

tate mass transport while smaller pores increase the surface area, are of great interest for electronics, catalysis, and sensors. However, synthesis of these materials remains a challenge. G.W. Nyce and colleagues from the Lawrence Livermore National Laboratory have reported the synthesis of ultralow-density gold monoliths with multimodal pore structure by combining templating and dealloying techniques, as reported in the February 6 issue of *Chemistry of Materials* (p. 344; DOI: 10.1021/cm062569q).

The researchers electrolessly deposited gold on polystyrene (PS) beads (10 μm and 1 μm) in the presence of the stabilizer poly(vinyl pyrrolidinone) (PVP) to favor growth of individual gold particles, 100–150 nm in size. They then isolated the gold-covered PS beads, re-dispersed them in distilled water, and casted them to create a PS-gold monolith by depositing the PS/Au particles in a plaster of paris mold to remove water slowly from the suspension. The relative polydispersity of the particles, high suspension concentration, and high rate of sedimentation resulted in randomly packed PS/Au spheres with void spaces among them. After that, the researchers prepared $\text{Ag}_{0.85}\text{Au}_{0.15}$ and $\text{Ag}_{0.7}\text{Au}_{0.3}$ alloys by electroless deposition of silver on the PS/Au spheres, varying the gold and silver mole ratios during plating conditions. Casting the Ag/Au PS beads and heating the monolith in an inert atmosphere at 400°C removes the PS template and alloys the Ag/Au layers, creating large cylindrical $\text{Ag}_{0.85}\text{Au}_{0.15}$ monoliths with densities of 0.8 g/cm^3 . The monoliths are composed of hollow homogeneous $\text{Ag}_{0.85}\text{Au}_{0.15}$ shells, roughly of the same size as the original PS bead template, but with 23% less mass. The dealloying process to remove the Ag proceeded by introducing a dilute nitric acid solution into the monolith and slowly increasing the concentration of nitric acid. The monoliths were then washed in distilled water to remove residual nitric acid, placed in acetone to remove water completely, and dried by supercritical CO_2 extraction ($T_c = 31.1^\circ\text{C}$, $P_c = 7.4 \text{ MPa}$).

The cylindrical gold monoliths were 0.45 cm in diameter and 0.8–1-cm high, with densities of 0.28 g/cm^3 , surface areas of 1.48 m^2/g , and composed of dealloyed hollow spheres ~9.6 μm in diameter and a nanoporous shell 200-nm thick. The researchers observed little volume changes during template removal and dealloying/drying steps.

The generality of this approach to prepare other hierarchical metallic porous materials is being investigated by the research team to develop new alterna-

tives to traditional powder/slurry catalysts that could be reused, minimizing environmental waste.

JOAN J. CARVAJAL

Patterned Silicide Nanowires Grown without Metal Catalysts

Fabrication of functional nanoelectronic devices requires manipulation or assembly of nanowires. Typical *in situ* patterning techniques distribute in a pattern metal nanoparticles that catalyze nanowire formation. By using a very different approach, A.L. Schmitt and S. Jin of the

University of Wisconsin–Madison have recently demonstrated patterned FeSi nanowire growth without the use of metal catalysts. The researchers said that FeSi “is particularly fascinating as the only transition metal compound Kondo insulator,” has “highly-correlated electrons,” and “forms a silicon-based magnetic semiconductor alloy” ($\text{Fe}_{1-x}\text{Co}_x\text{Si}$). Patterned nanowires made from these silicides would be an important step toward silicon-based nanospintronics devices.

As reported in the January 23 issue of *Chemistry of Materials* (p. 126; DOI:

Cost-Effective Portable Spin Coater



Two-Stage Spinning

Dispense liquid during Stage 1
Spin-up and flatten during Stage 2

Adjustable Speed

Stage 1
500 to 2500 rpm
2 to 18 seconds

Stage 2
1,000 to 8,000 rpm
3 to 60 seconds



Type CG



Type LR



Type CR

Vacuum Chucks

Wide Range of Vacuum Chucks Available To Hold Different Substrates in KW-4A Spin Coater

KW-4A SERIES PRODUCT LINE



UV Curer
KW-4AC



Hot Plate
KW-4AH



Spin Coater
KW-4A



Dispenser
KW-4AD





CHEMAT TECHNOLOGY, INC.
9036 Winnetka Avenue, Northridge, CA 91324
1-800-475-3628, Fax: 818-727-9477
website: www.enlabproducts.com; www.chemat.com
email: marketing@chemat.com

10.1021/cm0621161), Schmitt and Jin used standard photolithography and acid etching to produce silicon substrates covered mostly with a 100-nm layer of SiO₂ but with a periodic array of holes covered in a thin oxide layer of 1–2 nm. The researchers used optical and atomic force microscopies to characterize the substrate. They have previously shown that chemical vapor deposition of a precursor—*trans*-Fe(SiCl₃)₂(CO)₄—over silicon substrates covered with a thin (1–2 nm) layer of silicon oxide allows the growth of FeSi nanowires without the use of metal catalysts. Now with silicon substrates covered with both thin (1–2 nm) and thick (100 nm) oxide, FeSi nanowires can be grown selectively in the holes where the oxide is thin. The researchers hypothesize that the thin oxide layer promotes one-dimensional silicide growth and concomitantly restricts thick-film formation. They said that oxide thickness will also be critically important to the growth of other silicide nanowires.

As shown with scanning electron micrographs, nanowires can be selectively grown in arbitrary patterns by employing various photomasks and the sizes of the patternable nanowire islands range from several micrometers to hundreds of micrometers with pitches ranging from 10–100 μm. Only a handful of nanowires grow in the smallest patternable feature, ~4 μm. The researchers said that their method “will allow for the patterning of many other transition metal silicide nanowires” and “the ability to selectively grow nanowires in controlled locations is important for applications such as biological nanosensing, optical-electronic detection, light-emitting diodes, and field-emission displays.”

STEVEN TROHALAKI

Large Arrays of Organic Semiconductor Single Crystals Fabricated

Organic single crystals have served as excellent materials for fabricating field-effect transistors that show very good device performance relative to corresponding organic thin-film transistors. These transistors have significant potential for applications such as active matrix displays and sensor arrays. They are also ideal for characterizing charge transport characteristics of the materials. However, forming large arrays of separate devices using organic single-crystal materials has proven to be a challenge.

A.L. Briseno (Stanford University and the University of California, Los Angeles), Z. Bao (Stanford University), R.J. Tseng (University of California, Los Angeles), and their colleagues have developed a

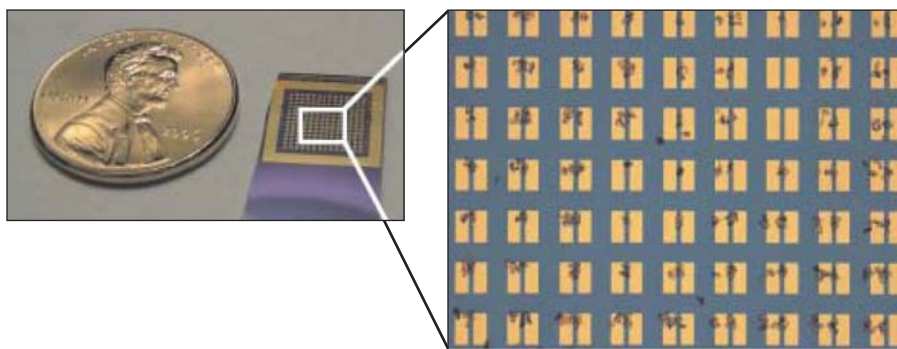


Figure 1. Optical micrograph of arrays of functional single-crystal transistors produced by printing films of OTS domains onto arrays of source–drain electrodes, followed by growth of organic single crystals in the printed domains. Reproduced with permission from *Nature* **444** (7121) (December 14, 2006) p. 913; DOI: 10.1038/nature05427. ©2006 Nature Publishing Group.

method for easily fabricating large arrays of a variety of organic single-crystal materials directly onto transistor source–drain electrodes. They have used microcontact-printed regions of octadecyltriethoxysilane (OTS) as controllable nucleation sites for the vapor-grown organic single crystals (see Figure 1). They report their results in the December 14, 2006, issue of *Nature* (p. 913; DOI: 10.1038/nature05427).

In the method developed by the researchers, thick OTS films (~13±2 nm) are printed by microcontact printing onto a clean SiO₂/Si substrate using a polydimethylsiloxane (PDMS) stamp with a relief structure in the desired pattern. Single crystals of the appropriate organic materials are then grown on the OTS-printed areas using a vapor transport method. The materials grown include a broad range of organic crystals including high-mobility *p*-type materials such as rubrene, pentacene, and tetracene, as well as *n*-type materials including C₆₀, fluorinated copper phthalocyanine, and tetracyanoquinodimethane. In the case of pentacene, for example, crystal growth was achieved in as little as 5 min. with crystal growth restricted to the OTS-stamped regions. The growth of discrete crystals was achieved by controlling the feature size of the printed OTS regions such that only one crystal nucleation event was supported.

Furthermore, the researchers demonstrated crystal nucleation and growth of large arrays of rubrene and pentacene crystals directly onto transistor source–drain electrodes. In several cases, a single crystal was seen to bridge the channel region between each pair of source and drain electrodes. More than 99% of the devices with at least one crystal bridging the drain and source electrodes exhibited a

field effect. In one case, random testing of 22 devices in a 14 × 14 rubrene-based transistor array yielded an average saturation regime mobility of ~0.6±0.5 cm²V⁻¹s⁻¹ with on/off ratios greater than 10⁷, which are comparable to those of amorphous silicon transistors and high-performance organic thin-film transistors. In addition to the rigid SiO₂/Si substrates, the method was also demonstrated for flexible polyimide and poly(ethylene terephthalate) (PET) substrates. It was shown that these patterned single-crystal transistors on flexible substrates could endure strenuous bending, which makes them potentially useful in flexible electronics applications.

The study also investigated the mechanisms of organic single-crystal formation and the selectivity achieved was attributed primarily to the high roughness of the thick OTS-stamped film. This view was supported by atomic force microscopy observations showing a much higher rms roughness for the stamped OTS regions than for the bare SiO₂ regions. The researchers said that this view is in agreement with classical nucleation theory as well as “modern phase field theory, which similarly predicts heterogeneous nucleation to favorably occur on rough surfaces.” The use of a high substrate temperature, only about 20°C lower than that of the evaporation source, was also useful, resulting in a higher thermal redesorption rate in the bare SiO₂ surface, suppressing crystal nucleation. The researchers are currently exploring the use of a combined nucleation/alignment layer in order to control the orientation and alignment of the crystals in addition to the nucleation location and nucleation density.

GOPAL RAO