

temperature for 1 h. It was then ground and polished to 0.5 mm thick.

SHG was obtained by pulses of 3.6 ns at 1.064 μm (beam ω) and 3 ns at 532 nm (beam 2ω) from a Q-switched Nd:YAG laser. The samples were prepared with both beam ω and beam 2ω incident. The samples were probed with beam 2ω blocked. Behind the sample, two heat-absorbing filters and a 532-nm bandpass filter allowed a photomultiplier to detect only the SHG signal with beam 2ω blocked. The signal was averaged by an oscilloscope.

The intensity of SHG, normalized by the maximum intensity of second-harmonic waves from 1-mm-thick Y-cut quartz, increased rapidly and saturated after 50 min. The maximum intensity was seven times larger than that of the quartz and four orders of magnitude larger than that of $15\text{Nb}_2\text{O}_5\text{-}85\text{TeO}_2$ under the same optical poling conditions. As-made samples showed no SHG.

The signal from the chalcogenide glass was stable, unlike other glasses. The signal from Bi_2O_3 -based glasses decreased to 80% after 10 min. For $15\text{Nb}_2\text{O}_5\text{-}85\text{TeO}_2$, the signal decreased to 5% after 10 min.

The researchers suggest that the non-linear coherent field of $\omega + 2\omega$ creates free electrons that are trapped by active sites in the glass, which breaks the inversion symmetry of the microstructure and allows SHG.

Selecting the proper glass composition could increase the conversion efficiency and stability of the SHG, the researchers said. They believe that with their technique "it is possible to achieve practically useful nonlinear optical frequency-conversion devices with a chalcogenide glass fiber."

ELIZABETH A. SHACK

Nonvolatile Memory Observed in Chromium-Doped SrTiO_3 Single Crystals

Materials that exhibit reversible resistive switching are potential candidates for random-access memory (RAM). Various metal-insulator-metal-oxide structures display switching and show memory retention of more than 18 months. Y. Watanabe and colleagues, members of the IBM research team at Zurich Research Laboratory, examined single crystals of one such oxide, Cr-doped SrTiO_3 . Using these single crystals as a model system, the researchers determined that microstructural defects in the thin films are not a significant contribution to the switching effect. Instead, the researchers conclude that a bulk electronic change is necessary for memory switching to occur.

As reported in the June 4 issue of

Applied Physics Letters, at 4 K the crystal has an initial resistance of 1 $\text{G}\Omega$ up to 100 V. Sweeping to 200 V causes a drop in resistance leading to a hysteretic current-voltage characteristic. Stressing the crystal with pulsed or dc voltage causes an additional resistance drop by several orders of magnitude. This creates a conductive state which allows for memory switching. By applying a positive voltage pulse, the oxide is switched to a low-impedance state with a resistance of 500 Ω . Applying a negative voltage erases the "information" written to the device and switches the oxide back to a high-impedance state with a resistance of 5000 Ω . This effect is also seen at room temperature. Once the conductive state is established, the switching behavior of the single crystal is reproducible. After more than 10^5 read pulses, no change in the readout signal was seen, indicating that these single-crystal oxides have the potential to be alternative non-volatile RAM.

The conductive state is created by exposing the insulating crystal to high voltages. During temperature cycling experiments, the low state tended to change to the high state. This suggests to the researchers that the conductive state originates from an excessive amount of injected carriers. This was verified by Cr-doped SrZrO_3 thin-film experiments. A good scaling of the current versus electrode area from 0.5 mm square to 100 mm square is observed, which indicates to the researchers that this is not a defect-dominated process. The researchers said that the high resistance of the single crystal at low voltage confirms that the bulk determines the current flow across the insulator and that the transition to the conductive state originates from a change in the bulk property.

JENNIFER L. BURRIS

(Pb,Sr) TiO_2 Thin Films Prepared by LSMCD as Potential DRAM Materials

Researchers at the Department of Chemical Engineering at the Korean Advanced Institute of Science and Technology and Samsung Electronics Co. have prepared high-quality thin films of (Pb,Sr) TiO_2 (PST) on Si wafers and Pt-coated Si wafers by liquid source misted chemical deposition (LSMCD). Seong I. Woo and co-workers found that LSMCD produced high-quality films that exhibited a high dielectric constant, good paraelectricity, and low dielectric loss after annealing at a relatively low temperature of 550°C. According to the researchers, these properties make the "PST thin film a promising material for ULSI-DRAM [ultralarge-scale integration dynamic random-access memory] capaci-

tors and other microelectronic device applications."

As reported in the May 2001 issue of *Chemistry of Materials*, the researchers used lead acetate, strontium acetate, and titanium isopropoxide as the metallic precursors for the film. A solution of the precursors in acetic acid and 1-butanol was misted using an ultrasonic nebulizer and the mist transported to the deposition chamber by a stream of argon. The films were grown on Si(100) wafers and Si(100) wafers coated with 100 nm of Pt. The films were baked at 400°C for 10 min and annealed between 500°C and 700°C for 5 min. All heat treatment was performed in air. Films with thicknesses of 60, 90, and 130 nm were prepared.

Scanning electron micrographs of the PST films revealed smooth, dense, and uniform surfaces devoid of any gaps or cracks. X-ray diffraction and Auger electron spectroscopy also showed that the polycrystalline film exhibited uniform grain size and composition throughout its thickness. Wavelength dispersive spectroscopy was used to confirm that the composition of the film was identical to the composition of the precursor solution used for misting.

Measuring the capacitance and current as functions of applied voltage in the PST showed that the films exhibited paraelectric behavior, low leakage currents, and high dielectric constants. The researchers predict that the leakage current and paraelectricity in the films could be further improved by postannealing under oxygen and reducing the amount of Pb in the films, respectively. The electrical properties measured for the PST films compare favorably to those of (Ba,Sr) TiO_2 (BST) films, which are considered the most promising material for ULSI-DRAM capacitors. The BST films, however, must be annealed at 700°C while PST films can be annealed at 550°C. This reduction of annealing temperature is important in electronics fabrication because high annealing temperatures can damage sensitive electronic components.

GREGORY KHITROV

Self-Assembled Diblock Copolymers Applied in Semiconductor Capacitor Fabrication

Advances in microfabrication technologies over the last few years have allowed reductions in the physical size of integrated-circuit (IC) components. Shrinking the size of the memory cell has facilitated dynamic random-access memory (DRAM) chips with near-gigabit storage capacities while maintaining similar sizes to their 1-MB

ancestors fabricated no more than 10 years ago. These technological improvements demand corresponding advances in silicon processing at nanometer scale, rendering self-organizing systems as attractive candidates for processes in future IC assembly. Taking the challenge of on-chip capacitor fabrication, a joint research team from IBM T.J. Watson Research Center and the University of Massachusetts has combined a self-organizing diblock-copolymer system with semiconductor processing to produce silicon capacitors with increased charge storage capacity over planar structures. Capacitor design is a difficult task in IC processing since decreasing the physical dimensions results intrinsically in reducing the capacity of storing electrical charge. This issue is fundamental to DRAM cell design, as well as on-chip decoupling capacitors and ferroelectric memories.

As reported in the July 2 issue of *Applied Physics Letters*, the research team used the diblock-copolymer film as a mask for creating electrode topography, combining the concept of surface roughening (already implemented in DRAM using rugged polycrystalline silicon) with the demonstrated ability of diblock copolymers to be used as masks for dry etching. The choice for materials used was for the diblock copolymers composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA) which, under suitable processing conditions, separate and self-reassemble into a hexagonal lattice of PMMA cylinders in a matrix of PS with a lattice periodicity well below photolithographic resolution limits. Reactive ion etching using this type of mask produced a patterned capacitor electrode with increased surface area, yielding a capacitance increase of 30% over planar structures. The capacitor dielectric was thermally grown silicon dioxide onto which an aluminum gate electrode was deposited to form a metal oxide semiconductor device. The PS-PMMA diblock copolymer had an average molecular weight of 73,000 g/mol, polydispersity index of 1.04, and PMMA weight fraction of 30%. Scanning electron microscope images were used at various steps during the process to confirm its development and control. The hemispherical-shaped capacitors obtained proved to have a $29 \pm 6\%$ increase in capacitance over planar structures.

The process established by the researchers is compatible with standard semiconductor processing techniques and is scalable to large wafer dimensions. Their results illustrate the potential for self-organizing block-copolymer templates to add functionality to silicon technology.

CLAUDIU MUNTELE

Thin-Film Fullerene PV Cell Doubles Previously Achieved Power Conversion Efficiency

P. Peumans and S.R. Forrest at the Center for Photonics and Optoelectronic Materials at Princeton University have fabricated an organic thin-film photovoltaic (PV) cell with an efficiency nearly twice that of previously fabricated cells. The researchers measured an external power conversion efficiency of $3.6 \pm 0.2\%$ under AM 1.5 spectral illumination of 1.5 suns on this cell made of copper phthalocyanine (CuPc) and C_{60} . As stated in their article published in the July 2 issue of *Applied Physics Letters*, "The improved results are primarily a consequence of the long exciton diffusion length of C_{60} ."

The researchers fabricated these novel double heterostructure PV cells in a superstrate configuration using precleaned glass precoated with transparent, conducting indium tin oxide (ITO). The team treated the glass/ITO, which had been solvent-cleaned, with an O_2 plasma and subsequently spin-coated the glass/ITO with a film of 3,4-polyethylenedioxythiophene:

polystyrenesulfonate (PEDOT:PSS). Next, they grew the donor-like CuPc, the acceptorlike C_{60} , and then the bathocuproine (BCP) films at room temperature in high vacuum ($\sim 1 \times 10^{-6}$ Torr). They deposited the Al cathode by thermal evaporation.

Since C.W. Tang developed the efficient heterostructure in 1986, researchers investigating thin-film organic PV cells have been making frequent advances, such as the development of the polymer bulk heterostructure donor-acceptor cells in 1995. The team at Princeton had made previous advancements, in part, due to the ability of the BCP to transmit electrons while blocking exciton recombination at the cathode. However, the incorporation of the fullerene, C_{60} , with a diffusion length of $77 \pm 10 \text{ \AA}$, instead of other previously used acceptor materials, such as 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI), with a diffusion length of $30 \pm 3 \text{ \AA}$, is what propelled the efficiency of this cell far beyond the others. The increased diffusion length allowed for enhanced carrier collection across the solar spectrum. While significantly increasing the effi-



Institute for Soldier Nanotechnologies

The Army announces its intention to create a University Affiliated Research Center (UARC) to develop nanometer-scale science and technology solutions for the soldier. A single university, along with industry partners, will host this center to emphasize revolutionary materials research toward an advanced uniform and protective ensemble concept. In anticipation of the Broad Agency Announcement, the Army will host two pre-competition informational meetings to be held in the August - September time frame on the East and West Coast. Registration information, the meeting times and directions to the meeting location are available at the ARO web site:

<http://www.aro.army.mil/soldiernano/>

Questions may be posted by contacting QA@arl.aro.army.mil. The questions and answers will be posted at the above web site.

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