

quency conversion and possibly to super-continuum generation, increasing the possibility to design nonlinear fibers for dedicated applications and potentially enabling the generation of single-cycle optical pulses in the visible.

IULIA MUNTELE

**Magnetostatic Energy May Explain Unusual Ferromagnetic Transition in Erbium**

Erbium metal exhibits unusual behavior at the ferromagnetic transition. The first-order transition between ferromagnetic (F) and antiferromagnetic (AF) phases near 19 K demonstrates superheating and supercooling as well as an unusual mechanism behind the phase change. In material with small amounts of impurity, the phase transition is resolved into at least four subtransitions apparently connected with metastable phases occurring within a range of about 2 K. C.S. Durfee and C.P. Flynn at the University of Illinois at Urbana-Champaign account for this phenomenon in terms of magnetostatics which favors transitions through ferrimagnetic intermediaries.

As reported in the July 30 issue of *Physical Review Letters*, some features of

the ferromagnetic nucleation in erbium can be explained by conventional methods. However, the researchers determined that the magnetostatic self-energy of the transformed nucleation droplet is enough to supercool the droplet to more than an order of magnitude greater than the observed 1 K. They report that this behavior indicates that nucleation of the erbium phase cannot occur by the normal process of spherical droplets. The researchers instead propose the use of spheroidal droplets of large eccentricity. In spite of the increased surface area (by ~200%) of the spheroidal droplet over that of the spherical droplet, the magnetostatic self-energy is greatly diminished, reducing the barrier to nucleation. These anisotropic shapes represent the preferred path for droplet growth during the nucleation process. The researchers found that for 1 K supercooling, the length of the critical droplet along its major axis is now an order of magnitude larger than expected; however, the magnetostatic energy is still far too big and requires an impossibly large supercooling.

The researchers believe the answer lies in the metastable states accessed during the F-to-AF phase transition and consider

ferrimagnetic intermediate (FI) phases, with 2, 4, or 6 spins aligned out of every 8. They believe this explanation offers a low energy route between AF (0 excess spins) and F (all 8 spins aligned) and that magnetostatics again plays a critical part. For the first ferrimagnetic phase the magnetostatic energy is reduced by a factor of 16 with a spheroidal droplet radius that has a surface energy 70% greater than a spherical nucleus. The barrier to nucleation for this FI droplet is now comparable with that of a spherical droplet in which the magnetostatic contribution is neglected. The researchers suggest that this explains the four-stage magnetic transition that has been observed.


JENNIFER BURRIS

**Volatile Metal Alkylamides Serve as Precursors for Vapor Deposition of High-Dielectric-Constant Gate Insulator Materials**

The speed and capacity of computers have been doubling every year or two, following Moore's law. These improvements in the power of microelectronics have been achieved largely by shrinking their dimensions. The smallest components in circuits are gate insulators,

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which are made of silicon dioxide only about 1.5-nm thick (about four atomic layers of SiO<sub>2</sub>). Further decreases in the thickness of the SiO<sub>2</sub> 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 SiO<sub>2</sub>.

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, HfO<sub>2</sub>(SiO<sub>2</sub>)<sub>x</sub>.

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  $\Delta n$  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