Selective Ionization Process Reduces Hydrogen in Contamination During Plasma Doping

Ka-Ngo Leung, the leader of the Plasma and Ion Source Technology Group in the Ernest Orlando Lawrence Berkeley National Laboratory's Accelerator and Fusion Research Division, has developed a selective ion source that can improve the semiconductor manufacturing process and decrease the cost of flat-panel displays. "Although the technology can help improve the manufacture of conventional silicon-based semiconductors," Leung said, "its primary application will be the manufacture of flat-panel displays."

The transistors that control each pixel in flat-panel displays are formed from semiconductors consisting of silicon doped with phosphorus or boron. A method called ion shower is used to dope a layer of silicon with phosphorus or boron, causing two problems. One is that the energy of the beam is so high that the silicon-coated glass blank is heated too much by the accelerated hydrogen ions or other unwanted ions in the mixture causing damage to the glass surface. A second problem is damage caused by the buildup of excessive electrical charges in the plate from the unwanted ions.

To resolve these problems, Leung developed an ion source technology that uses just enough energy to selectively ionize only the phosphine (or diborine, B_2H_6, or other gas), but not enough to ionize the hydrogen gas. This eliminates most of the unwanted impurities from the ion stream because they are electrically neutral, and reduces both the excess heating and the charging problem.

The technology also solves the problem of contamination from a tungsten filament used by conventional ion sources to inject the gas containing the dopant with electrons. Leung's technology injects electrons using radio frequency (rf) induction discharge. "We create plasma using rf induction discharge and then inject electrons into the main chamber to ionize the source gas," Leung said. "The device is called an rf plasma cathode."

Ink Jet Printer Heads Heat Near 10^9°C/s

In confirming the mechanism by which the thermal ink jet printing process works, researchers at Cornell University have measured a heating rate of nearly 10^9°C/s.

"We knew that the print heads would have to be heated very fast to avoid forming multiple bubbles and that we would be at the edge of prior experimental art with measuring such fast transients, but we were surprised by just how high the heating rates actually were," said C. Thomas Avedisian, Cornell University professor of mechanical and aerospace engineering.

Tiny droplets of ink forming characters or other images are propelled onto paper from print heads that are about 60 μm on a side . The droplets are created and propelled by rapidly heating the ink in contact with the printheads causing the liquid to boil sharply.

The vapor bubble—of steam in the experiment's case but of ink vapor in a printer—squeezes the liquid above the bubble partially through a nozzle. Then the bubble collapses rapidly when the power is turned off, pinching off the liquid and forming the droplet. In the commercial product, about 100 of the tiny print heads, or resistors, made of a mixture of tantalum and aluminum, sit on a 1/4-inch (0.6-cm) silicon chip. The researchers study one of these tiny heaters in their experiments.

For the process to work effectively, a single bubble must be produced on the print head when it is heated. "If the resistor is heated too slowly, multiple bubbles can form on it much the same way that water boils in a teapot, and that decreases print quality," Avedisian said. Increasing the heating rate suppresses the familiar teapot-like boiling in favor of the more preferred mode—by molecular density fluctuations in the liquid that create only one bubble.

To achieve this, the ink must be heated to well above its normal boiling point (100°C for water at atmospheric pressure). The researchers anticipated that temperatures close to 300°C would have to be reached, which is a theoretical limit for water at 1 atm. For the liquid to reach such high temperatures above the boiling point without boiling, the researchers calculated that surface heating rates higher than 100 million degrees per second would have to be realized for the bubble jet print head.

The problem for the researchers was to measure the surface temperature on the time scale of the heating process, about 5 μs, and to acquire enough data during the transient to draw meaningful conclusions.

To measure surface temperature, the researchers first measured the electrical resistance of the heater pad during the time it takes for a bubble to form and collapse, and then calibrated the heater resistance with temperature.

To Avedisian's knowledge, "No one had previously measured heating rates this high for such tiny surfaces in a boiling process. Higher heating rates have, however, been measured for laser heating solids in air."

"The importance of knowing the surface temperature is that it establishes physical mechanisms for boiling, and models can be formulated based on such mechanisms for improving printers," Avedisian said.

Final Call for European Projects

The third and final call for proposals under the current European Community Brite-Euram Programme in Framework IV is published in the *Official Journal of the European Communities* (December 17, 1996). This will be the largest of the three calls under the program, with a total of 476 million ECUs ($520 million) available for funding collaborative materials-based research work, compared with 400 million ECUs, which was available in each of the previous calls. More than 450 projects have so far been approved for funding across Europe in this program. (See *MRS Bulletin,* February 1996, p. 8 for more on this program.)

NSF Career Grants Integrate Teaching and Research

Mohan Krishnamurthy, assistant professor of Metallurgical and Materials Engineering at Michigan Technological University, has received an award from the National Science Foundation's (NSF) Faculty Early Career Development (CAREER) Program. He is expected to receive $275,000 over five years, beginning May 15, 1996.

Krishnamurthy's research project addresses fundamental issues in the control of nucleation and ordering processes during epitaxial growth of semiconductor thin films, to create arrayed nanostructures (dimensions ~10 nm). His particular interest is in utilizing strain-driven morphological transitions to fabricate so-called self-organizing or naturally forming structures. Semiconductor nanostructures are thought to possess unique electronic and optical properties.

Krishnamurthy received his PhD degree from Arizona State University and served as a postdoctoral researcher at the University of California—Santa Barbara before coming to Michigan Tech in 1994.

The CAREER Program encourages scientists and engineers to integrate their research and education efforts early in their careers. The grants, about 3–5 years in duration and ranging from about $70,000 to $300,000, are awarded to junior-level university faculty.

NSF Invests $105 M in New Materials Research Centers

The National Science Foundation (NSF) has made 13 awards for Materials Science and Engineering Centers (MRSEC), bringing to 24 the number of centers nationwide that support materials research and education over a broad spectrum. NSF support for these new centers will amount to $105 million over the next five years.

Tom Weber, director of NSF's Division of Materials Research, said that the centers encourage research of broad scope and complexity. "With these awards, we encouraged investigators to take risks, and to spot new developments in materials research," said Weber. The centers will ultimately become a national network of university-based centers.

The new awards complete NSF's transition to the Materials Research Science and Engineering Centers program, which replaces the Materials Research Laboratories and Materials Research Groups. The new centers meet the traditional criteria of a high standard of research and strong interaction among disciplines, but also stress the relevance of research to society and technology. "The centers still do fundamental research, but they are linked much more explicitly to industry and other sectors," said Weber. The centers integrate graduate and undergraduate education with their research, and many of them also support precollege education.

Awards for the new centers were based on intellectual breadth of research and the ability to stimulate interdisciplinary education. They are also fully integrated with the academic programs of participating institutions.

Following are the new awards at a glance:

- Arizona State University ($4.18 million/56 months): Research addresses new phases of materials, such as glasses, using high pressure techniques; investigators are also designing team-taught materials education courses.
- Brown University ($5.35 million/56 months): Research focuses on how fracture and deformation occur by examining micromechanics and nanomechanics of materials; the center will involve nationwide outreach to junior high and high school students.
- University of California—Santa Barbara ($13.75 million/55 months): The center's broad program targets research on molecular and atomic interfaces of soft materials, such as plastics and colloids, and complex materials, and supports a vigorous educational partnership program with area school districts.
- Carnegie Mellon University ($3.57 million/57 months): Research pursues a greater understanding of the properties of polycrystalline materials through the "Mesoscale Interface Mapping Project." This project uses automated microscopic techniques to map grain boundaries in metal alloys and ceramics, which are important in understanding strength, failure, or fracture of materials.
- Cornell University ($17.75 million/54 months): Research in this center ranges from fundamental condensed matter science to materials with potential technological application, such as thin films on glass, which are important to display materials and novel optical materials; the center strongly emphasizes shared facilities accessible to a wide range of users.
- University of Houston ($4.14 million/56 months): The research advances the basic science and engineering needed to design, synthesize, and process new materials for fuel cells, catalytic reactors, and membrane reactors; the center focuses on the industrial context of new materials developments.
- Johns Hopkins University ($3.45 million/52 months): Research addresses the design of novel devices and structures, such as granular solids, as well as magnetic and superconducting materials with applications in communications; the center involves undergraduates extensively in its activities.
- University of Maryland, College Park ($8.28 million/57 months): A common theme running through the center's research is the fundamental understanding and potential application of thin films and surfaces for electronic and photonic purposes; the center emphasizes the involvement of young women and minorities in science.
- Northwestern University ($13.05 million/54 months): This broad-based program targets research on ultrahard coatings, novel semiconductors, electroceramic thin films, polymers, and molecular materials. The center offers research opportunities for high school science teachers and is developing "Materials World Modules" for classroom use.
- University of Pennsylvania ($13.5 million/54 months): This interdisciplinary program addresses research on polymers, liquid crystals colloids, and emulsions, and emphasizes the interface between biological and materials science; the center offers wide opportunities for undergraduate research, and coordinates with the Princeton MRSEC.
- SUNY at Stony Brook ($3.74 million/56 months): Research focuses on thermal spray coatings, which are crucial to the operation of many engineering components and systems; the center collaborates with the Massachusetts Institute of Technology and a number of industrial laboratories.
- SUNY at Stony Brook/Polytechnic University/City University of New York ($3.24 million/56 months): This diversified center is a partnership between SUNY, Polytechnic University, three CUNY colleges, Brookhaven National Laboratory, and researchers at three industrial research laboratories; the focus is on the design of polymer interfaces and the program emphasizes research participation by undergraduates and gifted high school students.
- University of Wisconsin—Madison ($10.56 million/56 months): Research targets the interfaces of superconducting materials and the growth of thin films for potential electronic and optical applications; the center also produces instructional materials for pre-college, college, and graduate curricula.

NSF invests more than $43 million per year in the 24 centers' research and education. Awards are made initially for up to five years, with competitive review at the fourth year and again every four years thereafter. The next competition is set for fiscal year 1998.

AlN-Polymer Composite Combines Low Dielectric Properties and High-Thermal Conductivity

Development of new electronic devices accelerates demand for materials with high-thermal conductivity and good dielectric properties. These properties often seem to be mutually exclusive. Scientists at Advanced Refractory Technologies, Inc. (ART), an advanced materials supplier, have developed aluminum nitride composites (ANC) which possesses the high-thermal conductivity benefits of aluminum nitride in conjunction with the low dielectric properties of polymers.

By prefabricating a network of AlN, a high-performance composite which incorporates both AlN and a polymer is possible. This technology differs from traditional AlN fabrication in that the AlN is fabricated into a porous preform into which a polymer is infiltrated, creating a dense structure. The resultant thermal conductivity has not been attainable by traditional AlN/polymer composite fabrication.

The properties of the ANC include moderately high-thermal conductivity (25–45 W/mK), low dielectric constant (5–7), a coefficient of thermal expansion which approximates that of silicon, and good electrical resistivity (10^{14} Ω cm). ANC can be tailored for a specific application by choosing a particular polymer that, in combination with the AlN preform, provides the desired properties.

Carbon Fiber's Microstructure Linked to Adsorption Properties

Using a scanning tunneling microscope, researchers at the University of Illinois at Urbana-Champaign have seen the porous microstructure within an activated carbon fiber, and related this microstructure to the fiber's adsorption properties. The scientists

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described a labyrinth of narrow tubes twisting and turning through the fiber, creating an interconnected, microporous network in which macropores on the surface branch into smaller mesopores, which branch into smaller micropores. Many of the pores, which ranged in size from less than 1 nm in width to more than 50 nm, formed tubes that extended more than 30 times their width. Adsorption takes place within the narrow confines of these pores and tubes.

The adsorption properties of a carbon fiber are directly related to the size and distribution of the pores, said Chris Mangun, doctoral student in materials science. Activated carbons with smaller pore sizes, for example, are much more effective at removing contaminants at low concentrations.

The commercial fibers used in the study were spun from a phenolic polymer. The fibers become activated when some of the carbon is etched away through an oxidation reaction. The nature of the reaction—which includes such factors as reagent, time, and temperature—controls the pore structure and surface chemistry, which in turn control the adsorption properties of the fibers.

"For a long time, surface area was presumed to be the measure of carbon's ability to adsorb contaminants," Mangun said. "Now we are saying that pore size, pore shape, and pore-surface chemistry are just as important. And these characteristics can be altered to meet specific adsorption requirements."

Temperature Variations During Processing Cause Phase Separation and Degradation of Properties

Minor temperature variations that occur during the processing of metal alloys, composite materials, and advanced plastics can have major effects on the properties of the finished materials, said Steve Granick, materials scientist at the University of Illinois at Urbana-Champaign. Granick has found that the temperature at which ingredients blend can vary if the temperature throughout the mixture is not kept constant. Because temperature plays a vital role in how things mix, variations in that temperature can degrade the performance of the final product. He and his colleagues Jiro Kumaki of the Hashimoto Polymer Phasing Project and Takeji Hashimoto of Kyoto University published their findings in the September 2 issue of *Physical Review Letters*.

The scientists heated a pot of polystyrene-polybutadiene-dioctylphthalate to which they applied small thermal gradients. Because the entire pot was above the solution's thermodynamic coexistence temperature of 80°C, the polymer should have looked smooth. Instead, the scientists found that the thermal gradients created little pockets of locally enriched concentrations that phase-separated at their own unique thermodynamic coexistence temperatures. The phase separations occurred when the solution was over 20°C above the predicted thermodynamic coexistence temperature.

Because it may not be possible to maintain a constant temperature, Granick said, scientists and engineers should include the effects of a shifting thermodynamic coexistence temperature when designing a new material.

Luminescent Efficiency Linked to Trapped Electrons in Oxygen Vacancies

Liquid crystal displays have the tendency to appear blank if looked at from angles other than straight on, placed in direct sunlight, subjected to rapid changes in temperature, or accelerated rapidly. In addition, their batteries run down quickly because the entire screen is backlit and then blocked out in sections to provide images. A phosphor field emission display—traditionally used to create light in most television screens—only energizes pixels that provide information. While studying the mechanism by which a phosphor emits light, scientists at Sandia National Laboratories have found that the amount of green light emitted by zinc oxide does not depend upon the thickness of the crystal but upon the density of oxygen vacancies. Single electrons that remain in the vacant spaces emit green light when a mild electric current is introduced.

"Our work has shown for the first time that the electronic properties at a material's surface have a dominant effect on its luminescent efficiency," said Sandia scientist Bill Warren. "Now we're changing the chemistry of the surface to achieve the greatest luminescence."

Zinc oxide was chosen because of its simple, two-component lattice. While most phosphors comprise three, four, or five elements in complex lattices, the scientists believe that development of other phosphors will benefit from the knowledge gained by studying zinc oxide. Other phosphors include those that emit blue and red light, the primary colors which combine with green to form full-color TV or computer images.

"Zinc oxide does not quite have the right chromaticity—it doesn't look naturally green," said Sandia scientist David Tallant. "But the color can be balanced. It also can be used in monochrome displays. We used that material to tune up a method to study other phosphors."

Previous methods of generating light from phosphors, like those used in most television sets, require large voltage drops across bulky cathode ray tubes to blitz relatively large volumes of phosphor. The voltage required—approximately 25 kV—is incompatible with battery-powered portable units, and the efficiency of light generated by that method declines rapidly when incoming energy drops below 5 kV.

By activating the phosphor surface, the scientists believe they can produce phosphors that operate at 0.5 kV. The scientists now use a few thousand volts to better benchmark efficiencies at lower voltage. Less power can readily be applied because new technology has developed microscopic structures shaped like tiny cones that deliver small amounts of low voltage current to each red-blue-green pixel on a phosphor screen less than a millimeter away.

"The portable display-building community wants a device that operates at low voltage, a material whose surface dominates its properties, and an understanding of how surface defects that generate light can be used to improve device performance," said Tallant.

"At low voltages, the surface properties of phosphors dominate their light emissions, and surface engineering becomes a key element in improving device performance," said Karel Vanheusden, a scientist at Sandia and postdoc at the University of New Mexico.

To obtain a fundamental linkage between luminescence and specific defects or dopants, the scientists used photothermal deflection spectroscopy which measures optical absorption in a powder by measuring the increase in heat of a liquid in contact with the powder. The heat increase causes a change in the liquid's refractivity. That change bends a laser beam passing through it. The amount of bending, when related to the amount of heating, measures changes in temperature to 10^{-4}°C, and can be calibrated to reveal the amount of light initially absorbed by the phosphor powder. The technique is further refined by measuring the amount of light absorbed at particular wavelengths.

While light is usually measured by the amount that passes through materials, so much light is dispersed by powders that accurate absorption measurements are difficult to perform.

Molten Co-Pd Found to be Magnetic

Iron, cobalt, and nickel, when heated, lose their magnetism long before they begin to melt. Until recently this seemed to be unavoidable among magnets; however, researchers at German Aerospace Research Institute (DLR) in Cologne have discovered that molten metal can be magnetic. They heated a cobalt-palladium alloy to over 1500°C, at which point it liquefied and lost it magnetism, as expected. The researchers then allowed the molten metal to cool and prevented it from solidifying by keeping the sample in suspension with the aid of an electromagnetic field. The molten sphere remained liquid because there were no walls of solid surfaces on which the first crystals could precipitate.

In this way the scientists were able to cool the liquid sample to almost 400°C below it melting point while at the same time preventing atoms from taking on the rigid formation characteristic of solids. Nonetheless, the liquid alloy still became magnetic when the temperature dropped below the magnetic alignment temperature of 1119°C. The tiny elementary magnets apparently aligned and oriented themselves, although the atoms themselves were still in random motion. Strong attraction to a bar magnet showed that the liquid sphere was almost as magnetic as in its solid state.

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AVS Announces 1996 Awards

The American Vacuum Society (AVS) has selected 27 AVS members and graduate students to receive awards and honor for 1996. The AVS established its annual awards program to encourage excellence in research and innovation in technical areas of interest to the AVS. Among the major award recipients is Brian E. Bent (Columbia University) who received the Peter Mark Memorial Award for seminal research leading to molecular-level understanding of the mechanisms and kinetics of surface chemical reactions relevant to heterogeneous catalysis and to materials deposition. He passed away after notification of his award; a family accepted the award in his place. Peter J. Feibelman (Sandia National Laboratories) is the recipient of the Medard W. Welch Award for his insightful predictions and explanations of surface phenomena based on first principles calculations. William R. Wheeler (Tencor Instruments) is the recipient for the Albert Nerken Award for a lifetime of fundamental vacuum hardware and instrumentation innovations, particularly the enabling invention of the Conflat flange. Gerald J. Lapeyre (Montana State University) is the recipient of the Gaede-Langmuir Award for his outstanding contribution to the development of photoemission spectroscopy with synchrotron radiation and, in particular, for his innovative use of photon tunability and angle resolution, which influenced several generations of surface scientists.

The following members have made outstanding contributions in areas of interest to the AVS and have been named Fellows: David Aspnes, North Carolina State University; Brian Bent, Columbia University; Donald Carmichael, Vacuum Technology, Inc.; Scott Chambers, Pacific Northwest National Laboratory; Guy Davis, Dacco Science, Inc.; Gert Ehrlich, University of Illinois; Peter Feibelman, Sandia National Laboratories; Frances Houle, IBM Almaden Research Center; Gerald Lapeyre, Montana State University; John Rabalais, University of Houston; Federico Sequeda, University of Columbia; Charles Tilford, National Institute of Science and Technology; and William Wheeler, Tencor Instruments.

Experiment Indicates Large Superheating of Frozen Water-Methane Compound

Traditional techniques for making methane clathrate yielded too little or too loosely structured material to be suitable for testing or measurement. Bill Durham of Lawrence Livermore National Laboratory and Laura Stern and Stephen Kirby of the U.S. Geological Survey aimed to make "large-volume, low-porosity, cohesive polycrystalline clathrate aggregates with a uniform fine grain size and random crystallographic grain orientation." To do this, they mixed fine, granular ice and cold, pressurized methane gas in a constant-volume reaction vessel which they slowly heated under strictly regulated conditions. Methane clathrate takes at least 7–8 hours to form using this method and essentially consumes the water ice as it forms.

The researchers found that the ice did not liquefy as predicted when the melting temperature was reached and surpassed. According to the scientists' article published in the September 27 issue of *Science*, clathrate was formed only after many hours, with the temperatures inside the reaction vessel reaching 289 K before the last of the ice was consumed.

The researchers concluded that a kind of "armoring effect" accompanying clathrate formation suppresses the melting of the ice due to a superficial layer of hydrate enveloping each seed ice grain. A control experiment using neon, which does not form a clathrate, instead of methane under identical conditions showed no such anomaly. The ice melted as predicted.

The scientists said that they have not verified the phenomenon of superheated ice by measuring its physical property characteristics, and that while their results are implausible, they have no alternative explanation.

Lead Isotope Analysis Recasts Archaeologists' Thinking about Peoples of Ancient West Mexico

After studying ore samples from 15 deposits in West Mexico, Oaxaca, and Eastern Mexico (Veracruz) and samples of 171 copper artifacts from a variety of Mesoamerican archaeological sites, researchers determined the ratios of lead isotopes in each sample. The researchers plotted $^{208}Pb/^{204}Pb$ in creating lead isotope fields. Lead isotope analysis "can be used to identify ore sources for artifacts made from copper and copper alloys by matching the isotopic signatures of ore lead to those of the artifacts," Dorothy Hosler, Associate Professor of Archaeology and Ancient Technology in the Department of Materials Science and Engineering and Andrew W. Macfarlane, a research affiliate in the department and an associate professor at Florida International University wrote in the September 27 issue of *Science*. The lead-isotope results show that most of the Mesoamerican artifacts sampled were made of metal smelted from West Mexican ores. These analytical data combined with historical and archaeological evidence show that the West Mexicans were exporting artifacts throughout the Mesoamerican region which encompasses central and southern Mexico, Guatemala, Belize, western Honduras, and El Salvador.

Among the archaeological evidence that supports this conclusion is that "as far as we know, other Mesoamerican peoples did not develop the technical expertise to make these artifacts," Hosler said. She said that West Mexican bells, for example, are difficult to cast, as her students demonstrated when they spent two weeks trying to cast copies of the bells. Until now, archaeologists had thought that the West Mexicans were relatively isolated and had little impact on other Mesoamerican peoples during the period of ~1200–1521 AD. □

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