

Nanoscale Technique Prints Metal Films with Reusable Stamps and Tailored Surface Chemistry

Traditional nanolithographic techniques such as electron-beam or deep-UV nanolithography are limited to patterning small regions of specialized materials on rigid, ultraflat inorganic substrates. These restrictions are unacceptable for nascent applications in fields such as plastic electronics and biotechnology. Consequently, researchers are aggressively investigating alternative “soft lithography” methods, such as near-field phase-shift lithography, microcontact printing, and dip-pen lithography. In the July 15 issue of *Applied Physics Letters*, Y.-L. Loo and co-workers at Lucent Technologies described a nano-transfer printing (nTP) technique that is used to transfer metal films with features as small as 100 nm from the raised regions of a stamp onto substrates. This is reminiscent of woodcut printing, but on the nanometer scale. The high-resolution method is fast, can cover large areas, provides good adhesion, and is conducted under ambient conditions. Moreover, unlike its competing technologies, this soft lithography method is a one-step process and purely additive: It does not require any etching, resists, or post-patterning deposition.

The scientists produced rigid stamps by conventional patterning and etching of hard substrates such as glass or GaAs and created flexible stamps by casting a prepolymer of poly(dimethylsiloxane) (PDMS) in a patterned resist mold. They “inked” the stamp simply by evaporating the desired metal. Substrates can also be either rigid or conformal, and materials have included silicon dioxide and PDMS.

Intimate contact between the film and the substrate transfers the metal film through a common condensation reaction between hydroxyl (–OH) groups present on both surfaces. In order to accumulate the hydroxyl groups, the researchers applied either oxygen plasma or UV radiation to the native oxides.

This surface-chemistry restriction on the materials is not severe. Thus far, the researchers have successfully used nTP to print films of aluminum, whose surface spontaneously oxidizes, and, surprisingly, gold, after dusting it with titanium to obtain the requisite oxide layer.

“By exploiting other interfacial chemistries,” Loo said, “nanotransfer printing may be suitable for patterning a wide range of single- and multilayer conducting, dielectric, and semiconducting films.”

To appraise nTP’s potential application to plastic electronics, the scientists patterned

Au/Ti contacts and interconnects for organic transistors and complementary inverter circuits. The devices performed as well as top-contact devices fabricated with conventional shadow-mask gold electrodes.

RICHARD N. LOUIE

Diblock Copolypeptide Amphiphiles Form Rapidly Recovering Hydrogels

Protein-based hydrogels are used in a number of applications including drug delivery, tissue replacement, and cosmetics. Researchers at the University of California, Santa Barbara and the University of Delaware, Newark have synthesized diblock copolypeptides, composed of hydrophobic and hydrophilic domains, that form rigid hydrogels at very low concentrations (0.25–2.0 wt%). Gelation depends on the amphiphilic nature of the polypeptides as well as on the particular conformation of the hydrophobic domain. The porosity, thermal stability, and rapid recovery from network disruption make these materials attractive for a variety of biotechnological and biomedical applications.

As reported in a letter to *Nature* in the May 23 issue, a team led by University of California researcher Timothy J. Deming employed metal-mediated α -amino-acid N-carboxyanhydride polymerizations to control both the polypeptide chain lengths and composition of the amphiphiles. Poly(L-lysine-HBr) or poly(L-glutamate sodium salt), both highly charged polyelectrolytes at neutral pH, make up the hydrophilic blocks. The hydrophobic blocks are composed of poly(L-leucine) or poly(L-valine), which form rodlike α -helices and crystalline β -sheets, respectively. Copolypeptides of identical compositions to those that formed hydrogels but with random sequences did not form hydrogels at all.

Rheological measurements were made to investigate the nature of gel formation, the absolute strength of the gels, and the dependence of gelation on molecular parameters. The research team found that the hydrogels were one or more orders of magnitude stronger than an aqueous gelatin gel of the same weight percent. No visible thinning was observed up to 90°C; most protein gels generally start to dissolve at 60°C. No gelation occurs when the secondary structure (α -helix or β -strand) of the hydrophobic domain is precluded, either by incorporating a racemic mixture of amino-acid residues or simply by decreasing the degree of polymerization. This suggests that the self-assembly process is conformation-specific, similar to protein assembly, the

research team said. The addition of salt—for example, 25 mmol NaCl—weakens the gels, presumably through charge-screening of the polyelectrolytes. After large-amplitude oscillations were applied to break down the gel structure, recovery was probed by measuring the storage and loss moduli in the linear, small-deformation regime as a function of time. After about 10 s, the hydrogels recovered 80–90% of their strength, followed by a slower reorganization, after which the full initial storage modulus was restored. The researchers attributed this rapid recovery to the relatively low molecular mass of the copolypeptides, which enables them to reorganize quickly.

Gel morphology was visualized using cryogenic transmission electron microscopy (CTEM) and laser scanning confocal microscopy. Hydrogel formation appeared to coincide with the intergrowth of microscopically phase-separated domains of 1–25 μ m in size. CTEM visualization of the vitrified gel domains revealed a complex membrane assembly responsible for network formation at the nanoscale level. Gel porosity was verified with microrheological experiments, in which the Brownian motion of micrometer-sized tracer particles dispersed in the sample was measured. In a (L-lysine-HBr)₁₆₀(L-leucine)₄₀ gel, 0.5- μ m tracer particles diffused freely, while the motion of 1.0- μ m particles was restricted, which is taken as a measure of the lower size limit of the voids. This microscopic heterogeneity persisted after prolonged standing, heating, centrifugation, and bulk shear.

The researchers said that the very low mass fractions in these polypeptide gels, together with their microporous structure and recovery properties, may allow them “to fill...[a] unique niche between conventional polymer and surfactant hydrogels.” These gels also possess the “advantageous features of proteins, such as degradability and functionality, which [make] them attractive for biomedical applications,” said the researchers.

STEVEN TROHALAKI

Anode-Supported SOFC Performs Well at Intermediate Operating Temperatures with a Lanthanum Ferrite-Based Cathode

A group of researchers at Pacific Northwest National Laboratory in Washington has fabricated a strontium-doped lanthanum ferrite cathode that has a comparable performance with typical cathode materials, but at intermediate temperatures of 650°C to 750°C. A typical solid-oxide fuel cell (SOFC) configuration

employs a yttrium-stabilized zirconia (YSZ) electrolyte, kept thin (5–10 μm) to reduce ohmic losses at lower temperatures and supported by a planar Ni-YSZ anode (0.5 mm thick). However, cell performance of such SOFCs may suffer at intermediate temperatures because of the reduced electrochemical activity of the cathode. Researchers S.P. Simner, J.F. Bonnett, N.L. Canfield, K.D. Meinhardt, V.L. Sprenkle, and J.W. Stevenson investigated the use of La-ferrite and La-nickelate cathode compositions, rather than the much-researched La cobaltite, to facilitate matching of the coefficients of thermal expansion (CTEs) between the cathode and other cell components (thus enhancing thermal cycling characteristics) and to reduce chemical interactions. Cobaltites are well known for their high CTE and reactivity with YSZ to form electrically insulating zirconate phases.

As described in the July issue of *Electrochemical and Solid-State Letters*, the researchers prepared $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (LSF-20), $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSFN-3020), and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF-6040) in addition to a mature interlayer material, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC-20) to be incorporated between the cathode and YSZ electrolyte. Sintering temperatures were optimized for each cathode: LSF-20 (1150°C for 2 h), LNF-6040 (1200°C for 2 h), and LSFN-3020 (1150°C for 2 h). Power densities were based on a screen-printed cathode with a diameter of 22 mm. Current-collection was achieved by the use of screen-printed platinum grids with embedded platinum gauze for the cathode and screen-printed NiO grids with embedded Ni gauze for the anode.

Despite its lower electrical conductivity, as compared with LNF-6040 and LSFN-3020, LSF-20 exhibited the highest cell performance at each temperature (850–950 mW/cm² at 750°C and 0.7 V). The researchers suggest that possible reasons for this result might be that LSF-20 has a greater activity for the reduction of oxygen or that its finer grain size can catalyze the reduction of oxygen through greater surface area. An interesting observation, unresolved at this time, is a power-density performance increase during the first 40 h of operation that levels off by 200 h and remains constant after that until the end of the test at 300 h. CTEs for the new cathode materials showed that LSF-20 had the best match with the anode while the others had slightly higher values. Thus, LSF-20 shows comparable performance to higher-temperature cathodes while resisting cell delamination by matching the CTE of the anode.

DONALD CARTER

Magnesium Diffusion in Silica Enhanced by Na and Retarded by Al

Silica-forming ceramics can be beset by certain cations present in the ceramics either as impurities or as sintering additives. Both alkali and alkaline-earth cations are known to break the silica network structure, allowing nonbridging oxygen anions to form, thereby weakening the silica network. For example, researchers have learned that in NBD 200 silicon nitride, a commercial ball-bearing ceramic pressed with ~1 wt% magnesia, sodium impurities are responsible for increased oxidation, compared with other sodium-free magnesia-containing silicon nitrides.

Aluminum surface alloying by implantation results in a marked improvement in oxidation resistance in the NBD 200. This may be due to the ability of intermediate cations (including aluminum) to convert non-bridging oxygen anions back to bridging ones. Consequently, Priya Mukundhan and Henry Du at Stevens Institute of Technology, and Stephen Withrow at Oak Ridge National Laboratory, have implanted fused silica platelets with combinations of sodium, magnesium, and aluminum at room temperature to definitively study their interactions.

As reported in the June issue of the *Journal of the American Ceramic Society*, the

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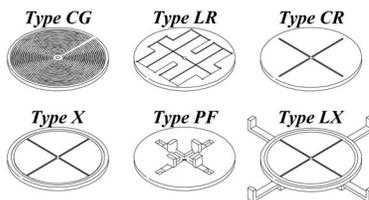
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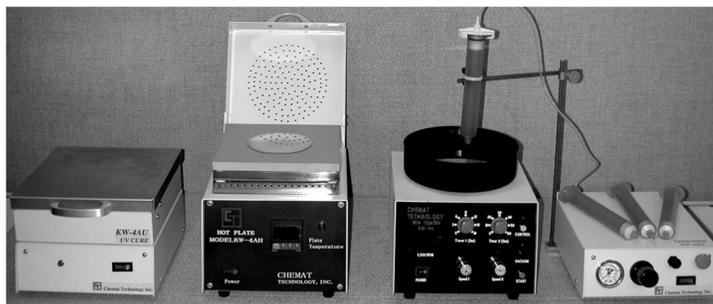
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researchers annealed the samples in 1 atm flowing oxygen at 900°C. Following the implantation with one, two, and then all of the elements, secondary ion mass spectrometry depth profiles were taken of both the annealed and unannealed samples. The researchers found that when magnesium was implanted on its own, it did not diffuse after annealing. They also found that the magnesium moved most when it was co-implanted with just sodium, and less when aluminum was also implanted. The researchers said, "These findings corroborate the roles of sodium, magnesium, and aluminum in the oxidation behavior of NBD 200 silicon nitride ceramic."

PAMELA JOHNSON

Protein Promotes Nucleation in Water Microdroplets

Ice crystallization in micro-sized water droplets plays an important role in nature. Researchers at the National University of Singapore have made a quantitative measurement of the interfacial effect of impurities on ice nucleation kinetics. Using microdroplet suspension to minimize the effects of the container and foreign particles, Du Ning and X.Y. Liu found that the protein lysozyme promotes freezing as a result of its effects on the interfacial kinetics of nucleation. The crystallization of microdroplets has significant implications for natural processes or systems such as climatic systems and the freezing and antifreezing processes within plants and animals.

As described in the July 15 issue of *Applied Physics Letters*, a 0.4- μ l droplet of deionized water was suspended between two layers of oil of different densities. To study the nucleation kinetics, the researchers measured the amount of time it took for an observable amount of the new phase to appear at several different temperatures. This induction time included both the time for crystals to nucleate and the time for them to grow to an observable size. However, because ice crystals grow much faster than they nucleate, the growth time can be neglected, and the time measured in the experiment was considered to be the nucleation time only.

At a constant nucleation rate, a smaller water droplet has a longer induction time. In bulk water, a small change in volume during the experiment has a negligible effect, since the total volume is so large. However, for microdroplets, the change in volume can double the induction time. The researchers included the size effects by multiplying the induction time by the volume of the water droplet, allowing a precise and reproducible measurement of the nucleation kinetics. The effects of pro-

teins on ice nucleation kinetics was also studied. The researchers found that the addition of lysozyme at 0.05 wt% to the droplets had two effects. First, it raised the energy barrier for removing impurity molecules from the surface, which inhibited nucleation. Second, the lysozyme decreased the interfacial free energy. This made the nucleation time increase less rapidly with the supercooling temperature and promoted nucleation. Because this latter effect is dominant, the net effect of the lysozyme is to promote nucleation.

ELIZABETH A. SHACK

Possibility of the Formation of Mesostructured Silica Titania Mixed-Oxide Thin Films with High Titania Load Demonstrated

The ability to prepare mesostructured thin films is a prerequisite to the implementation of many technological applications such as sensors, catalysts, and microelectronics. A group of researchers at the Institute of Materials Chemistry within the Vienna University of Technology, Austria, and the Advanced Materials Laboratory at the University of New Mexico has developed a method for the morphology-controlled synthesis of mesostructured silica titania mixed-oxide thin films with a high titanium load (Si:Ti ratio as high as 5:1) and good distribution of titanium atoms in the silica pore wall.

As reported in the June 17 issue of *Chemistry of Materials*, Nicola Hüsing of Vienna and co-workers used a titanium-coordinated surfactant as a structure-directing agent in their rapid and continuous technique for the formation of mesoporous silica titania mixed-metal-oxide thin films. The underlying principle is based on the evaporation-induced self-assembly of a modified amphiphile in combination with simultaneous sol-gel processing of the inorganic species. The researchers used the hydrophilic head group of oligo(ethylene oxide) alkyl ether surfactants {Brij56 [C₁₆H₃₃(OCH₂CH₂)₁₀OH]/Brij92 [C₁₈H₃₅(OCH₂CH₂)₂OH]} for coordination to the titanium alkoxide. The thus-modified surfactant performs two essential functions, acting as both a structure-directing agent and a coordinating ligand to lower the reactivity of the titanium alkoxide.

Deposition of the thin films was performed by a dip-coating method from the sol. After calcination at 450°C for 3 h, transparent, crack-free, and optically uniform silica titania films with a thickness of 200–250 nm were obtained. The researchers confirmed a well-defined, ordered structure and a good distribution of tetrahedrally coordinated titanium

atoms in the silica pore walls by low-angle x-ray diffraction, transmission electron microscopy, and UV- and Fourier transform infrared spectroscopy.

The researchers examined the thermal stability of the films in the temperature range of 450–1000°C. After annealing at temperatures above 450°C, amorphous titania converts to anatase and, later on (at 800°C), to rutile. The research team concluded that the proposed approach opens the way to a variety of mesostructured mixed metal oxides.

ANDREI A. ELISEEV

Spontaneous Emission from CdSe/CdS Core-Shell Quantum Dots Modified in the Presence of a SiO₂/Si Interface

The ability to precisely control the optical and electronic properties of nanomaterials by simply changing their size has led to potential application of these materials in areas such as biological chips, solar-energy conversion, catalysis, and light-emitting diodes. The desire for greater understanding of the properties of these unique materials has spawned further research. A group of researchers led by Min Xiao in the Department of Physics at the University of Arkansas has demonstrated a method to control the photoluminescence (PL) intensity of CdSe nanocrystals by adjusting their position with respect to a SiO₂/Si interface. They studied the spontaneous-emission lifetime of CdSe/CdS core-shell quantum dots as a function of distance between the dots and a polished Si surface. The researchers observed a damped oscillatory behavior in the lifetime of the PL as the separation distance between the nanomaterials and the surface was increased. According to Xiao, "Control of spontaneous emission from semiconductor structures may be useful in future applications of optoelectronic devices."

As described in the July 15 issue of *Optics Letters*, the researchers used CdSe nanocrystals, 4 nm in diameter and passivated with a CdS shell, to increase the PL efficiency of the materials. The nanomaterials were added to a solution of poly(methyl methacrylate) and spin-coated onto a layer of SiO₂ thermally grown on a silicon wafer. The thickness of the SiO₂ layers was varied between 20 nm and 400 nm. The researchers then excited the CdSe film with 400-nm laser radiation and measured the PL intensity decay at 605 nm through the use of a time-correlated photon counting system.

The researchers found that the spontaneous-emission lifetime showed a damped oscillatory dependence on the separation distance between the nano-

material film and the SiO₂/Si interface. The researchers said that the interface causes this behavior in two ways. First, the interface reflects some of the PL radiation, producing constructive and destructive interference between the directly emitted and reflected radiation. The PL intensity increases (and lifetime decreases) for samples in which the thickness of the SiO₂ layer allows mostly constructive interference. The opposite is true when destructive interference predominates. Second, the interface causes a damped oscillatory fluctuation in the local density of the optical modes that, in turn, has the same effect on the PL intensity and lifetime. This semiconductor-interface-induced optical-mode density fluctuation has been predicted by quantum mechanical calculations and previously observed for single-atom emitters.

GREG KHITROV

Single-Phase Ba₂Ti₉O₂₀ Fabricated after Addition of 5% B₂O₃

The compound Ba₂Ti₉O₂₀ is known for its good microwave properties, including a high-dielectric constant. Synthesis of Ba₂Ti₉O₂₀ by solid-state reaction is a challenging procedure because of the likelihood of the formation of intermediate stable compounds and of decomposition in different phases. Different techniques have been developed to obtain single-phase Ba₂Ti₉O₂₀, including the use of solid-state additives, chemical methods such as sol-gel fabrication, and the addition of precursors. Among other additives, B₂O₃, known for improving dielectric properties and optimizing sintering conditions in other materials, is a common addition in electronic glass applications. For these reasons, it was chosen by a group of scientists from the National Taipei University of Technology and the National Taiwan Ocean University as a solid-state additive in the fabrication of Ba₂Ti₉O₂₀, as they described in the June issue of the *Journal of the American Ceramic Society*.

S.-F. Wang of Taipei and co-workers started the fabrication of Ba₂Ti₉O₂₀ from powders of 81.8% TiO₂ and 18.2% BaO. After mixing in methyl alcohol for 6 h, the powders were dried and then calcined at 1000°C for 8 h. At this point, x-ray diffraction (XRD) analysis detected two phases: BaTi₄O₉ and BaTi₅O₁₁. Powders were then mixed again with different additions of B₂O₃ in methyl alcohol for 8 h. Further mixing with 3.5 wt% of a 15% poly(vinyl alcohol) solution allowed the fabrication of disks that were later sintered at different temperatures for 6 h. A liquid-displacement method permitted the measurement

of the density of the resulting materials. Powders with 5% addition of B₂O₃ showed a higher density after sintering at temperatures below 1100°C, as compared with the material without additive.

Results after differential thermal analysis show that the material with 5% B₂O₃ has an endothermic peak at 840°C. At this temperature, B₂O₃ forms a liquid eutectic that enhances the densification process. At temperatures higher than 1100°C, evaporation of B₂O₃ precludes the increasing densification, as compared with the material without B₂O₃ addition. Comparing results from XRD analysis, the material without B₂O₃ addition revealed the presence of BaTi₄O₉ and Ba₂Ti₉O₂₀. In the case of the material with 5% B₂O₃, only Ba₂Ti₉O₂₀ was detected after sintering at temperatures as low as 900°C.

For additions of up to 10% B₂O₃, XRD revealed the formation of BaTi(BO₃)₂ and TiO₂ after sintering at temperatures below 1200°C. At higher temperatures, BaTi(BO₃)₂ decomposed and its product BaTiO₃ combined with TiO₂ to form Ba₂Ti₉O₂₀.

SIARI S. SOSA

Low-Temperature 2D-to-3D Transition in Layered Metals Correlates with the Presence of Coherent Quasi-Particles within the Layers

The transition between metal and insulator is of particular interest when materials with reduced dimensionality exhibit two- or one-dimensional characters within a three-dimensional system. Using electronic-transport measurements and angle-resolved photoemission, researchers at Brookhaven National Laboratory, the University of Connecticut, Princeton University, and Osaka University have explored the behavior of 2D metals that change to 3D materials at low temperature and proposed new means for understanding this behavior. Their findings were described in the June 6, 2002, issue of *Nature*.

In their letter, T. Valla and co-workers suggest that the crossover from full to reduced dimensionality is correlated with the presence or absence of coherent quasi-particles within the layers of the material. The researchers studied the layered metallic materials (Bi_{0.5}Pb_{0.5})Ba₃Co₂O₇ and NaCo₂O₄ that become effectively 3D materials at low temperatures, below the crossover temperature of ~100–200 K.

The technique of angle-resolved photoelectron spectroscopy (ARPES) employed in this study has the advantage of directly measuring the single-particle spectral function that appears in the equation describing conductivity. It also is able to

investigate deeper states, unlike transport probes, which may be crucial to understanding higher-temperature behavior. Valla and co-workers observed a dramatic correlation between dimensionality crossover and measured features of the spectral function measured by ARPES. A sharp quasi-particle peak is apparent in the low temperature 3D state and broadens and disappears as the temperature increases and the system becomes effectively 2D.

Although the researchers speculate that a variety of competing mechanisms may play greater or lesser roles in effecting the crossover to the 3D ground state, the proposed importance of coherent quasi-particles provides new insight into this phenomenon. Valla said, "The existence of quasi-particles has been at the core of our understanding of transport phenomena in solid-state materials for decades and the behavior observed in this work points toward the necessity of modifying the conventional picture."

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