber, a hot filament chemical vapor deposition chamber, and various apparatus for single crystal growth.

— Theory and Simulation —

CVD Reactions

We have extensive capabilities to model complex chemically reacting flows such as occur in chemical vapor deposition manufacturing processes. Our numerical simulations can include the coupled gas-phase and gas-surface chemistry, fluid dynamics, heat, and mass transfer to provide predictive models of a chemical process.

Electronic Structure and Linear Scaling

We have developed state-of-the-art massively parallel electronic structure algorithms, based on ab initio pseudopotentials and plane-wave/ gaussian basis functions. In close collaboration with experimental efforts, these codes are used to develop a fundamental understanding of new physical phenomena and materials, including compound semiconductor band structure, point defects in semiconductors, surface electronic structure, enhanced reactivity of nanoparticles, and adsorbate interactions on surfaces. To allow the investigation of more complex systems and phenomena, we are also developing new computationally efficient algorithms, e.g., selfconsistent linear scaling density functional theory, and variable- and real-space gridding.

Low-Temperature Plasmas

We have extensive capabilities to simulate the time

and space evolution of low-temperature plasmas, focusing on new theoretical techniques for achieving rapid convergence and on direct comparisons with experimental results.

Optical Design

We have capabilities in novel optical designs, including resonators for application-driven laser geometries and in the application of binary optics. These capabilities are coupled to in-house microoptics construction facilities and state-of-the-art optics testing.

Wave Propagation

We have developed advanced simulation codes for understanding wave propagation in optical parametric oscillators and amplifiers for the purpose of designing highly efficient, missionoriented tunable laser sources.

Semiconductors

Expertise in this area includes: Ab initio pseudopotential bandstructure, semiconductor transport and photo-luminescence, Monte Carlo surface epitaxial growth and sputtering, and binary collision TRIMRC code to simulate ion-solid interactions. Workstations, CRAY-YMP, and massively parallel computational facilities are used.

Physical & Chemical Sciences Center FY97 Budget - By Customer





Recent Awards and Prizes Physical and Chemical Sciences Center

National and International Awards

- 1997 Peter Mark Award for "Pioneering studies of atomic-scale, kinetic and thermodynamic aspects of the morphology of Si surfaces, and significant innovations in scanning tunneling microscopy that make such measurements possible" American Vacuum Society (B. S. Swartzentruber)
 - Edward Orton, Jr., Memorial Lecturer Award American Ceramics Society (T. A. Michalske)
- 1996 DOE Young Independent Scientist Award (B. S. Swartzentruber)
 - The Medard W. Welch Award for "His insightful predictions and explanations of surface phenomena based on first principles calculations" - American Vacuum Society (P. J. Feibelman)
- 1993 International New Materials Prize for "Originating the Field of Strained-Layer Superlattice Electronics and Optoelectronics" - American Physical Society (G. C. Osbourn)
 - ---- Shock Compression Science Award The American Physical Society (R. A. Graham)
- 1990 E. O. Lawrence Award, Materials Science DOE (S. T. Picraux)
- 1989 Davisson-Germer Prize "For his pioneering work in developing the theory of electromagnetic fields at surfaces" American Physical Society (P. J. Feibelman)
 Weyl International Glass Science Award International Glass Commission (T. A. Michalske)
- 1986 Ross Coffin Purdy Award American Ceramics Society (T. A. Michalske)
- 1985 E. O. Lawrence Award, Materials Science DOE (G. C. Osbourn)

DOE Basic Energy Sciences, Material Science Awards

- 1996 Outstanding Scientific Accomplishment--Solid State Physics "Development of Atom-Tracking Scanning Tunneling Microscopy for Direct Measurements of Surface Dynamics" (B. W. Swartzentruber)
 - Significant Implication for Department of Energy Related Technologies--Materials Chemistry "Nanoclusters for Energy Applications" (J. P. Wilcoxon, P. P. Newcomer, D. E. Bliss,

G. A. Samara, and A. Martino)

- 1994 Sustained Outstanding Research--Solid State Physics "Surface Atom Energetics" (P. J. Feibelman)
 - Sustained Outstanding Research--Metallurgy and Ceramics "Science of Surface Processes in Beam-Enhanced Growth" (E. Chason, J. Y. Tsao, J. A. Floro, K. M. Horn, T. M. Mayer, P. Bedrossian, D. K. Brice, A. J. Howard, S. T. Picraux, D. L. Buller, and K. J. Penn)
 - Significant Implication for Department of Energy Related Technologies--Materials Chemistry "Real Time, *In Situ* Materials Growth Monitors Using Remote Optical Probes" (K. P. Killeen, S. A. Chalmers, W. G. Breiland, and T. M. Kerley)
- 1993 Sustained Outstanding Research--Metallurgy and Ceramics "Strained Layer Superlattices and Artificially Structured Semiconductors" (P. Gourley, I. Fritz, E. Jones, K. Lyo, J. Nelson,
 - R. Schneider, G. Osbourn, B. Biefeld, and R. Dawson)
 - Significant Implication for Department of Energy Related Technologies--Metallurgy and Ceramics "Interfacial Force Microscope" (J. Houston and T. Michalske)

- 1992 Sustained Outstanding Research--Materials Chemistry "CVD Sciences" (W. G. Brieland, M. E. Coltrin G. H. Evans, P. Ho, and R. Kee)
- 1991 Sustained Outstanding Research--Metallurgy and Ceramics "Advanced Ion Beam Techniques for Materials Analysis" (B. L. Doyle, S. T. Picraux, J. A. Knapp, and S. M. Myers)
 - Outstanding Scientific Accomplishment--Solid State Physics "Surface Diffusion by Atomic Substitution" (G. L. Kellogg and P. J. Feibelman)
 - Significant Implication for Department of Energy Related Technologies--Metallurgy and Ceramics "Exceptionally High-Strength Aluminum Alloys" (D. M. Follstaedt, R. J. Bourcier, M. T. Dugger, and S. M. Myers)
- 1990 Sustained Outstanding Research--Metallurgy and Ceramics "Model of Hydrogen-Defect Interactions in SiO₂ and at the SiO₂-Si Interface" (K. L. Brower, S. M. Myers, P. M. Richards, and H. J. Stein)
- 1989 Significant Implication for Department of Energy Related Technologies--Solid State Physics "Development of Tl-Ca-Ba-Cu-O High Temperature Superconducting Thin Films and Demonstration of Novel High-Performance Devices" (R. J. Baughman, D. S. Ginley, J. F. Kwak, B. Morosin, and E. L. Venturini)
- 1988 Significant Implication for Department of Energy Related Technologies--Solid State Physics "Boron Carbides: Novel Refractory Materials as Very High Temperature Semiconductors" (D. Emin, T. L. Aselage, G. A. Samara, B. Morosin, D. R. Tallant, E. L. Venturini, A. N. Campbell, C. Wood (JPL), and C. Beckel (UNM))
- 1987 Significant Implication for Department of Energy Related Technologies--Materials Chemistry "Laser-Initiated Chemical Etching and Deposition for Applications to Microelectronic Circuits Processing" (K. E. Greenberg and A. W. Johnson)
- 1986 Outstanding Scientific Accomplishment--Metallurgy and Ceramics "Icosahedral Surface Alloys—Formation and Properties" (D. M. Follstaedt and J. A. Knapp)
 - Significant Implication for Department of Energy Related Technologies--Materials Chemistry "Selective Photochemical Etching of Semiconductors Using Surface Electronic Properties" (C. I. H. Ashby)

Other Awards

- 1997 R&D Award for "Development of a Biological Microcavity Laser" (P. L. Gourley)
 R&D Award for "Bringing to the market one of the top 100 technologically significant new products of 1997" (W. G. Breiland)
- 1995 Norbert J. Kreidl Award from the New Mexico Ceramics Society Glass Division (K. S. Simmons-Potter)
- 1994 R&D 100 Award for "Interfacial Force Microscope" (J. E. Houston and T. A. Michalske)
- 1993/94- J. J. Thomson Award for "Temporal and Spectral Gain Dynamics in an Actively Modelocked Semiconductor Laser" (W. W. Chow)
- 1987 R&D 100 Award for "External Micro-Ion Beam Analysis System" (B. Doyle and N. Wing)
- 1986 R&D 100 Award for "Carbon-Resistance Particle Analyzer" (B. Wampler)

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