

## Palo Alto Report

### 1986 MRS Spring Meeting Explores Materials for Semiconductors, Electronic Packaging, Ceramic Matrix Composites, Chemical Sensors

The third annual MRS Spring Meeting was held April 14-18 in Palo Alto, CA, featuring 9 technical symposia, Symposium X (reviews for the nonspecialist), and 13 short courses. Over 1,300 scientists attended the week-long event—making this meeting 30% larger than the 1985 Spring Meeting.

Complementing the technical sessions throughout the week were special highlights, including the Plenary Address, "Materials Studies in the Examination of Works of Art," by Dr. Pieter Meyers, Director of the Conservation Center, Los Angeles County Museum of Art. Meyers showed how materials analysis is being used to authenticate works of art and to study media, techniques, and artistic styles of the masters. (See an abridged version of Dr. Meyer's lecture in upcoming issue of the BULLETIN.)

Eight students received Graduate Student Awards, and the new Southern California Section of the Materials Research Society received its charter in ceremonies preceding the Plenary Session.

Other events included afternoon and evening poster sessions, in which scientists were afforded the opportunity to discuss their work in a relaxed atmosphere. One poster session, conducted by Symposium H (Better Ceramics Through Chemistry) took full advantage of the Southern California weather by holding an evening poster session poolside at the Hyatt Palo Alto. Symposium F (Materials Issues in Silicon Integrated Circuit Processing) held a Tuesday evening Chili Cook-off, offering at-



**Graduate Student Award winners. Bottom row (left to right): Burtrand I. Lee (Symposium H), Leslie Ann Kolodziejski (Symposium B), Karen K. Gleason (Symposium E), Stephanie Koch (Symposium A). Top row (left to right): Kent Budd (Symposium H), Douglas A. Doughty (Symposium C), Jeffrey C. McCallum (Symposium D), Chris Gronet (Symposium F).**

tendees a sampling of various spicy recipes, including one appropriately named "rapid thermal" chili.

The following articles summarize the technical highlights of the Meeting. Look for details on many of these topics and more in the proceedings volumes noted. Complete studies on some of the newest developments will also appear in forthcoming issues of *Journal of Materials Research*.

#### Heteroepitaxy on Si Technology (Symposium A)

*Symposium Organizers: J.C.C. Fan (Kopin Corporation) and J.M. Poate (AT&T Bell Laboratories)*

This symposium, the first ever held on this emerging field, was exceptionally well received. A maximum attendance of 100 was expected. Instead, 200 people enthusiastically participated. There were 35 talks, including several late-news papers. The topics were divided into semiconductors (primarily GaAs) on Si, insulators (primarily CaF<sub>2</sub>) on Si, and metals (primarily silicides) on Si.

Successes in these areas would result in inexpensive high-speed ICs, optical interconnects, and 3-D devices and circuits. Major technological advances have already been achieved in this embryonic field. Very encouraging results were presented on devices such as high-speed transistors,

lasers, LEDs, and detectors, indicating that the heteroepitaxial layers are of good device quality. Although substantial improvements in material quality are still needed before commercialization of this technology, there was great expectation and excitement among many of the participants that these advances will come.

Material improvements will be realized when basic principles of nucleation on Si substrates are better understood. Therefore, the fundamentals of nucleation, especially during the initial stages of epitaxial growth, were emphasized at the symposium and drew much active discussion.

About 200 people participated in an evening panel session on "The Future of GaAs on Si." A wide variety of topics was covered, ranging from the potential applications of GaAs on Si to various techniques to solve the material growth and device processing problems of such a composite structure. The panel was composed of M. Akiyama (OKI Electric), J. Goodman (Stanford University), H. Kim (Ford Microelectronics), R. Koyama (Tri Quint Semiconductor), H. Kroemer (University of California-Santa Barbara), and H. Morkoc (University of Illinois). John C.C. Fan was the moderator. A major highlight of the evening was the unveiling of a 5-in.-diam-

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**Plenary speaker Pieter Meyers discusses materials characterization techniques in authentication, attribution, and provenance determination of works of art.**



**MRS President Gordon Pike (second from left) presents certificates of appreciation to 1986 Spring Meeting Chairs (left to right) Rod K. Quinn, Wei-Kan Chu, and Malcolm J. Thompson.**

eter GaAs on Si wafer (grown by OMCVD) by H. Kim. A summary of the panel discussion will be included with all the invited and contributed papers in the forthcoming proceedings volume.

The symposium was so successful because of the excellent contributions from many participants, especially from the invited speakers: M. Akiyama, H. Ishiwara, H. Kröemer, H. Morkoc, Y. Ohmachi, S. Sakai, R.T. Tung, K.L. Wang, and T.H. Windhorn. *Symposium Support: Air Force Office of Scientific*

*Research (K.J. Malloy and Gerald L. Witt).*

*Proceedings: Volume 69 of the Materials Research Society Symposia Proceedings series.*

**Plasma Processing (Symposium C)**

*Symposium Organizers: J. Coburn (IBM Almaden Research Center), R.A. Gottscho (AT&T Bell Laboratories), and D. Hess (University of California-Berkeley)*

The third symposium on Plasma Processing continued the tradition established

in previous meetings of emphasizing fundamental aspects of plasma chemistry. Talks on plasma processing in general, diagnostic techniques, modeling, amorphous film deposition, radiation effects, and ion-enhanced chemistry constituted the bulk of the meeting. In each session, a variety of invited speakers served as the focal points for specific issues.

On the first day, Ken Herb (AT&T Bell Laboratories) and Clarence Tracy (Motorola) gave talks on the current state of plasma processing. Herb emphasized materials considerations in plasma process development while Tracy described the variety of problems currently confronting the process engineer. In the afternoon, Michael Isaacson (Cornell) described the state of the art in nanometer-scale lithography with an emphasis on the fundamental limitations to high resolution.

On the second day, the sessions focused on plasma diagnostics and metastable materials. Unfortunately, Vince Donnelly (AT&T Bell Laboratories) was unable to deliver his invited talk in person; however, his manuscript, which will appear in the proceedings volume, describes recent advances in optical diagnostic techniques, such as time-resolved emission actinometry and laser-induced fluorescence. Alan Garscadden (Wright-Patterson Aeronautical Laboratories) delivered a wide ranging talk which helped to tie together current diagnostic capabilities, both in the discharge and in more well-defined environments (such as the ion cyclotron mass spectrometer), and theoretical approaches to modeling gas-phase discharge chemistry. The diagnostic session also featured a paper by D.K. Doughty and J.E. Lawler (University of Wisconsin), who described the use of rare gas, Rydberg opto-galvanic, and laser-induced fluorescence spectroscopy to study the properties of the cathode fall region in dc glow discharges. As a result of this work, Doughty received an MRS Graduate Student Award.

The metastable material session mostly dealt with deposition and characterization of such materials as amorphous silicon and carbon. Jeffrey Reimer (University of California-Berkeley) led off with a talk describing the plasma deposition of amorphous materials and methods of characterization, with emphasis on nuclear magnetic resonance techniques for determining hydrogen content, bonding, and spin densities. Bernard Meyerson (IBM Yorktown Heights) presented an entertaining view of pitfalls in characterization and properties of amorphous carbon or diamond-like films. In all, six talks dealt with amorphous carbon deposition and four talks dealt with deposition of insulating films such as silicon nitride and silicon dioxide.

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**Symposium A Organizers (left to right): J.C.C. Fan and J.M. Poate.**

**Microcosm of MRS**

The symposium on "Heteroepitaxy on Si Technology" organized by John C.C. Fan and John M. Poate is an excellent case study of the spirit of MRS symposia. The subject matter represents a new, emerging field. Fan and Poate saw the budding interest in this field and about a year ago proposed to organize such a symposium—the first of its kind in the world. There was very little indication how this symposium would be received, and yet in the true spirit of MRS, the Meeting Chairmen (W-K. Chu, R.K. Quinn, and M.J. Thompson) accepted it anyway. Fan and Poate then decided to invite the key investigators in this field to the symposium.

With 35 papers, they organized a 2½ day symposium and discussed the subject in significant detail. The attendance reached 200, much higher than expected based on the number of papers at the symposium. The large attendance illustrates the remarkable interest in this new field.

The success of this symposium is really a microcosm of the enormous success of MRS as a whole. The ability of MRS to serve the materials science community with rapid and timely symposia on important emerging topics is well demonstrated. MRS symposia can respond to the needs of materials scientists rapidly. The future of MRS is very bright.

Most of Thursday was devoted to modeling various aspects of the plasma chemistry. Several invited talks and nine contributed papers made this topic one of the central themes of the meeting. David Graves (University of California-Berkeley) began the session with a description of his fluid model for an rf (radio frequency) discharge with a large dc bias; he has been able to solve simultaneously the equations of continuity for ions and electrons, Poisson's equation, and the electron energy transport equation. Some of his insights pertain to where and how power is dissipated in the rf discharge. John Keller (IBM East Fishkill) presented a model for rf sheaths and models for describing etching of Si and SiO<sub>2</sub>. Mark Kushner (Spectra Technology) described a model for the plasma deposition of amorphous Si: the output of a Monte Carlo simulation of the electron kinetics was used in a fluid description of the heavy particle homogeneous and heterogeneous chemistry. Good agreement with experimentally determined deposition rates was obtained.

On the last day, sessions were devoted to the effects of radiation on surface and device properties and surface chemistry. Gottlieb Oehrlein (IBM Yorktown Heights) led off with a discussion of (reactive ion etching) RIE-induced damage in polysilicon.



**Symposium B Organizers (left to right): V. Keramides and L.R. Dawson.**

He described the use of Rutherford backscattering to characterize the damaged layer, and x-ray photoelectron spectroscopy to characterize fluorocarbon contaminating overlayers. Leonard Feldman (AT&T Bell Laboratories) gave a talk which covered the fundamental aspects of ion-surface interactions and showed that while the damage in SiO<sub>2</sub> films was unmeasurably small in plasma-deposited films, it was substantial in sputter-deposited films. Tom Mayer

(University of North Carolina) gave a talk in the afternoon which included recent experimental studies of Si etching by a combination of ion and neutral beams under conditions where a fluorocarbon film was being deposited on the surface. The net deposition or etching rate was monitored using quartz crystal microbalances; Mayer showed that the underlying Si could be etched despite the growth of the fluoro-

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**Symposium C Organizers (left to right): R.A. Gottscho, D.W. Hess, and J. Coburn.**

carbon film. Mayer also described a simulation technique for trench etching which takes into account the depletion of neutral reactant and the angular dependence of chemical sputtering. The last invited talk was given by Bob Walkup (IBM Yorktown Heights), who discussed mechanisms for electron and photon stimulated desorption. Most of the talk dealt with classical trajectory studies of Na or F ion desorption from a NaF lattice after a photon or electron-induced Auger process produced either  $\text{Na}^{3+}$  or  $\text{F}^{2+}$  on the surface. The remarkable result was that, without defects, desorption was found to be highly unlikely because of dynamic distortion of the lattice.

Overall, the meeting was successful in bringing together a diverse group of scientists interested in plasma-related problems. Substantial progress was reported in the areas of discharge modeling, diagnostics, materials characterization, amorphous film growth, and mechanisms for radiation-enhanced chemistry.

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*Proceedings: Volume 68 of the Materials Research Society Symposia Proceedings series.*

### Materials Characterization (Symposium D)

*Symposium Organizers: Marc-A. Nicolet (California Institute of Technology) and N.W. Cheung (University of California-Berkeley)*

There is always room for new ideas.

That a symposium on materials characterization is a good place to see how true this is may surprise those who consider the development of analytical tools a realm of hard work, little glamour, and poor return. Applause and recognition of the masses go to the football players, not to the team that levels the ground and erects the stands. But there is no football game without the field. There is no materials science without tools of characterization. Those who push the limits and capabilities of the tools we all use are a dedicated lot. They deserve our respect. It is they who ultimately determine how fast the knowledge of materials progresses. To succeed, they must be excellent scientists, have a grasp of fundamentals, and a love for clarity and accuracy. They also have to be first-rate experimentalists with a heart to battle adversities most of us shun: chase backgrounds, track weak signals, eradicate interferences, and stamp out effects of dirt and drift.

They were there, at the materials characterization symposium, to report how they fight and win these battles, and what elegant things their creations can do. They also demonstrated vividly that materials characterization is challenging and fascinating, with plenty of room for the scien-

tist with a creative mind and an entrepreneurial spirit.

Want a proof? Drive across the desert and look at the dancing fugitive patch of water reflecting the horizon far down the straight, hot highway. Quite simple, of course. It's a *fata morgana*, that layer of air heated by the burning sun, that bends the rays of light and misleads the eye. Over the sand, next to the highway, there is no mirage. Of course. The air isn't that hot there because the sand is white. It's all very obvious. Kid's stuff.

But do you get a hint?

Maybe not.

But someone's mind started wandering. "My laser can heat a sample too. I can probe the heated layer above it with another laser beam of grazing incidence. I'll see lateral differences by noting that there is a mirage here on that minipavement, but not there on that microdesert." Get the hint now? It's called PTS, for photo thermal spectroscopy, and it's powerful, nondestructive, contactless and easy (once you know how). The layer of hot gas over the minihighway can be as thin as  $1\mu\text{m}$ . A temperature rise of  $10^{-6}\text{C}$  is enough to be seen. Add days and nights to the scheme with a chopper and you can see time-dependent processes in the sample. Also, when that illuminated spot of  $1\mu\text{m}$  in size heats up, the material expands and buckles. That, too, can be measured and serve for analysis. But to *feel* it takes someone with a fine touch like Nabil Amer (Lawrence Berkeley Laboratory) who reviewed the topic. He has a very fine touch indeed. One that senses  $10^{-3}\text{\AA}$  of buckling!

Our senses cannot extrapolate common experiences into the realm of the microscopic world. To turn an idea into a useful tool requires the support of a scientific mind and of patient experimentation. What remarkable and unexpected vistas these analytical tools can open was the content of 15 invited talks at this symposium, spread over three morning sessions. Each talk reviewed an advanced analytical technique for materials characterization. Each in its own way was as remarkable as PTS and Nabil Amer. Their sum impressed the listener by the variety of techniques that now exists, by the level of their sensitivity and sophistication, and by the seemingly endless possible variations, combinations and improvements.

Sixty posters of contributed papers constituted the main part of the symposium, distributed over two afternoons with authors in attendance and another full day of walk-in display. Techniques of materials characterization differ from topical subjects in that the principles and effects embodied in them cover almost all aspects of physics. The poster session is a format well suited to accommodate such a variety of content and interest. The customer walks in and seeks out familiar merchandise first. But when it's over, as in the real market, the basket often contains unexpected goodies. That's the idea. Snacks and wine facilitate the transactions.

The posters covered many different analytical techniques, with authors predominantly from the United States, where contributions from industry and govern-

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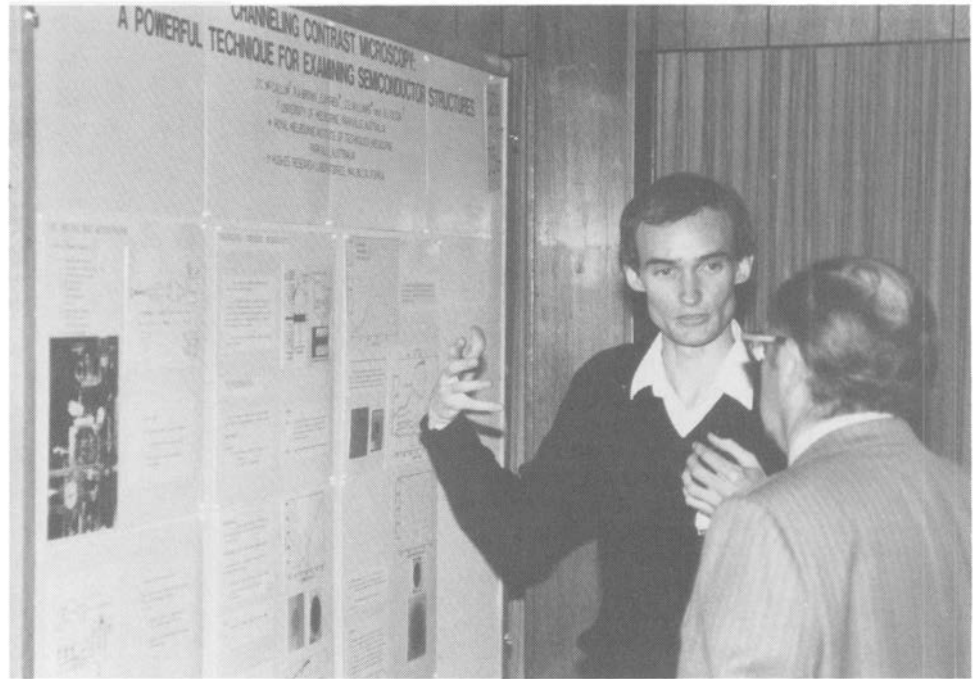
Symposium E Organizers (left to right): D. Adler, Y. Hamakawa, and A. Madan.

ment laboratories prevailed. Contributors from abroad came predominantly from universities. The field of magnetism was not represented. This contrasts with its industrial dominance on the West Coast. Perhaps this will be covered in a future Spring Meeting of the Materials Research Society.

Maybe next time you drive through straight, barren countryside, in the hot desert or in cold snowdrifted plains, your mind may start wandering as well. What other possibly useful phenomena are there in the sky? If shrinking the *fata morgana* by many orders of magnitude can lead to an invited talk in the Materials Characterization Symposium at the 1986 Spring Meeting of the Materials Research Society, where would it lead if someone were to shrink the *aurora borealis*?

*Symposium Support: National Semiconductor, National Electrostatics Corporation, and Office of Naval Research (L.R. Cooper).*

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Poster Session.

**Materials Aspects of Amorphous Semiconductor Technology (Symposium E)**

*Symposium Organizers: D. Adler (MIT), Y. Hamakawa (Osaka University), and A. Madan (Glasstech Solar)*

This symposium was concerned with both the properties of amorphous-semiconducting materials and the characteristics of devices based on these materials. The symposium was packed with both papers and attendees, with a participation in excess of 300 scientists listening to the 120 presentations.

As has been true for the past ten years, the major interest in both the materials and the device areas was amorphous silicon alloys, although a lively session on chalcogenides took place. Some controversial aspects involving the electronic structure of hydrogenated amorphous silicon (a-Si:H) formed the basis of rather intense discussions, suggesting the need for future work in this area. Great progress in device technology in the past year was also evident.

The opening session was concerned with growth and structure, primarily that of a-Si:H deposited via glow discharge decomposition, chemical vapor deposition (CVD), and photo-assisted CVD. There has been a great deal of progress in understanding the decomposition of silane and the gas-phase reactions while diffusing or drifting to the film surface, but the details of the surface reactions are somewhat mysterious at present. Interest in photo-assisted CVD is waxing, as is that in using triode deposition systems and more exotic gas mixtures (including rare gases), in all cases to try to exploit the greater flexibility in process parameters.

The next main topic discussed was electronic structure and defects, and here the controversy was liveliest. The recent progress in ab-initio calculations has been very promising, fostering the hope that detailed theoretical analysis might be able to settle the remaining conflicts in the near future. There seems to be little doubt that the dangling bond is of great importance in a-Si:H films, but some fundamental characteristics of this defect remain controversial in both magnitude and even sign. There is growing evidence that it acts more often as a trap rather than a recombination center, as ordinarily expected. Its position in the gap remains uncertain, as does its state of charge. Even the concentration of dangling bonds remains a subject of contention.

A fundamental topic in amorphous silicon alloys is the origin of the photo-induced effects, which involve the creation of metastable defects after carrier recombination. These effects now appear to be both temperature dependent and very sensitive to the quality of the original material. This is one area where we appear to be farther from an understanding this year than last.

Because of their potential importance for devices, a-Si-Ge alloys and a-Si-C alloys are of prime interest. The quality of these alloys, whose bandgaps can be tailored for the desired application, has typically been somewhat inferior to those of a-Si itself. Many of the problems appear to be dramatically alleviated by the incorporation of fluorine in addition to hydrogen as a network relaxer.

One area of progress has been that of a-Si interfaces, including both the free

surface and the interfaces with insulators and metals. A spur to some of this progress has been the study of multilayer structures, including the so-called "superlattices" (i.e., periodic multilayered structures), whose study has mushroomed over the last two years. Recent progress has included an understanding of the persistent photoconductivity observed in some of these structures, lasting for many hours at room temperature after removal of the light.

The device part of the symposium once again concentrated on solar cells, particularly their efficiency and stability. Now that these fundamentally low-cost cells have become commercial (already representing one third of the total 1985 photovoltaic market), the emphasis has been on stacked cells with different bandgap alloys. Progress has been phenomenal. A single a-Si-Ge:F:H alloy cell has achieved 10% efficiency, a tandem structure has reached 12.5% efficiency, while a triple-junction dual-bandgap device has exhibited 13.0% efficiency under AM 1 (100 mW/cm<sup>2</sup>) illumination at 300 K. Equally impressively, these devices retain about 90% of their initial efficiency after 2500 hours of exposure (over a year of actual operation). Large-area (> 100 cm<sup>2</sup>) devices have now reached the magic 10% level. New ideas abound, including the use of a superlattice structure (with its increased bandgap) as a p-type window for the cell. It now appears that the light-induced degradation saturates relatively quickly. Stability can be greatly improved by using alloys that incorporate fluorine, and particularly by using multiple-junction cells.

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Another extremely active area of device research is that of flat-panel displays. Here it is the large-area deposition capability of amorphous silicon alloys that is advantageous. Although thin-film transistors (TFTs) can be employed, a simple alternative for the switching element is an ordinary diode, similar in structure to a solar cell. TFTs are still needed for on-substrate drivers to reduce the external circuitry, and a promising new device structure based on double injection was presented as a late-news paper. This device, called a double-injection field-effect transistor (DIFET), uses an  $n^+$  source and a  $p^+$  drain, the voltage-induced double injection then leading to a factor of 20 increase in output current over conventional MOSFETs.

There was continued interest in amorphous-silicon alloy photoreceptors, which have better mechanical properties than the presently used amorphous chalcogenides and allow for simple wavelength modulation. This year, multilayered structures and heterojunctions attracted the most attention. There was also impressive progress in amorphous-silicon-alloy image sensors.

Finally, amorphous chalcogenides have not been forgotten. A revival of interest in their reversible amorphous-crystalline transitions for use in updatable optical data storage and erasable video disks has occurred, again opening the possibility of ultra-high bit densities for mass memories.

All in all, the symposium appeared to be very successful, with attendance remaining high even at the end of the fourth full day (particularly impressive considering that it was the only day accompanied by the famous California sun). We look forward to a similar symposium next April in southern California.

*Symposium Support: AMOCO, ARCO Solar, Energy Conversion Devices, EPRI, Fuji Electric Co., Glasstech Solar, Kanegafuchi, Mitsubishi Electric Co., Sanyo Electric Co., SERI, SOHIO, Solarex, and 3M Company.*

*Proceedings: Volume 70 of the Materials Research Society Symposia Proceedings series.*

### Materials Issues in Silicon Integrated Circuit Processing (Symposium F)

*Symposium Organizers: M. Wittmer (IBM), J. Stimmel (National Semiconductor), and M. Strathman (Charles Evans & Associates)*

Symposium F, "Materials Issues in Integrated Circuit Processing," sought to bring together all the materials issues pertinent to modern integrated circuit processing. The inherent properties of the materials are becoming an important concern in integrated circuit manufacturing.

The session on silicon materials science revealed the advanced stage of knowledge which topics such as point defects, intrinsic and extrinsic gettering, and diffusion kinetics have achieved. Adaptation of this



Symposium F Organizers (left to right): M. Wittmer, M. Strathman, and J. Stimmel.

knowledge to specific integrated circuit processing technologies is beginning to be addressed.

The session on epitaxy included invited papers on epitaxial insulators and infrared detectors. Heteroepitaxy on silicon is receiving great attention and the results presented in this session suggest that 3-D integrated structures are an increasingly realistic possibility. Progress in low-temperature silicon epitaxy and epitaxy of thin films with abrupt interfaces was also reported.

Diffusion and ion implantation were well represented. Regrowth of implant-damaged layers and the nature of the defects which remain after regrowth were discussed in no less than seven papers. Substantial progress was also reported in the understanding of amorphizing boron implants and the use of gallium implants for the formation of shallow  $p^+$  layers.

The contact and interconnect and rapid thermal processing sessions were the best attended sessions, due perhaps to strong current interest within the manufacturing community. Two excellent presentations on electromigration explored the basic electromigration failure mechanisms and called into question the efficacy of the popular layered metal interconnect materials. Spirited debate is expected during the coming year. Several papers addressed selective deposition of tungsten, and more data were presented on the troubling issue of encroachment and substrate tunnel formation. Two novel materials, ZrN and TiB<sub>2</sub>, were reported on and showed promise for future device applications. Titanium

silicide researchers are turning more of their attention to the electronic properties of Ti-silicon interfaces and the knowledge of the physical properties of these interfaces has been advanced considerably over the past years.

Rapid thermal processing received much attention, with many investigators in the United States, Europe, and Asia active in this field. Considerable mention was made of the adjustments which must be made to conventional integrated circuit processing to successfully integrate rapid thermal processing. A good example is the activation of shallow boron implants, where careful attention to details of the implantation process is required to realize the true potential of rapid thermal annealing. Silicide anneals are a second example, where control of annealing ambient, metal film thickness and film purity are now recognized as key process parameters. Several papers on laser-assisted processing highlighted the increasing practicality of this field.

A session on dielectrics concluded the symposium. High-pressure processing, in many ways a companion to rapid thermal annealing, was reviewed and recent results were reported on reflow of glasses, formation of thermal nitrides, and nitridation of thin oxides. Optimization of thin gate oxides, a key area for device scaling, rounded out the session.

The 1986 Spring Meeting was the first MRS meeting in which the above issues have been organized as a specific symposium. The presentation of 85 high-quality invited and contributed papers in Palo Alto

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is an indication of the relevance of basic materials science to integrated circuit manufacturing. As symposium organizers, we hope that the success of Symposium F signals the development of a closer relationship between the Materials Research Society and the microelectronics manufacturing community.

*Symposium Support:* CVC Products, Gasonics Corporation, General Ionex Corporation, IBM, Lam Research Corporation, Machine Technology, Materials Research Corporation, National Electrostatics Corporation, Peak Systems, Prometrix Corporation, Temescal, and Varian/Extrion.

*Proceedings:* Volume 71 of the Materials Research Society Symposia Proceedings series.

### Better Ceramics Through Chemistry (Symposium H)

*Symposium Organizers:* C.J. Brinker (Sandia National Laboratories), D.E. Clark (University of Florida), and D.R. Ulrich (Air Force Office of Scientific Research)

This symposium addressed the synthesis, structure, and applications of ceramic materials derived from molecular precursors (rather than minerals dug from the ground). The symposium consisted of 22 invited papers and approximately 75 contributed papers in the form of oral presentations and posters. Session topics included: solution chemistry, gels and powders, characterization, drying and consolidation, structure, non-oxides, MO and MD calculations, and novel materials. On the final day, a joint session entitled Materials for Electronic Packaging was held with Symposium G, Electronic Packaging Materials Science. As the symposium title suggests, one purpose of the meeting was to unite chemists with ceramists and materials scientists to achieve a synergistic result. We believe that this synergism was realized.

The symposium was organized to follow the evolution of structure from its inception in solution through gelation (or precipitation), drying, heating, and consolidation, to arrive finally at a ceramic body which hopefully exhibits technological advantages over its conventionally processed counterpart.

The theme of the meeting was well conveyed by the first two papers (by Walter Klemperer and Vera Mainz, both of the University of Illinois) which collectively described the synthesis and structure of well-defined, oligomeric units (e.g., cubic octamers) which serve as "molecular building blocks" for silicate gels and glasses. The solution behavior of model oligomeric species was also investigated in studies of silicate and borate gel formation by Carol Balfe and Jeff Brinker (Sandia). Bruce Bunker (Sandia) showed how investigations of the aqueous corrosion of silicate and borosilicate glasses could provide chemical insight into the mechanisms of hydrolysis

and condensation involved in sol-gel processing.

Solution chemistry and synthesis resulting in powder formation was addressed in the afternoon session. One new approach to powder synthesis was described by Mufit Akinc (Iowa State University) in which liquid-liquid immiscibility is exploited. Powder size, shape, and sinterability appear to be tailorable through control of the droplet characteristics in oil in water emulsions. One prominent theme of this session was monodispersity. This issue was discussed by P.D. Calvert (University of Sussex), Jan-Ho Jean (MIT), and Robert Heistand (Dow Chemical). Roland Cannon (Lawrence Berkeley Lab) distinguished between the conditions leading to powder formation versus gel formation in  $ZrO_2$  and presented intriguing results concerning crystallite orientation within precipitated powders.

Characterization of chemically derived ceramics was the topic of the Tuesday evening session. NMR spectroscopy ( $^1H$ ,  $^{29}Si$ , and  $^{27}Al$ ) was shown to be the method of choice for *in situ* investigations of hydrolysis and condensation kinetics as well as structural analyses. Bruce Kay (Sandia) impressed upon the audience the complexity of the solution chemistry of silica, but presented a kinetic model which successfully predicted the speciation of TMOS (tetramethylorthosilicate) during the initial stages of hydrolysis and condensation. David Avnir (University of Jerusalem) used probe molecules (Pyrene) to obtain information concerning pore size, cage size, and

surface fractality during the sol-gel-zerogel transition.

On Wednesday, Tom Shaw (IBM) and George Scherer (DuPont) presented two papers which described drying of powders and gels. Scherer presented a model based on capillary stress, redistribution pressure, and condensation reactions which successfully predicts trends in warping observed during drying. Shaw used a percolation-invasion model to describe the structural characteristics of drying fronts invading randomly packed arrays of monodisperse particles. Dave Tallant (Sandia) presented an overview of Raman investigations on silicate materials which identified cyclic tetramers and trimers as the species responsible for the  $D_1$  and  $D_2$  defects observed in gels and high surface area powders.

The session on structure of random and ordered systems included five papers which utilized small angle scattering (neutron, light, and x-ray) to probe structures on length scales of about ten to several hundred Å. Dale Schaefer (Sandia) presented overview of fractal aspects of silicate sols and gels. He delineated the conditions in which percolation clusters, cluster-cluster aggregates, or colloidal particles are obtained depending on the synthesis method employed. Drake (Exxon) used small angle scattering combined with molecular probes to explore silica surfaces. Keith Keefer (Sandia) showed how varying the functionality and spatial distribution of silicate monomers resulted in condensed structures ranging from dense colloids to uniformly

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**Symposium H Organizers (left to right): C.J. Brinker and D.E. Clark. Not shown: D.R. Ulrich.**



Tuesday evening's Chili Cook-off.

porous clusters to mass and/or surface fractals under conditions in which condensation is reaction-limited. George Onoda (IBM) and Alan Hurd (Sandia) investigated particle packing in two dimensions. Hurd employed ac fields and various electrode geometries to obtain either one or two dimension packing.

The session on non-oxides showed how Al-N (Interrante, Rensselaer Polytechnic Institute), B-N (Paine, University of New Mexico), and Si-N (Blum, SRI) molecular analogues to cyclohexane could be synthesized and used as precursors to aluminum nitride, boron nitride, and silicon nitride, respectively. Joe Ritter (NBS) used a novel reductive dehalogenation approach to produce a variety of boride and carbide powders. This approach appears to be generally applicable to a wide variety of compositions.

A prominent theme of the Thursday afternoon session was the question: Are gel-derived glasses different from ordinary glasses? Discussion of this subject by Al Cooper (Case Western Reserve), Mike Weinberg (Jet Propulsion Lab), Shyama Mukherjee (IBM), and Lisa Klein (Rutgers) led to the following conclusions: gels processed below  $T_g$  (defined by viscosity  $\approx 10^{13.5}$  poises) are structurally different from their melt-prepared counterparts; however, the structures of gels processed above  $T_g$  rapidly approach those of conventionally melted glass. Due to the strong dependence of properties such as crystallization, viscosity, and phase separation on composition, one must be very careful to make such comparisons on glasses and completely densified gels of the exact same

composition (including OH). Of course, if heterogeneities are promoted in solution, e.g., in diphasic systems, the approach to equilibrium above  $T_g$  will be retarded. This may be beneficial in synthesizing polycrystalline ceramics by a glass-ceramic approach.

The mechanisms of hydrolysis and condensation as well as the structure of model molecules which may be considered "molecular building blocks" in silicate systems were the general topics of the session on applications of molecular orbital (MO) and molecular dynamics (MD) calculations. One controversial conclusion which emerged from these studies was the result of an MNDO calculation suggesting that the condensation of silicic acid in basic conditions does not occur by an  $S_N2$  mechanism but rather through a cyclic dimer involving one bridging hydroxyl.

The joint session on materials for electronic packaging had as its main theme the use of gel-derived thin films in microelectronic applications. These films were shown to be useful in passivation (Bagley, Bell Communications) or in electro-active applications such as piezo-electric, ferroelectric, electrochromic, photochemical, etc. (Jacques Livage, University of Paris and Kent Budd, University of Illinois). Uma Chowdhry (DuPont) summarized requirements for improved substrate materials (low dielectric constant, low thermal expansion, high thermal conductivity). She demonstrated the potential of chemical synthesis routes to these materials by preparing  $MgO \cdot Al_2O_3 \cdot SiO_2$  gels which densify by viscous sintering and subsequently crystallize to produce dense cor-

dierite ceramics.

The theme of the final session was new directions and novel materials. Several papers described hybrid organic-inorganic systems prepared either by using alkyl substituted alkoxide precursors (Helmut Schmidt, Fraunhofer Institute of Silicate Research and C. Parkhurst, MIT) or by subsequent impregnation of porous gels with polymers (E. Pope, University of California-Los Angeles) and organosilane precursors to silicon carbide (B. Lee, University of Florida). The latter two approaches resulted in novel low temperature and high temperature composites, respectively. The former approach appears useful for preparing low temperature protective coatings and sensor materials. Finally, Peter Morgan described some relatively simple, but to date ignored, routes to prepare aluminate and aluminosilicate materials which exhibit rather unconventional crystallization behaviors.

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### Materials for Chemical Sensors (Symposium I)

*Symposium Organizers: J.N. Zemel (University of Pennsylvania) and S.C. Chang (GM Research Laboratory)*

Sensor research is rapidly emerging as a scientific and technological discipline with important ramifications for the future in modern microelectronic information proc-

*continued*



Technical Session.





Symposium I Organizers (left to right): J.N. Zemel and S.C. Chang.

essing systems. As for all modern technological areas, significant material problems are just beginning to emerge from the current body of research. Twelve speakers were invited to present overviews of their research and the material problems central to their sensor studies. Approximately 60

people attended the 1½ day session.

The symposium was comprised of the following papers:

Multi Ion Sensors by I. Lauks, M. Sayers and T. Dietz, Integrated Ionics, Inc.

Some Effects of Gas Exposures on the Electrical and Physical Properties of Cata-

lytic Metal-Insulator-Silicon Systems by Thomas Fare and Ingemar Lundstrom, Department of Physics and Measurement Technology, Sweden.

Approaches to Ionophore-Based Optical Sensors by W. Rudolf Seitz, University of New Hampshire.

Materials for Solid-State Gas Sensor by A.L. Micheli and S.C. Chang, General Motors Research Laboratory.

Polyimide as a Material for Capacitive Moisture Sensors by Denice D. Denton and Stephen D. Senturia, Massachusetts Institute of Technology.

Potentiometric Gas Sensors by M. Kleitz and E. Siebert-Mantel, Laboratoire d'Ionique et d'Electrochimie des Solides associe au CNRS.

Application of Pyroelectric Materials in Non-Optical Sensor Research by Jay N. Zemel, University of Pennsylvania.

Chemically Selective Coatings for Surface Acoustic Wave Vapor Sensors by Hank Wohltjen, Microsensor Systems, Inc.

Electropolymerized Organic Films for Sensor Applications by Jiri Janata, University of Utah.

Sensing Toxic Environmental Gases/Vapors by Joseph R. Stetter, Argonne National Laboratory.

Optical Waveguide Sensors and Materials by J.F. Giuliani, U.S. Research Laboratory.

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