

which are made of silicon dioxide only about 1.5-nm thick (about four atomic layers of SiO₂). Further decreases in the thickness of the SiO₂ would result in unacceptably high leakage current that would drain batteries and overheat chips. To continue the advancement of microelectronics, materials with higher dielectric constant (*k*) and higher thickness will be needed to replace the SiO₂.

This is the main research focus of Roy G. Gordon and co-workers at Harvard University. In the August issue of *Chemistry of Materials*, the research team reported the use of chemical vapor deposition (CVD) and atomic layer deposition (ALD) techniques to deposit metal silicates and metal oxides. The researchers use reactions between the vapors of metal alkylamides and tris(*tert*-alkoxy)silanols. For CVD, a reaction chamber is supplied with continuous flows of the vapors of tetrakis(dimethylamino)hafnium and tris(*tert*-butoxy)silanol, which were dissolved separately in tetradecane solutions and then flash-vaporized. With substrate temperatures ~250–350°C, the deposited product is a hafnia-silica glass, HfO₂(SiO₂)_x.

For ALD, pulses of each vapor are dosed alternately and separately into the reaction chamber, producing the same composition with very uniform thickness, even inside small holes. ALD showed high growth rates of 0.3–0.4 nm per deposition cycle, a level higher than traditional ALD reactions. This ALD procedure can also be modified to deposit metal oxides by replacing the pulses of tris(*tert*-butoxy)silanol vapor with water vapor. By varying the ratio of silanol pulses to water pulses, the ratio of silicon to hafnium can be controlled from $x \sim 0$ to 3. Rutherford backscattering measurements showed impurity levels of nitrogen and carbon to be very low (<2 at.%). Additional attractive characteristics included relative smoothness (<0.5%) and lack of cracks and pinholes in the thin films over domains of 300 nm, as determined by atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. No special pretreatment was needed for silicon and glassy carbon substrates.

Volatile amides are known for many metals, including Li, Na, K, Be, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Ge, Sn, Pb, Sb, and the lanthanide and actinide metals. Thus, according to the researchers, similar techniques could be used to deposit metal oxides and silicates for these metals.

In contrast to many CVD and ALD techniques, this process uses no metal chlorides, which can result in chloride

impurities and possible substrate/equipment corrosion. Also, some metal chlorides, such as those of yttrium and lanthanum, are not volatile enough for use in CVD or ALD.

This technique may provide a way to continue Moore's law improvements in computing power by using high-*k* materials to replace leaky gate insulators of silicon dioxide.

MATHEW M. MAYE

Model Explains Capillary Condensation of Fluids in Disordered Mesoscopic Materials

Using a mean-field density functional theory for a disordered lattice-gas model during their investigation of the phenomenon of capillary condensation of fluids in disordered mesoporous materials, researchers have discovered that the hysteresis loop can present itself both in the presence and the absence of a true equilibrium phase transition and that capillary criticality is not linked with the vanishing of the hysteresis loop. Furthermore, as Edouard Kierlik and co-workers from the Laboratoire de Physique Théorique des Liquides at the Université Pierre et Marie Curie and the Department of Chemical Engineering at the University of Massachusetts have reported in the July 30 issue of *Physical Review Letters*, the system can "jump" from one grand potential minimum to another along the adsorption and desorption isotherms such that thermodynamic behavior is erratic.

According to the researchers, their simulations indicate the presence of a large number of metastable states inside the main hysteresis loop. According to researcher Martin Luc Rosinberg of Université Pierre et Marie Curie, these metastable states are responsible for the typical history-dependent behavior of fluids adsorbed in disordered porous solids. The value of the solid-fluid interaction is crucial for determining whether an underlying equilibrium first-order phase transition actually occurs (i.e., a jump in the density of the adsorbed fluid).

The work of Kierlik and co-workers provides a means for understanding the experimentally observed hysteresis loops and temperature-dependence of sorption isotherms in capillary condensation studies. The "scanning curves" obtained by changing the sign of the chemical potential along adsorption and desorption branches agree with experimental observations, whereas previous models have not properly captured such features. The researchers said that the ability to reproduce observed physical behavior is a critical factor in determining a model's predictive capacity.

On a broader scale, this research provides an instance where theory can contribute key understanding by focusing on information that lies outside of conventional "restrictions": Often, theory studies pursue simulations designed to obtain equilibrium information and to present thermodynamically consistent results. Many of the interesting features obtained in this study specifically fall outside such a "narrow" regime.

The researchers draw a connection between their results for capillary condensation phenomena and the macroscopic avalanche of low-temperature ferromagnets. The researchers hope that the observation of such features in capillary condensation of real materials will provide additional support for the applicability of the model Hamiltonian and assumptions employed in this study. Predicting as-yet-unseen features and explaining unusual observed behavior are the ultimate goals of most materials simulations, they said.

EMILY JARVIS

Silicon Nanowire Structure Displays Enhanced Optical Birefringence

To further enhance the use of birefringent crystals for controlling the polarization state of light in optical applications, an international group of researchers from the Technical University of München, Germany, and Koba University in Japan, has demonstrated a way of realizing a silicon-based optical device based on the anisotropic dielectric nanostructuring of silicon wafers. The merit of this experiment is the realization in the laboratory of a material with higher values of the anisotropy parameter Δn than of any other crystal found in nature.

As reported in the August 15 issue of *Optics Letters*, the method used to synthesize the Si wafers is anodic etching of bulk Si in 1:1 volumes of hydrofluoric acid and ethanol solution, resulting in a spongelike network of interconnected Si nanowires. The size of the nanowires is a function of the doping level of the substrate, the concentration of the etching agent, and the etching-current density. Transmission electron microscopy revealed that the pores resulting from etching propagate independently of the orientation of the substrate in a [100] equivalent crystallographic direction. To achieve in-plane anisotropy of the refractive index, the wafers were etched on the (110) plane, resulting in different refractive indices for light polarized along $[1\bar{1}0]$ and [001] directions. To determine $\Delta n = n_{[1\bar{1}0]} - n_{[001]}$, two methods were involved: transmission measurements in

polarization-resolved mode and Fabry–Perot oscillations in a reflection geometry with a Fourier transform IR setup. The variation of the refractive index in this setup is found to be six to seven orders of magnitude higher than in bulk Si lattice. To verify that the birefringence of the anisotropically nanostructured Si layers has a dielectric nature and is not induced by stress, the pores of the samples were inundated with various dielectric liquids, and the ratio of the perpendicularly polarized light to the parallel polarized light was measured. The researchers found that the result supported the dielectric explanation of the birefringence in anisotropically nanostructured Si layers.

CLAUDIU MUNTELE

Soft Chemistry Method Developed for Synthesis of Cubic Boron Nitride

A team of researchers from Shandong and Beijing Science and Technology Universities and the Chinese Academy of Science have synthesized cubic boron nitride (cBN) at low temperatures and low pressures. As reported in the August issue of *Chemistry of Materials*, they used a solvothermal method to obtain nanocrystalline powders.

Cubic boron nitride is an attractive material for many applications due to its hardness, high thermal conductivity, and high-temperature stability. Unfortunately, the conventional synthesis of cBN from hexagonal BN requires extremely high temperatures and pressures (1200–2000°C and 2.5–7.5 GPa), which limits the possible batch sizes.

“But theory predicts that cBN should be stable at temperatures below 1300 K and pressures below 2 GPa,” said D.L. Cui, a professor at Shandong University. So his group investigated soft chemistry methods for the low-temperature and low-pressure synthesis of cBN.

Their process utilizes an anion exchange reaction between BBr_3 and Li_3N , using benzene as a solvent. The mixtures were heated for 8–12 h in a stainless steel autoclave at 480°C. The product was filtered, washed with water to remove the LiBr, and dried under vacuum at 80°C.

Transmission electron microscopy showed particles of nearly cuboidal shape and sizes of ~30 nm. Characterization by x-ray and electron diffraction and Fourier transformation IR spectroscopy revealed that the samples consisted of a mixture of different BN phases, with the cubic phase as the major one. Some hexagonal and orthorhombic BN were observed along with the cBN. The extracted lattice constants were in good agreement with liter-

ature values. The sample stoichiometry of B:N was confirmed by x-ray photoelectron spectroscopy. No oxide impurities could be detected.

Graduate student X.P. Hao said, “We are still trying to improve our synthetic methods. By now, we can prepare almost pure cBN at even lower temperatures, around 200°C, and pressures of 0.3–0.5 MPa.”

CORA LIND

Resorcinarene Promotes Self-Assembled Arrays of 2D Gold Nanoparticles

Chemists from Purdue University have developed a macrocyclic surfactant that enables gold nanoparticles in the mid-nanometer-size (10–200 nm) range to self-assemble into two-dimensional (2D) hexagonal close-packed arrays. As reported in the August 15 issue of the *Journal of the American Chemical Society*, the work demonstrates that particles as large as 170 nm can be dispersed at the air-water interface and organized into well-ordered monolayers when coated with resorcinarenes, a macrocycle with several hydrocarbon chains.

“Many nanostructured materials with mid-nanometer length scales have useful optical or magnetic properties, but are difficult to work with because of strong interparticle forces,” said researcher Alexander Wei, an assistant professor in the Department of Chemistry. “The resorcinarenes provide us with greater synthetic control for harnessing these materials into periodic structures with size-tunable properties.”

Wei’s research group has illustrated this point by measuring the arrays’ optical extinction properties, which were shown to vary dramatically as a function of periodicity. The arrays also exhibit strong and size-tunable surface-enhanced Raman scattering (SERS), the details of which will be published in *ChemPhysChem* later this year. The researchers are currently investigating the arrays for their potential as chemical sensors.

YUE HU

Organic LED Utilizes Flrpic for Efficient Blue Electrophosphorescence

A research team led by S. Forrest at The Center for Photonics and Optoelectronic Materials (POEM) at Princeton University has engineered an organic thin-film light-emitting device that will emit blue light using endothermic instead of conventional exothermic energy transfer. In order to create the energy transfer, the researchers used a 4,4'-N,N'-dicarbazole-biphenyl (CBP) conductive host

molecule doped with iridium(III)bis(4,6-difluorophenyl)pyridinato-N,C^{2'})picolinate, Flrpic. The researchers report in the September 3 issue of *Applied Physics Letters* that, “[t]o our knowledge, this is the first report of efficient blue electrophosphorescence.”

Although the researchers had prior success with red and green electrophosphorescent devices, they encountered a materials selection challenge due to the higher energy requirements of blue electrophosphorescence. Typically, the electrophosphorescence occurs when an exciton moves from a high energy state of the host molecule to a lower energy state on the phosphor, giving up energy in the process. However, the energy difference between the preferred host molecule and blue phosphors is not sufficient for luminescence via this conventional exothermic energy transfer. When investigating other potential host molecules, they found that a potential dichotomy existed between host materials with suitable high energy triplet states and host materials with appropriate energy level alignments with the other materials in the organic light-emitting devices (OLEDs). Consequently, the researchers pursued endothermic energy transfer in which the combination of applied current and existing thermal energy pushes excitons from the host molecule to the phosphor. They likely would not have achieved the same results without using a host molecule characterized by a very slow decay of its exciton.

The researchers grew OLEDs on a glass substrate precoated with a ~130-nm thick indium-tin-oxide (ITO) layer. Using a degreased and UV-ozone ambient cleaned glass/ITO substrate, the researchers grew the organic and metal cathode layers without breaking vacuum using an *in vacuo* mask exchange mechanism. After depositing the organic and metal cathode layers, the researchers encapsulated the device using a UV-epoxy resin under a nitrogen atmosphere. When describing the process, the researchers noted that, “[m]aintaining vacuum throughout the entire process is critical to attain high efficiencies.”

The researchers were able to achieve high photoluminescent efficiencies in several materials. However, to achieve the blue emission they sought, they had to introduce fluorine atoms and replace one of the ligands. Although the blue light emitted is not yet an exact match to the National Television Standards Committee (NTSC)-recommended blue for use in video displays, their ability to achieve wavelength shifts by creatively interchanging materials indicates that this material has the potential for an exact