Broad Content Spurs New Collaborations at the 1992 MRS Spring Meeting

Attention at the 1992 MRS Spring Meeting focused on the interdisciplinary scientific content offered by 2,400 oral and poster presentations in 26 symposia. From cleaning semiconductors and synthesizing new materials to recycling paper, modeling fracture, and protecting national monuments from the destruction of war, the technical content ran particularly broad. Chaired by June Passaretti (Pfizer, Inc.), Lynn Rehn (Argonne National Laboratory), and Dale Schaefer (Sandia National Laboratories), the meeting ran from April 27 to May 1 and drew more than 2,600 attendees. In addition to the daytime sessions, four evening poster sessions buzzed with activity as researchers shared their research results and established collaborations across disciplinary lines. Short courses on topics related to the symposia and a packed equipment exhibit complemented the meeting.

An overflow audience attended a late news session on light emission from porous silicon. The session was triggered by experimental results ascribing the light emission to siloxene, a compound known since the 1860s for its extraordinary luminescence, rather than to quantum confinement arising from the silicon nanocolumns. Light also touched off interesting effects in holographic materials, photorefractive polymers, bandgap engineered structures, and even "smart pixels," which optimize the use of electronics and optics. Among other "smart" designs, silicon performed the unusual task of supporting the regeneration of nerves through micromachined holes, whose signals were read through on- board electrical sensors. This approach holds promise for developing advanced prostheses for amputees.

Rumors of superconductivity at 180 K faded after interesting but less dramatic results showed the excitement stemmed from weak magnetic and resistive anomalies around 180 K found in some atomically layered $Ca_{1-x}Sr_xCuO_2$ thin films.

Fullerenes joined the standard program in a symposium covering diamond, graphite, carbonaceous fibers, foams, and other novel forms of carbon. Fullerene research centered on endohedral fullerenes (which enclose metal atoms), which are expected to exhibit novel electronic and chemical properties. Fullerene crystals might even be useful in separating, storing and/or purifying gasses.

Synthesis and processing methods were considered throughout the meeting. Semiconductor processing was studied from surface treatment through metallization, ion beam processing, defect engineering, packaging, and reliability. New chemical strategies for synthesizing ceramics and nonsilicate materials emerged that rely on novel precursors and new methods. Microwave processing, offering reduced time and lower cost, surfaced as a potentially viable treatment for ceramics, polymers, and even for hazardous waste.

Plenary Address. Bassam Z. Shakhashiri, professor of chemistry at the University of Wisconsin-Madison spoke about science education in the United States, and the role scientists can play in the twin mission of maintaining the flow of talent into careers in science, technology, and mathematics and improving the science and technology literacy of all people. See the July *MRS Bulletin* for Shakhashiri's full address.

Materials Initiative Forum. A special session was held to inform the materials community about the role of various government agencies in the Bush administration's Advanced Materials and Processing Program proposed for FY 1993. The speakers were Karl Erb (OSTP), Iran Thomas (DOE), Samuel L. Venneri (NASA), Jagdish Narayan (NSF), and Lyle H. Schwartz (NIST). See the July *MRS Bulletin* for a full report.

Technical Sessions. For highlights of the symposia, read the summaries that follow. More detailed information is available in the published proceedings (listed elsewhere in this issue).

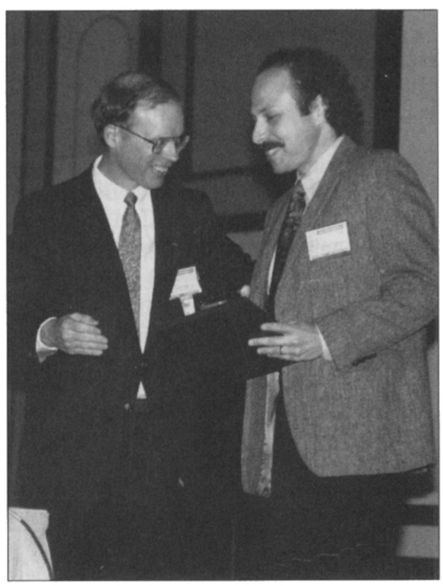
Amorphous Silicon Technology Improves for Solar Cells, Sensors
(See MRS Proceedings Vol. 258)

Amorphous Silicon Technology, Symposium A, continued to attract a large number of abstracts and attendees, keeping in step with ever expanding applications of this versatile semiconductor. Fundamental researchers and technologists joined forces to sort out materials issues that influence the behavior of solar cells, thin film transistors for flat panel displays, imaging and nuclear particle detectors, and other devices.

Hybrid solar cells overcame a 20% conversion efficiency threshold. The structures required the use of either polycrystalline or single crystalline Si as an integral part of the solar cell. The efficiency enhancement, using the amorphous Si layers, resulted in an absolute increase of 2%. Therefore, it was not entirely evident that significant benefit from an economic standpoint would accrue.

The mechanism of light-induced effects remains elusive. With many excellent contributions devoted to this important subject, various models and interpretations were presented and hotly debated, but a definitive model did not emerge.

Significant advances were reported in the image sensing area, such as high-resolution sensors (400 dpi) and three-color sensing, using thin film transistors, by a group from Xerox. In contrast, a group from Philips re-



David D. Awschalom (right), UC-Santa Barbara, accepts the MRS Outstanding Young Investigator award from MRS President Slade Cargill. Awschalom presented his work, "Spin Dynamics and Tunneling in Quantum Magnetic Systems," during Symposium X.

ported on impressive sensors fabricated using p-i-n junctions. The Xerox group also reported on a 2-D imaging array for x-rays.

Numerous papers were devoted to understanding growth kinetics during semiconductor film fabrication as it pertains to the ultimate electronic performance of devices. B. Drévillon of Ecole Polytechnique gave a comprehensive overview of the first 10 Å of a-Si:H growth using ellipsometric techniques while A. Shah of the Univ. of Neuchâtel reviewed high deposition rates (20 Å/s) using very-high-frequency plasma deposition (up to 100 MHz) and the resulting optoelectronic properties; these high-deposition techniques are directly relevant to the fabrication of thick (>40 μm) nuclear particle detectors and in the mass production of solar cells. Some research provided for lower saturated light-induced defects by manipulating the growth conditions. Novel preparation techniques were presented in a quest to produce a more stable material or a material with lower density of inherent defect states.

Extensive discussions centered on transport mechanisms in relation to defects, long-range potential fluctuations, measurement and interpretation of minority carrier diffusion length, modeling of conductivity, and photoconductivity phenomena.

Scientists and Technologists Work Together to Improve Surface Preparation

(See MRS Proceedings Vol. 259)

Surface cleaning and conditioning as used in semiconductor processing drew the attention of an international audience of 150–200 people in Symposium B, Chemical Surface Preparation, Passivation and Cleaning for Semiconductor Growth and Processing. Both scientists and technologists participated to understand and improve surface preparation. Since surface cleaning needs to be designed for a specific process, the program was organized by the process and its relationship to surface cleaning or conditioning prior to the process.

In the opening session on issues and applications, M. Liehr (IBM) and M. Morita (Tohoku Univ.) emphasized the continuing importance of wet-cleaning processes and the specificity of precleaning to the process that follows, e.g., for epitaxial growth versus oxidation. The consensus of the discussion was that wet chemical cleaning will continue to be important, but there are great interest and potential advantage in both vapor- and plasma-based dry-cleaning techniques. Given the unique ability of wet cleaning to removal particles, dry cleaning may find its role in one of several *in-situ* steps that follow wet cleaning.

Several presentations on CVD and oxidation demonstrated that oxide passivation is appropriate and effective prior to insulator deposition or growth. This is a consequence of the high thermal and chemical stability of the oxide passivation layer, which can become the first stage of insulator growth.

For epitaxial growth, the beneficial effects of hydrogen passivation from the preclean were well documented. Hydrogen- terminated Si surfaces were achieved by plasma processes, UV-enhanced processes, vapor processes, and wet chemical processes. Several reported on the effectiveness with which these processes prevented surface degradation in an air ambient and their correlation with epitaxial quality.

The session on UV- and plasma-enhanced cleaning included approaches to metal removal and other challenges in surface cleaning. Much attention was also directed to HF cleaning, this topic being the basis of an entire session and considerable portions of other sessions. Significant details of surface bonding after HF cleaning were investigated both experimentally and theoretically. Major issues surround the differences in behavior between Si(100) and Si(111) surfaces and the important role of surface roughening by surface cleaning processes. Several papers explained new diagnostic approaches for relevant characterization questions, including *in-situ* TEM, x-ray reflectivity, optical surface diagnostics, STM, and trace analysis.

The session on compound semiconductors addressed corresponding issues involving wet and plasma surface cleaning treatments to effect surface passivation on materials such as InP, GaAs, and II-VI alloys. Chalcogenide sulfur provides stable passivation in several cases.

The consequences of plasma etching, including damage and contamination, were highlighted in an invited talk by S. Fonash (Pennsylvania State Univ.). These issues arose in subsequent discussion as an area needing comprehensive coverage. Very little research affecting the problem of surface cleaning for patterned wafers was presented, though this remains the ubiquitous challenge in microelectronics technology.

Semiconductor Processing Meets Many Challenges

(See MRS Proceedings Vol. 260)

More than 180 papers were presented during Symposium C, Advanced Metallizations and Processing for Semiconductor Devices and Circuits II, by representatives of more than 15 countries and attendance exceeding 400 at its peak. This symposium focused entirely on materials and processing issues of metallizations in conjunction with microelectronics applications.

Interconnect challenges have changed since the first transistor was developed by J. Bardeen in 1948, which used eighteen-gauge wire and paper clips. M.A. Fury (IBM) described some of the challenges encountered, as feature sizes have shrunk by five orders of magnitude and device speeds have increased by nine orders of magnitude. Trends include shifts from wet to dry etching, development of new methods of planarization and alternatives, and material substitutions such as aluminum for bulk copper which may shift again to copper. In addition to materials challenges, progress may come from fundamental design changes, increased sophistication of modeling mechanical and thermal properties, and attention to manufacturing. This symposium provided a forum to discuss the recent advanced processes associated with the metallization of diamond, ceramics, Si, InP, GaAs and other compound-semiconductor thin films for applications in electronic, optonic and optoelectronic devices and ICs, as well as the fundamental materials science, interfacial phenomena, and transport mechanisms

Common Principles Drawn from Electrooptic, Photorefractive, and Photoconductor Research

(See MRS Proceedings Vol. 261)

The interaction of light with matter is one of the most exciting and rapidly growing areas of research today. The intense interest in optoelectronics and photonics is driven by the promise of optical technology. Fiberoptic telephone transmission and laser compact disks are just two examples of how optical materials and technologies have dramatically altered our lives in recent years. Just as silicon played the revolutionary role in electronics, other semiconductors are playing the same role in optoelectronics.

Symposium D on Photo-Induced Space-Charge Effects in Semiconductors: Photoconductivity, Spectroscopy and Electro-optics was established as an interdisciplinary forum to foster lines of communications among three separate research communities: (1) the electrooptic community, (2) the photorefractive community, and (3) the photoconductor community. Common physical principles operate in each of these fields. In particular, the generation of microscopic electric fields inside semiconductor materials caused by illumination with light plays a key role.

Researchers from AT&T, IBM, Rockwell, and Hughes provided overviews of their respective fields. A. Glass and D.A.B. Miller, both from AT&T, gave introductory talks on recent advances in electrooptic devices and holographic materials. One exciting new aspect of optical devices is called "smart pixels." Miller described devices that were combinations of electronics and optics, using the best of each quality. Optics wins out for longer range connections, while electronics wins out in the short ranges. This tradeoff naturally leads to devices with significant electronic processing within each pixel; hence the term "smart pixels."

In the new optical materials, interfaces play important roles. For quantum-well and other multilayer structures, the optical and electronic properties of the interface may dominate device performance. Many contributed papers covered the spectroscopy and analysis of semiconductor interfaces, including interfaces in silicon.

Photoconductivity is the root of much of the optical technology in semiconductors. The generation of charge carriers by light is the first of many steps in the operation of photorefractive and electrooptic devices, as well as photodetectors. Novel applications that rely on photoconductivity were described by M.G. Stapelbroek of Rockwell and by A. Kost of Hughes. The bandgap of silicon can be engineered by selective doping, producing interesting new responses to light. Carrying bandgap engineering to the other extreme, multilayer n-i-p-i structures with alternating doping levels and quantum wells provide photoconductive electrooptic devices with high sensitivity for nonlinear optics and optical control.

As with all semiconductor materials and devices, defects are ubiquitous and can play esential roles—detrimental or useful—in the performance of devices and materials. S. Ralph of IBM and M. Klein of Hughes highlighted the roles that defects can play. In the photorefractive effect, for instance, defects are the sites where photo-induced space-charge is trapped, providing the mechanism for light interaction in the crystal.

Closing the symposium was a session on optical materials and applications. The key speakers were D. Chemla of Lawrence Berkeley Laboratory, L. Chirovsky of AT&T, and M. Yamanishi of Hiroshima Univ. in Japan. Quantum-well structures in semiconductors present one of the most attractive materials systems for optical applications. The flexibility in the design and integration of the devices and materials allows for almost endless combinations that can be best engineered for the desired properties.

Federal agency leaders answer questions in a special session on the Advanced Materials and Processing Program proposed by President Bush for FY 1993. Pictured from left to right are panelists Karl Erb (OSTP), Iran Thomas (DOE), Samuel L. Venneri (NASA), Jagdish Narayan (NSF), and Lyle H. Schwartz (NIST), and MRS First Vice President Tom Picraux. (See the July MRS Bulletin for a full report.)

Going Beyond Defect Control in Semiconductors

(See MRS Proceedings Vol. 262)

Symposium E on Defect Engineering in Semiconductor Growth, Processing and Device Technology — the first of its kind at an MRS meeting—brought together academic and industrial researchers with a variety of perspectives on defects in semiconductors. While defect engineering plays a role in techniques such as impurity/defect gettering and the use of the EL2 level in GaAs, more extensive as well as subtle uses of defects are emerging. This symposium was intended principally to encourage creative applications of defects in all aspects of semiconductor technology. It appears to have struck a chord in the semiconductor community, with five days of well-attended sessions.

Talks on defects in bulk crystals and epitaxial films provided a thorough review of intrinsic point defects and oxygen-related lattice defects in Si, and also addressed the role of impurities in reducing grown-in defects in compound semiconductors. An example of defect-assisted growth of single crystals was described for ZnSe, an important II-VI material in optoelectronics. A presentation on GaAs MBE growth at higher than usual temperatures showed that resistivities $>10^6$ ohm-cm could be achieved in a manner analogous to low-temperature GaAs, which has attracted recent attention due to its highly defect-controlled properties. J.M. Woodall (IBM) introduced an interesting theory on the crucial role of surface Fermi level position during growth in establishing bulk crystal properties (surface Fermi level engineering).

A session devoted to defect characterization addressed using TEM and EDX for solving defect issues, and also newer, often non-destructive techniques that help map defects in both bulk semiconductors and finished integrated circuit wafers. One interesting presentation explored the analysis of individual defects and their mutual interaction spectroscopically via the quenched infrared-beam-induced current technique that has 1 μm spatial resolution. Other papers reported on the use of positron annihilation spectroscopy for defect identification and characterization in a variety of semiconductors.

An exciting session was devoted to atomic hydrogen interaction with semiconductors. The realm of hydrogen in crystalline semiconductors has evolved rapidly in recent years, with a plethora of phenomena concurrent with a deeper understanding of the interaction of hydrogen with defects. Papers following two excellent reviews demonstrated the role of H in dopant/defect activation/passivation and complex formation, and also enhanced diffusion and stability of hydrogenation processes. The universality of some H-passivation phenomena as well as their relative stability seem to augur well for potential device/processing applications, particularly in compound semiconductors.

A special evening session marked by an overflow audience addressed the yet-unresolved mechanism of light emission from porous Si. M.S. Brandt (Max-Planck-Institute für Festkörperforschung), set the stage for the controversy by showing a wide range of experimental results that ascribe the light emission to siloxene ($Si_6O_3H_6$, a six-Si atom ring molecule with three OH and three H ligands) — a compound known since the 1860s for its extraordinary luminescence—rather than to quantum confinement arising from the Si nanocolumns. While the ensuing debate did not resolve the issue, it certainly roused new ideas for theory and experimentation in this scientifically and commercially significant research area.

The session on gettering phenomena in semiconductors had papers describing broad classification schemes such as internal/external or bulk/surface, and reactions on the microscopic scale. Gettering kinetics and stability issues were also addressed. Another session covered defects and contamination induced by processing.

The nature and influence of defects in devices and their passivation was addressed in a separate session. Papers covered fluorine incorporation for Si/SiO_2 interface passivation, high-energy ion implantation for device isolation in mixed binary III-V semiconductors, and the influence of dislocations in strained-layer p-n diodes. A very interesting paper outlined the effects of metal contamination as detected sensitively by CCD imagers. An invited paper provided a broad review of the possibilities of using defects for applications in III-V materials.

Quantum wells, superlattices, and interfaces were considered in a session, where issues such as disordering effects promoted by vacancies and impurities were addressed along with passivation of defects in quantum wells. Three reviews in the session on gettering and related phenomena dealt with transition-element gettering, CZ Si defect control, and gettering stability at oxide particles in Si. A novel technique for gettering uses a porous Si back surface to minimize oxidation-induced stacking fault defects.

The final session on ion implantation, dry processing, and radiation effects contained an excellent review of defects produced by plasma processing of Si. The following papers covered ion bombardment damage and its assessment. Among the novel defect engineering ideas shown were the use of ion implantation for improving thin oxide integrity, hydrogen passivation of ion implant damage at Si/SiO_2 interfaces, and the use of a PH_3 plasma to suppress trap formation in InP.

Characterization of Surface Structure Reveals Mechanisms of Heteroepitaxial Growth

(See MRS Proceedings Vol. 263)

The study of surface structure and its effect on nucleation was a recurring theme in Symposium F on Mechanisms of Heteroepitaxial Growth. An impressive array of surface characterization techniques have been developed and were strongly featured among the 70 oral and 70 poster presentations. E.D. Williams (Univ. of Maryland), opened the symposium with an excellent description of step interaction processes on Si(111). This study used STM, and low-energy electron diffraction and imaging. Subsequent invited presentations by Y.W. Mo (IBM) and J.A. Venables (Arizona State Univ.) focused on the earliest stages of nucleation on Si surfaces using STM and *in-situ* growth in the electron microscope. Other new approaches to the study of surface-related processes were described by D.E. Jesson (ORNL), who used a novel high-resolution electron microscope imaging technique, and D. Kisker (IBM), who used *in-situ* growth analysis by x-ray synchrotron techniques.

An exciting array of novel synthesis and interface characterization techniques were described. R.W. Fathauer (Jet Propulsion Laboratory) and S. Mader (IBM) showed new techniques and geometries for producing metal silicide-silicon heterostructures. Improved prospects for GaAs epitaxy on Si were described by R. Bringans (Xerox), who used ZnSe interlayers, and R. Matyi (Univ. of Wisconsin-Madison), who described successful growth of Si/GaAs superlattices. An ingenious electron microscope technique for measuring interface structure in cobalt disilicide-silicon heterostructures using reflections forbidden in the bulk lattice was presented by A. Daykin (Univ. of Illinois-Urbana). X-ray crystal truncation rod analysis was used by D. Loretto (Lawrence Berkeley Laboratory) and co-workers for the study of calcium fluoride-silicon interfaces. W.M. Tong (UCLA) applied atomic force microscopy to the structure of metal-insulator interfaces. C. Volkert (AT&T) studied strain relaxation dynamics using laser reflectance measurements of wafer curvature.

The last day of the symposium was devoted to strain relief mechanisms in lattice-mismatched heteroepitaxy. D.A. Smith (IBM) described an elegant theoretical framework for these processes. F. LeGoues (IBM) and D. Perovic (Univ. of Cambridge) addressed the controversial question of misfit dislocation nucleation. C.W. Snyder (Univ. of Michigan) discussed the interplay between strain, dislocation nucleation, and surface morphology during growth, and D. Gerthsen (Research Center Jülich) detailed investigations of dislocation introduction into islands. S. Dregia (Ohio State Univ.) described strain relief mechanisms at very large mismatch, and C. Maissen (Swiss Federal Institute of Technology) described strain relaxation processes below room temperature in lead selenide. D. Malta (Research Triangle Institute) proposed an interfacial melting process in growth of Ge/Si heterostructures at high temperatures.

Materials Processing and Manufacturing Affect Electronic Packaging Technology

(See MRS Proceedings Vol. 264)

Symposium G on Electronic Packaging Materials Science VI continued the MRS symposium series started in 1984. This symposium focused primarily on two key areas of current technology where materials and processing issues play an important role: (1) polymers for multichip module packaging and (2) materials and devices for optical interconnects. Additionally, a special one-day session was devoted to low-end packaging where the system and technology issues are driven by cost and manufacturing issues.

The program included 75 papers. Keynote presentations surveyed technology trends and materials and processing issues, bringing into focus the interdependency of materials science and technology development for electronic packaging. This relationship was exemplified for the multichip module session by C.W. Ho of Digital Equipment Corp. and R.C. Sundahl of Intel. Ho and Sundahl, both in charge of packaging development of multichip modules, presented overviews on the status of low-power applications and desktop computers. The program on multichip modules moved into three areas: polymeric materials development, thermal and mechanical properties, and stress/adhesion and reliability.

The program on low-end packaging began with one talk by R. Pollak of IBM on technology trends and materials issues and another by V. Brown of Motorola on a new family of grid array packages. Also, M. Ishikawa of Sony Corp. described the development of consumer products, and then J.H. Lau of Hewlett Packard focused on solder joint reliability for fine-pitch surface-mount packaging.

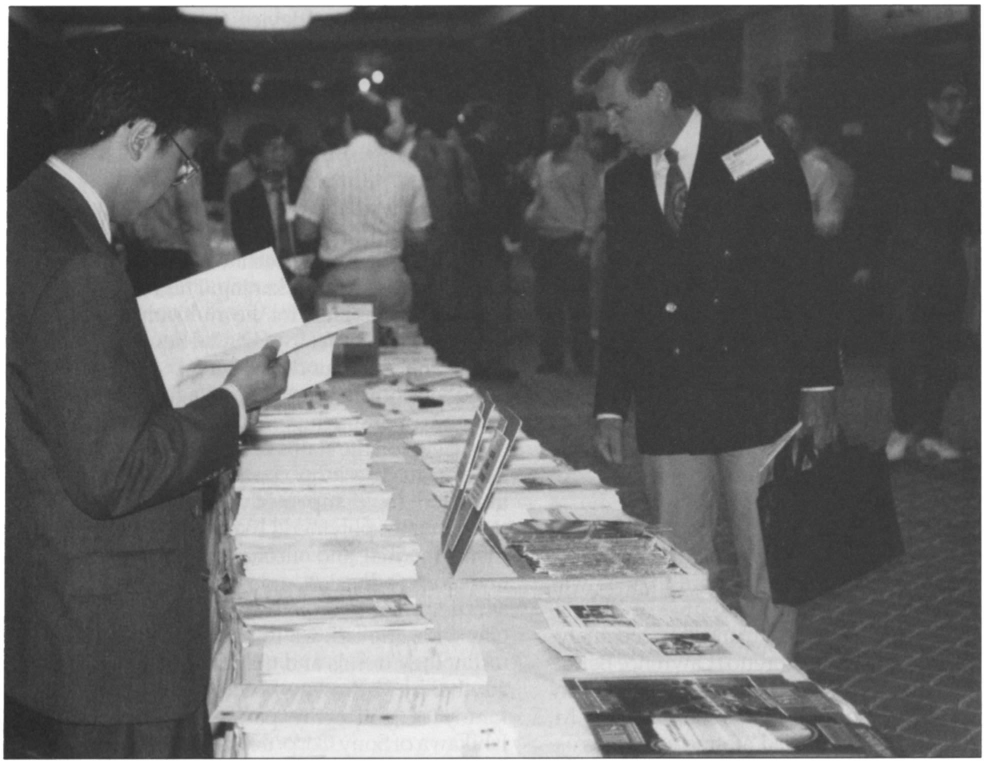
The program on optical interconnects started with four invited talks addressing the status of and materials issues for polymer applications to optical interconnects. On current technology, R.A. Nordin of AT&T gave the system designer's perspective on optical interconnects, followed by two reviews on optical interconnect and interfaces for system applications and two-mode bistability of semiconductor lasers and optical switching. The materials issues for technology was addressed by R.C. Lasky of IBM on single-mode optical fiber coupling loss and by J. McGroarty of Cornell Univ. on the alignment of electrooptical components. The program was completed with two papers by H. Fujimoto of Intel and J. Kenney of ROITech on materials and design for manufacturing of optical interconnects.

Current research activities reported in materials and processing for electronic packaging revealed some exciting results, particularly in the development of new polymeric materials for multichip modules and the understanding of molecular structures and chemical/physical properties of polyimide thin films and multilayered structures.

Reliability Takes Center Stage

(See MRS Proceedings Vol. 265)

Symposium H, Materials Reliability in Microelectronics II, drew overflow crowds, even after moving to a larger room. H.J. Frost



Meeting attendees gather materials science literature on equipment, services, publications, and meetings.

of Dartmouth gave an overview of mechanisms of mechanical creep in bulk materials, and how these mechanisms might change in thin films. Following talks considered stress-induced voiding of metal interconnects, electromigration-induced failures, and combinations of the two. A picture emerged of electromigration as a current-assisted creep phenomenon. Two new techniques for viewing voids in passivated interconnects were introduced — high-voltage scanning electron microscopy by P.A. Flinn and M.C. Madden of Intel, and environmental scanning electron microscopy by D.A. Smith of IBM.

A joint session with Symposium C, Advanced Metallizations and Processing for Semiconductor Devices and Circuits, focused on electromigration modeling and characterization. J.R. Lloyd of DEC gave a critical assessment of rapid testing techniques. Another session focused on the reliability of silicon dioxide and other dielectric films in microelectronics.

Recycling Wood-Based Waste Leads to Paper and Composites Development
(See MRS Proceedings Vol. 266)

One of the challenges confronting materials scientists, including wood scientists, is understanding the relationship between structure and properties at various scales. When we enter the arena of recycled wood materials, the problem becomes perhaps more acute, as we face a bewildering array of material sources, forms, and envisioned uses.

In order to establish categories for the utilization of recycled fiber and wood, it is useful, if not imperative, to consider their morphological features. Such consideration may be made at both the micro and macro scales for major classes of secondary wood and wood fiber. Paper and paperboard command attention as they represent the single largest stream of materials in municipal solid waste, accounting for approximately 40% by weight. Used pallets and demolition waste also present disposal problems of increasing significance. Forest and mill residues represent yet another major category.

Beginning with the fundamental structure of the materials comprising these diverse secondary resources, the objective of Symposium Ia on Materials Interactions Relevant to Recycling of Wood-Based Materials was to provide an overview of wood and fiber properties and processes relevant to waste utilization.

The quantities of industrial and municipal solid waste materials being landfilled urgently need to be reduced. Major components of municipal solid waste include waste wood, paper, agricultural wastes, and other biomass fibers. In 1986, approximately 65 million tons of 6,000 paper and paperboard products and 5.8 million tons of wood entered the municipal solid waste stream. These materials offer great opportunities as recycled ingredients in paper and wood-based composites. This symposium focused on research and development needs for maximizing the benefits of using recovered waste materials for composite products and paper.

There are several clear trends in the recycling of paper: (1) the amount of recycled paper is increasing and will continue to do so, (2) recycled fiber is being used in greater quantities, and (3) recycled fiber is being introduced into higher quality grades that previously had no recycle content.

One problem is that the quality of the recycled material seems to be deteriorating in terms of contaminant level and strength, while expectations for better properties of the end product, the recycled fiber, are increasing.

Researchers reviewed the major unit operations of recycling and general principles of papermaking system design. Properties of recycled fiber, methods for enhancing these properties, and achievable limits were also discussed.

Some of the broad topics discussed in the session on paper-to-paper included:

- New technologies for dispersing and removing inks, adhesive contaminants, and other foreign materials;
- Optimizing the properties of fillers to improve filled or coated paper recyclability;
- Measuring and controlling the bulk fiber and chemical transformations in cellulose due to recycling and papermaking; and
- Providing new enzymatic and bleaching technologies for "up-cycling" pulp fibers.

Though the recycling of paper products is not new to the paper industry, the upsurge in recycling interest has provided incentive to understand the chemical transformations taking place in traditional pulping, bleaching, and papermaking processes.

An entirely new class of materials was discussed in a second session on fiber-to-composites. This session highlighted material processing and properties development in the following areas:

- Wastepaper and wood particles as reinforcement of cementitious, gypsum, and fly ash composite materials;
- Alloyed properties of lignocellulosic materials and nonpolar polymers;
- Surface treatments and graft copolymers to improve interfacial adhesion between biomass fibers and hydrophobic polymers; and
- Properties of traditional fiber-based products, such as hard board, when made with recycled wastepaper.

Catalysts, Membranes, Alloys Developed for Energy Technology

A new symposium, Materials for Energy Technologies (Symposium Ib), focused on the design, synthesis, and characterization of enabling materials for the development of new energy sources and energy-conversion processes. Topics included catalysts and membrane materials designed for selective chemical conversions, novel porous electrode and separator materials for lightweight high-energy-density electrical power sources (batteries, fuel cells, capacitors), and crack-resistant alloys and composites that enable high-temperature/high-pressure energy-conversion processes.

J. Shelnutt and co-authors at Sandia and UC-Davis presented work concerning the design, synthesis, and characterization of novel substituted metalloporphyrin catalysts for the conversion of natural gas and carbon dioxide to alcohol fuels. They described success in incorporating a rigid binding site, similar to those found in enzyme catalysts, into molecular catalysts, which bind small gaseous molecules such as carbon dioxide and methane. Other presentations focused on the design, synthesis, and applications of unsupported nanometer-sized catalyst particles. Using inverse micelle synthesis, J. Wilcoxon and co-authors at Sandia National Labaoratory (SNL) and the Univ. of New Mexico described the preparation and characterization of a wide range of nanometer-sized catalyst formulations such as metals, metal oxides, metal sulfides and metal/metal alloys with narrow particle size distributions. J. Linehan and co-authors at Pacific Northwest Laboratory described the preparation and applications of nanometer-sized oxide and sulfide catalysts using reverse micelle synthesis and a new process, rapid thermal decomposition in solution (RTDS). The synthesis of nanocrystalline iron carbides using laser pyrolysis was described by A. Sethuraman and co-authors at the Univ. of Kentucky. M. Hampden-Smith and co-authors at the Univ. of New Mexico and Sandia National Laboratories presented exciting results on the synthesis of nanometer-sized molybdenum carbide and rhodium catalysts.

C. Liu and co-workers at Martin Marietta Energy Systems, Oak Ridge National Laboratories, reviewed the development of intermetallic materials for high-temperature applications. J. Kinney and co-workers at Lawrence Livermore National Laboratory and SNL showed work on the development of nondestructive evaluation of composite materials using x-ray tomographic imaging. Using x-ray tomography, the densification of chemical-vapor-infiltrated composites of Nicalon fibers reinforced with silicon carbide can be monitored in three dimensions. Also in this session, M. Allendorf and co-authors at SNL presented results on the theory, modeling, and determination of thermodynamic parameters important to CVD processes for composite fabrication and synthesis of refractory materials.

In the session on materials for fuel cells and fuel storage, T. Richardson and co-authors from Lawrence Berkeley Laboratory described the sol-gel synthesis and characterization of thin film solid oxide electrodes for fuel cells. S. Adler and J. Reimer from UC-Berkeley described the use of high-temperature NMR to characterize novel oxides and perovskite materials, and Y. Zhang and co-workers at Nankai Univ. reported on novel rare-earth materials for electrochemical and hydrogen storage applications.

Membrane catalysis, reactors sensors and separators were covered in a joint session with Symposium Ic, Materials for Separation Technology. Highlights from this session included a paper by Y. Ma and co-authors from Worcester Polytechnic Institute on inorganic membrane reactors and a paper by S. Morissette and co-authors from Argonne National Laboratory and Amoco Oil Co. describing chemical preparation and fabrication of perovskite membranes for partial oxidation reactions.

From Corrosion to War, Artifacts Need Protection

(See MRS Proceedings Vol. 267)

Both conservation and destruction were covered in Symposium J, Materials Issues in Art and Archaeology III. Topics ranged from the development of a reactive polymer that can protect artifacts from corrosion to the destruction of monuments in Iraq, Croatia, and regions involved in armed conflicts.

J.P. Franey, AT&T, described a polymeric system recently developed, patented, and licensed for sale that provides atmospheric trace gas corrosion protection. These reactive polymers consist of a blend of polymer resin (e.g., polyethylene, polypropylene, Acrilonitrile-Butadine-Styrene, PVC) with stable solid-state additives. They can be formed into bags, tubing, sheets, bubble-packs, trays, etc. and can provide corrosion protection for materials such as silver and copper that are susceptible to sulfur and chlorine gases.

The polyethylene bags are also colorimetric self-indicating when the pollutant scavenging is exhausted.

The session on cultural heritage in conflict discussed the 1954 Hague Conventions adopted to protect cultural property in the event of armed conflict. The measures taken by both the British Museum and the National Gallery in London to protect their national treasures during both World Wars were presented. The material losses of the Aleuts were discussed as was the aftermath of the Persian Gulf War. Two papers from Croatia dramatically depicted the destruction of properties during the recent conflicts there. Two theoretical papers covered the entropy of catastrophe and engineering lessons learned from natural disaster planning.

A session on treatment, deterioration, and structure in architectural materials contained papers on the hydric properties of some Spanish stones (L. Valdeón, Univ. de Oviedo), epoxy resins as stone consolidants (C. Selwitz, Getty Conservation Institute), the influence of minerals on the polymerization of alkoxysilanes (G.S. Wheeler, Metropolitan Museum of Art), silicone resins dispersed in water for stone protection (G. Biscontin, Universitá di Venezia), and chronological sequencing of Theotihuacan plasters (D. Magaloni, UNAM). E.P. Giannelis (Cornell Univ.) showed how polymer-ceramic nanocomposites can be assembled to provide barrier and specialized structures capable of diverse applications in conservation.

In the session on techniques for technical analysis: structure and composition, M. Notis presented work on digital wavelength dispersive spectrometry x-ray mapping and N. Tennent showed some new discoveries on nitrate stoichiometry in acetate/formate corrosion products on lead alloys. W.S. Taft and J.W. Mayer described a course at Cornell Univ. that takes on the highly unlikely task of jointly teaching art to science majors and scientific analytical methods to art majors. This course is very popular and draws about 150 undergraduates.

The third session addressed the behavior of materials used by artists. M. Mechlenburg, Smithsonian Institution, gave a clear, precise, and thought-provoking talk about applying mechanics to contemporary painting materials. Both his and G. Berger's previous work showed that oil films are highly responsive to both relative humidity and temperature fluctuations. New data show that acrylic polymer paints, favored by many contemporary artists, and today, matching oil paints as the medium of choice, are equally vulnerable, as are alkyds. This work has profound ramifications in storage and shipping. For example, the temperature in the cargo bay of a commercial jet airliner gets cold enough to subject contemporary art to huge stress factors, potentially large enough to do visible damage.

D. van der Reyden and T. Vitale of the Conservation Analytical Laboratory of the Smithsonian Institution gave their findings on modern transparent and coated papers and their conservation implications, the effects of water on the mechanical properties of paper, and the effects of drying on the mechanical properties of paper. V. Daniel, the

Getty Conservation Institute, talked about the moisture-buffering capabilities of museum cases and C.M. Guttman, NIST, about the protection of archival materials from the diffusion of sulfur dioxide through boxboard. S. Schiegl from the Univ. of Heidelberg elucidated the deterioration mechanism of ancient Egyptian pigments. Also presented were papers on the casting of an enormous bronze bell from casting remains discovered in a church in southern Italy, and a comparison to the eleventh century text of Theophilus as interpreted by C.S. Smith. A holistic approach to the analysis of archaeological deposits was given by O.S. Farrington, Birkbeck College, and reconstructing metallurgical processes at an Iron Age and Roman trading post by J.P. Northover, Univ. of Oxford. M.B. McNeil, Nuclear Regulatory Commission, described sulfate formation during corrosion of copper alloy objects.

H. Römich and J. Leissner, Fraunhofer-Institut, discussed stained-glass glazing and cleaning techniques. Particularly interesting was the use of the Fraunhofer-Institut's glass sensors to assess glazing without ventilation, and with exterior, interior, and interior/exterior ventilations. At least one cathedral showed evidence of internal sources of glass corrosion.

Energetic Beams Find Many Uses

(See MRS Proceedings, Vol. 268)

Energetic atoms and ions are used in a wide range of materials processing applications. Symposium K, Materials Modification by Energetic Atoms and Ions, provided a forum for discussing recent research on energetic particle effects in sessions covering thin film deposition, heteroepitaxy, reactive ion etching, ion implantation, and ion beam modification of surfaces.

The session on reactive ion etching featured work on expanding the range of materials that can be dry etched, understanding Si ion-induced etching processes, and limiting ion damage in etching of III-V semiconductors. Fundamental studies of complex chemistries for Si etching carried out using neutral and ion beams in UHV were described by J. Coburn (IBM Almaden). The use of new etch chemistries and ECR ion sources for III-V etching were also described.

The sessions on thin film deposition covered metals, oxides, nitrides, carbides, and semiconductors. Molecular dynamic simulations of very-low-energy (1–40 eV) ion impingement, graphically depicted on videotape, showed the basic processes induced by ion impact on metal (J.A. Sprague, NRL) and Si (M. Kitabatake, Matsushita). From an experimental point of view, ion-beam-assisted deposition, sputter deposition, and pulsed laser deposition approaches were described. A detailed characterization of amorphous Si:H deposition by magnetron sputtering, presented by J. Abelson (Univ. of Illinois), provided a quantitative picture of the various energetic particle fluxes present during sputtering. Experimental studies of very-low-energy ion irradiation during nitride and metal superlattice deposition, presented by J-E. Sundgren (Linköping), examined the effect on defects and interface mixing. Similarities in interface smoothing and intermixing with the simulation work of Sprague were evident. Y. Taga (Toyota) described the role of particle kinetic energy on the structure and properties of sputter-deposited metal and oxide films. I. Yamada (Kyoto Univ.) gave an overview of the development of large-scale production equipment for ion modification in Japan. Additionally, numerous talks described recent advances in the use of energetic particles to control film deposition and properties. Examples included controlling Ni film magnetic anisotropy, modifying Ge nucleation on Si, and SiGe alloy oxidation.

Topics in the sessions on ion implantation and surface modification ranged from broad beam implantation to focused beams, and energies ranged from hundreds of eV to MeV. T.A. Tombrello (California Institute of Technology) provided an overview of work on the use of MeV ions to modify electronic materials. Ion effects discussed included modification of surface reconstructions, mixing, amorphization, damage, surface hardening, film adhesion enhancement, and the modification of field effect transistors.

Carbon Foams, Diamond, and Fullerenes Share Venue

(See MRS Proceedings Vol. 270)

Carbon is unquestionably the most versatile element in the periodic table. Easily the largest group of unique compounds, the organics owe their existence to carbon's ability to simultaneously bond to itself and to many other elements. Moreover, after setting aside this class of materials, the properties of the pure carbon allotropes span an enormous range. From crystalline sp^3 bonded diamond to planar sp^2 bonded graphite to the hybridized ball and tube-shaped fullerenes, carbon research offers a unique richness and diversity. A broad cross section of these topics filled Symposium M, Novel Forms of Carbon.

In a session devoted to microporous carbon, A.P. Sylwester and R.W. Pekela described different approaches to the production of organic microporous precursors, from which carbon of tailored morphology can be made. Both the thermally induced phase separation (Sylwester) and organic aerogel (Pekela) processes allow engineering of density, porosity, and electrical conductivity. These materials, with controlled microporosity in the 10–20,000 Å size scale, have unique properties suggesting applications in separations, electrically conductive composites, and biomedical supports.

Several papers dealt with the nucleation of diamond crystals on various substrates by means of plasma-enhanced chemical vapor deposition and combustion flame synthesis. Low-temperature deposition of diamond using 80 W, 2.45 GHz microwaves in a CO-O_2-H_2 system was reported; good quality diamond films on silicon resulted, i.e., the full width at half maximum (FWHM) of the Raman peak ranged from 4.0 to 4.1 cm^{-1} for substrate temperatures of 684 to 1023 K (for natural diamond, FWHM=3.0 cm^{-1}). Crystal-

Graduate Student Award Winners — 1992 MRS Spring Meeting

Robert F. Jarvis Jr., University of California- Los Angeles, "Solution Synthesis and Photoluminescence Studies of Small Particles of Cadmium Telluride" (Symposium O).

John Robert LaGraff, University of Illinois at Urbana-Champaign, "The Chemical Diffusion of Oxygen in $YBa_2Cu_3O_{6+x}$ Via Electrical Resistance Measurements: Intrinsic and Extrinsic Mechanisms" (Symposium S).

Susan E. McKinstry, Pennsylvania State University, "Characterization of Ferroelectric Films by Spectroscopic Ellipsometry" (Symposium T).

Silvia L. Mioc, University of Illinois- Chicago, "Vacuum Electroreflectance: Overcoming the Difficulties of Photoreflectance and Electrolyte Electroreflectance" (Symposium D).

Suzanne E. Mohney, University of Wisconsin- Madison, "Phase Equilibria in the Metal-In-P Ternary Systems and Their Application to the Design of Metal Contacts to InP" (Symposium C).

Otto Z. Zhou, University of Pennsylvania, "Temperature Dependent Structural Studies of Rubidium Doped C_{60} Buckminsterfullerene (Rb_xC_{60})" (Symposium M).

Mehrdad Ziari, University of Southern California, "Optically Controlled Space Charge Fields Under the Electrode Region in Cadmium Telluride" (Symposium D).

line film deposition was achieved at 403 K.

Several groups gave results on the *in-situ* monitoring of diamond CVD, and the interaction between diamond and reactive gases. Researchers also focused on the synthesis and characterization of diamondlike or amorphous, hydrogenated carbon films. It is well-known that these materials exhibit extreme hardness, inertness to adverse environments, high wear resistance, and optical transparency. Additionally, a wide range of electronic, optical, chemical, and mechanical properties have been reported.

Two full days of fullerenes, fullerides, and fulleroids were highlighted by talks on synthesis and characterization of metallofullerenes, fullerene superconductors, diamond synthesis using fullerene substrates, water-soluble fullerene chemical derivates, fullerene-based polymer synthesis, and the trapping of gases in crystalline C_{60}. This part of the symposium was kicked off by R. Smalley of Rice Univ., who described recent work in his laboratory on endohedral metallofullerenes—fullerenes that enclose one or more metal atoms. Earlier work reported evidence of metallofullerenes of $La_x@C_n$ (the @ symbol is used to signify that the metal atom is contained inside the hollow carbon shell). The largest value of x for the smallest n found to date is $La_4@C_{110}$. Now the Rice group reports mass spectral observation of $U@C_{28}$, the smallest metal-containing fullerene discovered to date. The first reports of extraction and characterization of endohedral metallofullerenes containing a metal cluster, e.g. $Sc_2@C_{82}$, $Sc_3@C_{82}$ and $La_2@C_{80}$ were the subjects of talks by R. Johnson of IBM Almaden and R. Whetten at UCLA, respectively. In addition, the UCLA group reported that endohedral metallofullerenes are formed with every rare earth metal they have investigated, e.g., Y, La, Ce, Nd, Sm, Eu, Gd, Tb, Py, Ho, Er.

All the laboratories found that only certain size metallofullerenes are solvent extractable. The most common, and sometimes only soluble metallofullerene, is $M@C_{82}$, but $M_2@C_{80}$ and $M@C_{84}$ have also been extracted in some instances. The metallofullerenes of the most abundant fullerenes C_{60} and C_{70} are notoriously absent from the extracted soot, although they are detected in abundance in mass spectra obtained from raw carbon soot prior to solvent treatment. Could it be that C_{60} and C_{70} mostly form exohedral complexes under the present experimental conditions? If so, studies of such M_xC_{60} and M_xC_{70} molecular species may allow insights into the properties of metal-doped fullerene structures (M_3C_{60} stoichiometry) needed for superconductivity. The interest in metallofullerenes centers around the expectation that such materials should exhibit novel electronic and chemical properties and thus may find uses in electronics, solid-state chemistry devices, and also catalysis.

Along the theoretical front, A. Rosen of the Univ. of Göteborg calculated the electronic properties of endohedral (metal inside ball) and exohedral (metal outside ball) metallofullerenes. His results show that the ionization potentials and-or electron affinities of the metallofullerenes vary significantly depending on whether the metal atom is outside or inside the carbon shell. Such results suggest that measurements of the ionization potentials or electrol affinites may allow ascertaining the position of the metal atom. K. Raghavachari of AT&T reported the first calculations for the mono-oxides of C_{60}. His results suggest that a new isomer, a C_{60} in which an oxygen atom is inserted into one of the bonds formed by the fusion of a hexagon and pentagon in C_{60}, is the most stable. ^{13}C NMR of the mono-epoxide, $C_{60}O$, shows that oxygen is inserted into a double bond formed by the juncture of two hexagons in C_{60}, the second most stable $C_{60}O$ isomer examined by Raghavachari.

In other items of note, F. Wudl of UC-Santa Barbara reported preliminary results on the synthesis of C_{60}-based polymers, giving experimental support to the ball on a chain concept. L. Chiang of Exxon described electrophilic addition reactions in which he was able to synthesize polyhydroxylated C_{60}, a water-soluble fullerene derivative containing an average of 13-16 hydroxyl groups per C_{60} molecule. Such materials have promise as precursors for specialty chemicals and polymers. D. Brenner of NRL presented calculations that suggest that the curling up of the edges of a graphite sheet could be a precursor to formation of fullerenes or carbon tubules.

Chemistry Helps Build Better Ceramics

(See MRS Proceedings Vol. 271)

The focus of the symposium series on Better Ceramics Through Chemistry (Symposium N), now in its fifth year, has been steadily evolving. The early symposia emphasized silicate materials. This year the symposium emphasized different aspects of ceramics synthesis and processing, particularly the recent advances in chemical strategies for synthesis of ceramic materials and recent advances in the synthesis and characterization of nonsilicate materials.

The symposium started with molecular chemistry and then developed the connection between structure at the molecular level and the formation and characterization of bulk ceramic powders and films at the micro- and macroscopic levels. The week-long symposium was well-attended, with interest keeping the discussions going well into the night. A session devoted mainly to recent developments in preparing and characterizing new metal-organic precursors and their conversion to ceramic materials focused on the connection between the properties of the molecular precursors and the processing temperatures of the final materials. W.E. Buhro (Washington Univ.) offered some interesting alternative approaches to sol-gel processing, taking advantage of the enolization of acetone. He also described some photochemical routes to ceramic materials. Metal-organic precursor design, the central theme of many presentations, prompted valuable discussions of strategies (K.G. Caulton, Indiana Univ.; A.W. Apblett, Tulane Univ.; and W.S. Rees, Florida State Univ.) and the formation of high nuclearity species (H. Reuter, Institut für Anorganische Chemie). One of two evening sessions was devoted to hybrid organic/inorganic materials. Recent results from French (C. Sanchez, Univ. Pierre et Marie Curie) and German (U. Schubert, Univ. Würzburg) groups demonstrated strategies for the separation of hydrolysis and condensation steps in nonsilicon alkoxide compounds and showed quantum confinement effects of metal particles in insulating silicate matrices.

The session on novel routes to non-oxide ceramics included electrochemical routes to metal nitrides (R.M. Crooks, Univ. of New Mexico, and C. Rüssel, Univ. Erlangen-Nürnberg), vapor phase routes to metal nitrides (D.M. Hoffman, Univ. of Houston), and solution phase routes (L.V. Interrante, RPI). A joint session with Symposium P covered vapor phase routes to oxide ceramics. This session was the venue of some excellent presentations with notable overviews from T.T. Kodas, Univ. of New Mexico, and A.I. Kingon, North Carolina State Univ. Presentations on the synthesis, characterization, and reactivity of volatile, metal-organic barium CVD precursors (A. Gleizes, URA-CNRS and R.A. Gardiner, Univ. of Delaware) provided valuable examples of strategies to control oligomerization of large, polarizable cations through reactions with polyether ligands.

Presentations on particulate and polymeric sols began with an interesting discussion of aqueous inorganic precursors by J. Livage (Univ. of Paris), who rationalized complexation on the basis of the potential charge model and explained how anionic complexation of aqueous polyoxohydroxides could be used to tailor particle size and shape. The session on aging, drying, and consolidation of gels included an overview of the mechanics of gels by G. Scherer of Du Pont that was followed by an account of an exciting new process to prepare aerogels at room temperature and pressure presented by D.M. Smith (Univ. of New Mexico). In the session on thin films, S. Hirano (Nagoya

Univ.) discussed processing issues related to the formation of epitaxial ferroelectric niobate thin films, and K. Miller (UC-Santa Barbara) related lattice mismatch to thin film epitaxy. G.J. Exharos (Pacific Northwest Laboratory) described a number of optical spectroscopic techniques to characterize stress in supported thin films and commented on the effects of stress on crystallization phenomena. Many papers described strategies to introduce porosity into ceramic films for applications in sensors, membranes and catalysis: deposition of organosiloxane nanospheres (T. Bein, Purdue), immogolite tubular aluminosilicates (J.C. Huling, Univ. of New Mexico), weakly branched polymeric precursors (R.S.A. de Lange, Univ. of Twente), and zeolite/sol-gel composites (Y. Yan, Purdue).

Nanocomposites were discussed in the session on composite ceramics. A particularly enlightening discussion centered on the structure and properties of MDF cement as an organic/inorganic composite.

Inorganic Clusters Reveal Their Chemistry

(See MRS Proceedings Vol. 272)

Scientists interested in small inorganic particles came together in Symposium O, Metal and Semiconductor Colloids and Clusters, to exchange ideas on molecular clusters, colloidal binary compounds (metal oxides, sulfides), and colloidal metals, in the 1–10 nm size range (nanoscale clusters). Papers covered the preparation, structure, and physical and chemical properties of these materials.

The field of metal cluster chemistry and its extension into the so-called giant clusters and metal colloids was represented by speakers from several countries. Classical metal carbonyl cluster chemistry was developed in the silver-iron system by G. Longoni (Univ. di Bologna) to the synthesis and structures of macromolecules containing silver cores capped by $Fe(CO)_3$ groups to give molecules containing some 20 metal atoms. Even larger transition metal clusters were described by D. Fenske (Univ. Karlsruhe), who developed a synthetic method to form large clusters (up to 72 metal atoms) from the reaction of metal salts with silylated main-group elements, the metal cores being ligated at the periphery with various ligands. The chemistry of a giant palladium cluster, with the approximate formulation $Pd_{561}L_{60}X_{60}$ (L = dipyridyl, X = anion) was described by I.I. Moiseev (Russian Academy of Sciences), who also described the synthesis of oligomeric platinum clusters containing Pt_4 units. Studies of the well-known gold cluster $Au_{55}(PPh_3)_{12}Cl_6$ included reports of its electrochemical, structural and electronic properties.

Colloids of transition metals and their binary compounds were the subject of several papers. A detailed analysis of the effect of precursor chemistry on the formation of transition metal oxide clusters and colloids was presented by J. Livage (Univ. Pierre et Marie Curie) H. Bönnemann (Max-Planck-Institut für Kohlenforschung) reported the reduction of metal salts with tetraalkylammonium trialkylborohydrides to give very highly dispersed colloidal metal particles stabilized by the ammonium cations. These hydrocarbon soluble materials were evaluated as hydrogenation catalysts. M.J. Hampden-Smith and co-workers (Univ. of New Mexico) also used borohydride reducing agents in the preparation of highly dispersed rhodium and molybdenum colloids. Dimetallic colloidal metals were also reported. The physical properties of highly dispersed metal particles were discussed in several papers; for example, P.P. Edwards (Univ. of Birmingham) discussed the metal semiconductor transition in Group 11 metal colloids, and K. Kimura (Himeji Institute of Technology) reported the effect of metal particle shape and size range. The symposium also covered the preparation and characterization of nanometer-size semiconductor particles. Most of the 25 papers in this area focused on II-VI (CdS, CdSe, CdTe, ZnS) based materials, although other papers also covered nanoparticle Si and III-V systems (InP, GaAs). An important conclusion of the papers is that interfaces, surfaces, and particle host materials are clearly important in determining the details of size-dependent behavior of semiconductor particles. P. Alivisatos (UC-Berkeley) showed that the phase stability of particles depended on surface capping groups. J. Schroeder (RPI) also presented evidence for size-dependent stability changes in CdS and CdSe embedded in a glass matrix. M.G. Bawendi (MIT) and L. Brus (AT&T) discussed the importance of surface states near the valence band edge to the interpretation of luminescence in II-VI particles. J.H. Simmons (Univ. of Florida) stressed the relationship of quantum confinement effects to the host medium and presented evidence and calculations in support of the argument that electron wavefunctions extend significantly outside II-VI particles into the surrounding glass in semiconductor doped glasses. K-D. Rinnen (AT&T) showed that the optical ionization spectra of small silicon clusters is independent of cluster size.

A great deal of progress was reported in the preparation of II-VI and other particles, especially by chemical techniques involving novel precursors including organometallic block copolymers and molecular metal polychalcogenides. M.L. Steigerwald (AT&T) discussed the preparation of NiTe clusters, and K.H. Theopold (Univ. of Delaware) discussed the preparation of InP particles using chemical transformations of molecular precursors Emphasis was also placed on the control of particle size, stability, and electronic properties using organic molecules to terminate surfaces, for example the use by J.L. Coffer (Univ. of North Texas) of calixarenes for stabilizing CdS nanoparticles. Various new materials as host matrices for semiconductor particles were also discussed. For example, L. Spanhel (Institute für Neue Materialien) reported the use of organic-inorganic hybrid sol-gel precursors for the preparation of semiconductor composite materials. Grain size and grain boundary effects in metal and metal carbide particles were also reported.

Synthesis Begins with Aerosols

Aerosol processes for generating materials such as carbon black have been used since ancient times. Currently, large-scale industrial aerosol processes include generation of carbon blacks, TiO_2, optical fibers, and SiO_2. In general, nanophase-to-micron-scale metal and ceramic powders and films can be produced by evaporation/condensation, plasma reactions, laser reactors, hot-wall flow reactors, and solution or suspension spray processes. For the first time, Symposium P, Aerosol Precursors to Materials, brought together researchers working in these areas.

Vapor-phase synthesis of fullerenes, fullerides, and fulleroids was discussed in conjunction with Symposium M, Novel Forms of Carbon. These new materials can be viewed as clusters or precursors to certain aerosols, especially carbon blacks. The generation of fullerenes doped with a variety of species, methods of generation, and characterization were discussed. High production rates of fullerenes (C_{60}, C_{70}) can be obtained in hydrocarbon flames, though the yields were about 1%.

Aerosol particles or clusters on a nanometer scale (larger than fullerenes) form by routes such as evaporation/condensation, laser reaction, plasma reaction, and laser ablation. As pointed out by S. Friedlander (UCLA), production of nanometer-scale clusters and particles in the gas phase is a technology that is just beginning to be exploited for the generation of materials with controlled properties.

A session held jointly with Symposium N, Better Ceramics Through Chemistry, featured papers on spray pyrolysis, electro-spraying, gas-phase reactions, and thin film formation. This session demonstrated the overlap between chemical and aerosol routes to ceramics; potentially, a number of precursors used for CVD and liquid-phase routes can be used for gas-to-particle conversion and spray pyrolysis aerosol processes. Researchers from the Univ. of New Mexico discussed a new chemical approach for generating nanophase materials using intraparticle reactions in aerosol particles. R. Sievers of the Univ. of Colorado showed a novel way to administer respirable drugs. Material, such as lung surfactants for premature babies, is gently aerosolized by dissolution in supercritical carbon dioxide and the resulting aeroaol is then expanded through a nozzle. As the infant breathes the aerosol, the drug is deposited directly on the lung tissue.

In the session on powder synthesis by aerosol processes, several speakers demonstrated the utility of spray pyrolysis for generating high-quality metal oxide powders and films. Novel models simulating particle formation describe the evolution of particle morphology along with particle size. This area is advancing rapidly and new theoretical and experimental results are providing a solid foundation for the design and operation of these systems.

A session on novel techniques and materials covered several new applications of aerosol processes and diagnostics. The formation of silica nanodendrites on silica fibers and the formation of glass films by aerosol deposition for photonics were processes that rely on formation and deposition of aerosol particles onto surfaces. The final session, held jointly with Symposium W, Computation Methods in Materials Science, emphasized the role of cluster dynamics in aerosol processes.

Bassam Z. Shakhashiri, professor of Chemistry at the University of Wisconsin-Madison, delivers the MRS plenary address on science education. In his animated style, he stressed how scientists and engineers can help all citizens develop an understanding and appreciation of science and technology. (See the July MRS Bulletin for Shakhashiri's full address.)

Intermetallic Matrix Composite Research Spurred by Need for Strong, High-Temperature Materials

(See MRS Proceedings Vol. 273)

Robust activity in intermetallic composites has been motivated by several national initiatives which rely on new high-temperature materials that are strong, stiff, and light. The second MRS symposium on Intermetallic Matrix Composites focused on several of the materials and approaches being pursued to achieve these materials requirements.

In his keynote presentation, H.R. Gray provided an overview of the status of research and development of continuously reinforced intermetallic matrix composites. Critical technical issues discussed in this and subsequent presentations included coefficient of thermal expansion mismatch between the matrix and the reinforcement, chemical compatibility between the matrix and the reinforcement, matrix toughness, environmental resistance, and transverse properties. Economic concerns addressed two years earlier remain critical. Several papers addressed the potential of continuously reinforced composites based on the orthorhombic Ti_2AlNb phase, especially with respect to deficiencies noted for composites based on the α_2-Ti_3Al compound. A significant number of talks focused on $MoSi_2$ composites and *in-situ* composites as emerging classes of materials.

Testing techniques for probing the fiber/matrix interface were described by several speakers. An invited presentation detailing the stress distribution imposed by the fiber pushout technique was followed by several papers applying this experimental technique. Other techniques used to characterize the fiber/matrix interface included transmission electron microscopy and fiber pullout. A variety of processing approaches were discussed, including deformation processing, directional solidification of intermetallic eutectics, physical vapor deposition (to produce laminated composites), melt infiltration, and solid state displacement reaction. Creep, fatigue, and fracture properties of continuous and discontinuous intermetallic composites were also presented.

Nanostructures Show Big Advances

(See MRS Proceedings Vol. 274)

The breadth and diversity of applied technologies benefiting from fundamental research on nano-engineered materials was illustrated in Symposium R, Submicron Multiphase Materials. Highlights of the two-and-a-half day symposium included advances resulting in low-density dielectric materials, novel ceramic precursors, ferrite micro-composites, hydrophobic packaging materials, and toughened transparent polymer systems.

Polymer-derived ceramics with exceptionally low shrinkage on thermolysis were described by P. Greil (Technische Univ. Hamburg). Addition of an active filler that reacts with molecular fragments, which are released on thermolysis of suitable organometallic precursor polymers, will compensate for much of the shrinkage that would occur from complete volatilization of the thermolysis products. Complex ceramic shapes prepared directly from the green shape had linear shrinkages of as little as 7%.

Addition of a homopolymer that is miscible with the soft segment of an organic triblock copolymer can increase the modulus of the material when added in amounts below the solubility limit but with a sufficiently high molecular weight. Based on scattering results and physical property measurements, J. Koberstein (Univ. of Connecticut) postulated the modulus enhancement results from formation of an entanglement network. Given the relatively low cost of homopolymers, this finding may impact formulations for a variety of commodity thermoplastic elastomers.

Combining laser patterning methods with production of electrically conductive polymers may impact microlithography and printed wiring board technologies. J. Bargon (Univ. of Bonn) used the photodeactivation of the oxidant Fe(III)-chloride, dispersed in a PVC matrix layer, to create a latent image. Infusion of monomers such as pyrrole yielded conducting networks after polymerization in the unexposed regions. The resulting micron-scale conductive patterns can be reinforced by plating with suitable metals.

Layered Superconductor Research Heats Up

(See MRS Proceedings Vol. 275)

Nearly 280 papers were presented during the oral and poster sessions of Symposium S, Layered Superconductors: Fabrication, Properties and Applications. M.R. Beasley (Stanford Univ.) reviewed a broad range of artificially layered superconductors from the basic atomic layers of all three families of oxide superconductors to superlattices fabricated by molecular beam epitaxy and pulse laser ablation and layered structures of melt-textured bulk materials. The fundamental properties of these layered structures were discussed in a series of papers, which included studies of vortex dynamics and flux pinning (P.H. Kes, Leiden Univ.; N-C. Yeh, Caltech; and J. Clem, Iowa State Univ.), charge transfer and high-pressure effects (P. Chu, Univ. of Houston), thermoelectric and thermomagnetic effects (R.P. Huebener, Univ. Tübingen) and magnetization (J. Thompson, Oak Ridge National Laboratory). The nature of weakly linked grain boundaries, their properties and application for SQUID fabrication were also reviewed (P. Chaudhari, IBM).

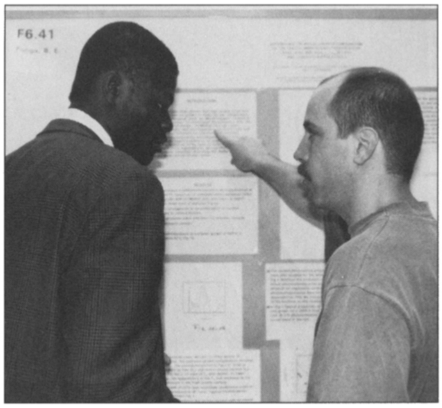
The rapid progress in the layer-by-layer synthesis of new superconducting materials was reviewed by T. Kawai (Osaka Univ.), who reported that the much publicized, but incorrect, rumors of the "discovery" of a 180 K superconductor were traceable to his findings of weak magnetic and resistive anomalies around 180 K in some atomically layered $Ca_{1-x}Sr_xCuO_2$ thin films.

Properties of one-unit-cell-thick Y-Ba-Cu-O (YBCO) layer sandwiched between Pr-Ba-Cu-O (PBCO) layers were presented by T. Terashima (Kyoto Univ.) and T. Frey (IBM). The development of an anisotropic multilayer technology was summarized by J. Rowell (Conductus Inc.). This was followed by a discussion of the design and fabrication of SQUID magnetometers by J. Clarke (UC-Berkeley) and of MISFE-type heterostructures by J. Mannhart (IBM, Zurich).

Interest continued in the processing of layered bulk materials and their development into practical conductors. Flux pinning and granularity in oxygen-deficient YBCO single and bicrystals (D.C. Larbalestier, Univ. of Wisconsin) and in polycrystalline YBCO, BSCCO, and TBCCO (K. Jagnnadham, North Carolina State Univ.) were discussed. Their correlation to the atomic structure and properties of grain boundaries was the subject of numerous poster presentations. Work on the development of practical oxide superconductors was highlighted by S. Jin (AT&T) and C.C. Tsuei (IBM) who reported the latest conductor fabrication techniques. Impressive progress on the processing of high critical current conductors of TBCCO and BSCCO materials was reported by J. Wang (SUNY-Buffalo), J. DeLuca (GE), and H. Mukai (Sumitomo Electric) during the final sessions of the symposium.

Defect Structure of Perovskites and Other Oxides Examined

Following several years of exciting development in the synthesis of thin film perovskites and other thin film oxides for electronic applications (e.g., high-temperature superconductors and ferroelectrics), Symposium T, Defect Structures in Crystalline Electronic Oxides, addressed defects in these materials, their characterization, measurement, and structure-property relationships. P.M. Smythe (Lehigh Univ.), R. Waser (Philips Research Laboratories), F. Greuter (Asea Brown Boveri) and J.P. Schaffer (Lafayette College) discussed electrically active defects in oxides, how they form, how they accumulate at grain boundaries, and how they can be characterized. In addition to Schaffer's talk on positron annihilation spectroscopy, other talks emphasized how this



Lively poster sessions during the 1992 MRS Spring Meeting offered attendees a chance to exchange research results in a relaxed environment.

technique, in combination with other methods, can identify the nature, density, and behavior of electronic defects. W.L. Warren and co-authors (Sandia National Laboratories) combined electron paramagnetic resonance and photothermal deflection spectroscopy to identify photoexcited Pb^{3+} and Ti^{3+} in PZT, showing that these two species, created from Pb^{2+} and Ti^{4+}, were related by similar creation and annihilation kinetics. This result has implications for the use of this material as an optical storage medium.

The symposium included a general session on perovskite structures and a session devoted to high-temperature superconductors. Thin film synthesis methods, both physical and chemical, are being applied to an increasing variety of perovskite structures and multilayers. Details of the interface structure are of great interest, and issues of strain accommodation and of growth behavior related to the specific chemical makeup of the interfacial layers were addressed by a number of papers, including papers by A. Kingon (North Carolina State) and S. Streiffer (Stanford Univ.).

G. van Tendeloo (Univ. of Antwerp) demonstrated the usefulness of high-resolution electron microscopy in characterizing extended defects in YBCO thin films, and K. Wasa (Matsushita) discussed growth defects in the Bi-oxide superconductors made by layer-by-layer sputtering. The growth behavior also influences the surface structure analyzed using scanning tunneling microscopy, as shown by M. Hawley and co-authors (Los Alamos National Laboratories). This technique was first used to identify spiral growth about screw dislocations in YBCO thin films. Current results show the propagation of spiral growth through $LaAlO_3$ on top of YBCO, the region where growth changes from c-axis to a-axis, and the in-plane alignment of a-axis films grown on $NdGaO_3$.

S. Trolier-McKinstry (Pennsylvania State Univ.), reported her results in applying spectroscopic ellipsometry to characterize optical properties and inhomogeneities in ferroelectric films. She demonstrated the utility of the technique for nondestructive depth profiling of thin oxide films.

Sensors, Actuators, and Micromachines Show their Smarts

(See MRS Proceedings Vol. 276)

Symposium U/Y, Smart Materials Fabrication and Materials for Micro-Electro-Mechanical Systems, was the first of its kind to be held at an MRS meeting. It was designed to produce a synergy between the rapidly developing fields of active and adaptive materials, and materials for microelectromechanical systems (MEMS). A dominant theme of the symposium was growth and characterization of active and adaptive materials and their application to thin film smart devices and in MEMS applications. As stated by P. Jardine of SUNY Stony Brook, the community needs to develop a "toolbox" of thin film growth and patterning techniques for a variety of dissimilar materials.

The active materials discussed were mainly ferroelectric materials and shape memory alloys. Talks initially focused on ferroelectric materials and issues raised in thin film microstructural characterization. Ferroelectric materials may play an important role both in sensing and actuation, and they are easily downsized for MEMS applications.

Shape memory effect materials, also termed ferroelastic materials, are gaining interest in both MEMS and smart applications. Ten papers were presented on thin film TiNi. There was general agreement among the authors that careful control of both oxygen, water, and nitrogen pressures are crucial in growing TiNi. David Johnson of TiNi Alloys Company reported on patterning issues of the thin film. The use of TiNi thin films as active materials in microvalves was also demonstrated. Cycling times for thin film TiNi were reported to be several orders of magnitude faster than for bulk material. Alternative deposition techniques such as dc and rf sputtering, ion-beam-assisted deposition, and thermal spray processing were also discussed. Finally, initial growth studies of ferroelectric-ferroelastic heterostructures were reported.

Many MEMS device applications use polycrystalline Si as part of the device structure. Several talks discussed recent efforts to characterize the mechanical properties, such as stress measurements within the polycrystalline materials, impact and wear testing, and the relationships between the mechanical properties and deposition conditions.

Sensing will become important in the evolution of smart devices. Development of fast organic dye sensors and electrochromic windows fabricated by sol-gel techniques were reported as were techniques to deposit alignable optical sensors. Materials fabrication for thin film chemical sensing routes were described by S. Semancik of NIST.

Micromechanical devices made from poly-Si were also discussed. N.C. MacDonald of Cornell Univ. described a new method for producing accelerometers using scanning tunneling microscopy technology driven by capacitive coupling between the elements, rather than with PZT, which may decrease hysteresis and increase the scanning range as compared to piezoceramic actuators.

Exciting developments in the application of micromachined technology were reported by G. Kovacs of Stanford Univ.. He reported that severed nerve trunks inside rats were regenerated through micromachined holes in Si arranged in an array. Nerves then followed the imposed geometry and signals from these individual nerve bundles could then be read through on-board electrical sensors on the Si-array. This revolutionary approach to sensing individual nerve cells has important applications in developing advanced prostheses for amputees.

New Light Shed on Photorefractive Polymers, Light Emitters, Biosensors

(See MRS Proceedings Vol. 277)

Chemists, physicists, materials scientists, and engineers gathered in Symposium V to discuss the fundamental and practical issues in the macromolecular host-guest approach to developing advanced materials with improved or novel optical, optoelectronic, photorefractive, electrooptical, nonlinear optical, or photocatalytic properties and applications.

New macromolecular host-guest materials discussed at the two-day symposium ranged from organic photorefractive materials, electrophotographic materials with tunable charge carrier mobilities, plastic laser materials that emit with high quantum efficiency in the visible range, host-guest Langmuir-Blodgett films for high density optical storage and for nonlinear optics, protein/glass sol-gel materials for use in optical biosensors, and polymer-dispersed liquid crystal films for electrooptical displace devices to zeolites for self-assembly of nanostructured catalysts and nonlinear optical materials and ferroelectric liquid crystal thin films for optoelectronics, and synthetic enzymes and ultrathin biomembranes for artificial photosynthesis and biomolecular recognition systems.

Considerable excitement surfaced in the discussion of large photorefractive properties in some polymer host-guest materials, first discovered and reported in 1991 independently by researchers at IBM Almaden Research Center and Eastman Kodak Company. Six invited speakers described work and recent developments on organic photorefractive materials in their laboratories. W.E. Moerner and J.C. Scott (IBM) reviewed the necessary and sufficient conditions for achieving photorefractivity in materials and described results on new polymer host-guest systems that meet these requirements. They also outlined the many potential advantages of the new class of photorefractive polymers and future directions for improving the materials. D.J. Williams and co-workers (Kodak) offered a new theoretical model of photorefractive effects and space-charge grating formation in photoconducting polymers and concluded that photorefractive polymers are fundamentally different from previously known inorganic photorefractive materials. N. Peyghambarian (Univ. of Arizona), J. Kumar (Univ. of Massachusetts-Lowell), and G. Hadziioannou (Univ. of Groningen) also presented invited papers on their work on photorefractive host-guest polymers.

Y. Okamoto (Polytechnic Univ.) described the preparation and properties of new lanthanide metal ion-polymer complexes that emit sharp blue (Eu^{2+}), green (Eu^{3+}), and red (Tb^{3+}) light with high quantum efficiencies. He also described the applications of these materials in lasers and electroluminescent devices. The results of efforts to explore and develop optically based biosensors were presented by S.A. Yamanaka (UCLA) who described the preparation and properties of stable, optically transparent, protein/silica glass composites that retain the bioactivity of the several proteins investigated. The characteristic reversible chemical reactions of the immobilized proteins can be optically monitored and hence can serve as the basis for new types of biosensors.

Computational Efforts Emphasize Material Structure and Properties

(See MRS Proceedings Vol. 278)

All types of materials and properties were discussed in Symposium W, Computational Methods in Materials Science. A number of talks addressed modeling of fracture in various materials. M.P. Anderson (Exxon Research and Development) explained a novel technique to numerically simulate the stress transfer and mechanical failure of composite materials. These simulations apply local constitutive relations and external forces to a discrete grid to analyze the effect of particle volume fraction and particle-matrix cohesive strength on deformation behavior. J.E. Angelo (Univ. of Minnesota) investigated hydrogen effects on fracture toughness using the embedded atom method. This technique involves calculating the overall energy change that occurs in a lattice when an atom is removed, added, or displaced. Monte Carlo simulation methods and molecular dynamics modeling for the transport of hydrogen in the material were combined to predict the extent of hydrogen segregation at two types of grain boundaries and the corresponding decreases in fracture toughness. J.A. Rifkin (Institute of Materials Science) performed direct atomistic simulations on arrays of about 10,000 atoms containing atomically sharp cracks. The variations in crack propagation modes were examined as a function of material composition, external applied stress, and temperature.

Another area of interest was the calculation and prediction of material structure. R. Kikuchi (UCLA) used a new formulation of the cluster variation method to calculate thermal expansion effects and phonon patterns in crystal lattices. This method determines the free energy functional of the lattice structure in terms of the atom locations that are individually displaced slightly from their lattice points, and then minimizes this free energy to obtain displacement patterns for the lattice structure. Thermodynamic phase stability and structural properties of Ti-Al fcc alloys were calculated by M. Astra (UC-Berkeley) using a first-principles approach that combines the cluster variation method and local density functional theory. The total energy of various configurations of atom clusters are calculated, and minimizing these energies yields the thermodynamically stable structures at various alloy compositions and temperatures. This technique is useful for theoretical prediction of the solid-state portion of the phase diagram for Ti-Al and similar alloys.

Polymer topics included configuration-dependent statistical properties, effects of surfaces on chain configurations, thermodynamic, elastic, and electronic properties of polymers, structure in liquid-crystalline melts, permeability of membranes, chain relaxations, adhesion of polymers to solid surfaces, polymer flammability, attack of atomic oxygen on polymers on spacecraft, and stress transfer and fracture in polymer-matrix composites. MRS

THANKS...

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