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Nanopatterning of Functional Solid Structures by Dip Pen Nanolithography

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Dip-pen nanolithography (DPN) is an exciting new development for the nanopatterning of molecular and inorganic functional structures. DPN can generate nanostructures at specific location through the controlled motion of an ink-coated atomic force microscope (AFM) tip. Until recently, the materials that can be directly patterned by DPN were limited to some small organic molecules due to stringent restrictions on the solubility, stability, adsorption and transfer properties of the inks that can be used. We have developed a new method for direct nanopatterning of a variety of solid nanostructure using appropriate sol precursor as DPN inks [1]. Considering the versatility of sol-gel process in preparing virtually any functional solid materials, our method opens many new opportunities for using these technically important materials at the nanometer scale. As an example, semiconductor nanodisk sensors are created by the site-specific DPN using sol inks of tin oxide. The intimate ohmic contact between the sensor element and the measurement electrode makes the method ideal for the sensor application. These sensors have short response time to chemical gases and recover quickly, and can recognize different gases when fabricated into an array. All these characteristics and their compact size are important to the on-site real-time detection of life-threaten gases.

The versatile DPN sol-inks are prepared by dissolving block copolymer surfactant, tin chloride and other metal salts in ethanol. The sol-to-gel transition happens when tin chloride hydrolyses inside the water meniscus formed between the gap of an AFM tip and the substrate in ambient environment (Figure 1). Proof-of-concept experiments on the nanopatterning of Al_2O_3, SiO_2 and SnO_2 are shown in Figure 2. Dots and lines at sub 200 nm-scale can be patterned routinely on both conductive and non-conductive substrates. Heat treatment (400°C, 2 hrs) removes the polymer surfactant and leaves only the inorganic composition. A SnO_2 nanodisk (height of 32 nm) is formed between measurement electrodes by holding an ink-coated tip at the same location for 30 s (Figure 3A). Energy dispersive X-ray analysis confirms its chemical composition as expected. AFM image of a spin-on thin film that is prepared using the same sol ink shows nanochannels (diameter of 100 nm) normal to the film. Transmission electron microscope image of a bulk sample after heating shows the existence of many nanopores (Figure 3B).

The current vs voltage curves of a SnO_2 nanodisk sensor are measured in air from 200°C to 300°C. The linear relations indicate intimate ohmic contacts between the nanodisk and electrodes, which are the results of the good flow ability of sol and the chemical bonds formed between the nanodisk and electrodes. The resistances of the nanodisk depend on the concentration of surface adsorbed oxygen ions. Thermal desorption of oxygen ions reduces the resistance of the nanodisk, and constitutes the basis for a miniaturized thermometer.

A significant character of the nanodisk sensors is their short response time and recovery time in gas detection: for 330 ppm acetic acid vapor, the resistance reaches minimum in 5 s, and recovers to its original value in 20 s (Figure 4A). A thin film sensor has a response time of 200 s and a recovery time of 700 s to 500 ppm acetic acid at 280 ℃ [2]. The response and recovery time to 200 ppm NO_2

are 20 s and 65 s (Figure 4B), which are much shorter than those of carbon nanotube and thin film sensors [3]. The fast response and recovery are due to the small sizes and well-developed channels.

Normal semiconductor sensors cannot discriminate different gases. We have created a sensor array with eight differently doped nanodisk sensors on a single chip (SnO_2, Ti-SnO_2, Co-SnO_2, Ni-SnO_2, Cu-SnO_2, Zn-SnO_2, Cd-SnO_2 and Pt-SnO_2). The molar ratios of the promoters to Sn are controlled at 0.05. A 5 µl liquid droplet of organic chemical is injected to produce a contaminated environment at 300 ºC. The sensor response to a certain gas is not the same due to the different reactivity of the gas on each sensor. The diversity in response pattern of each gas on the array constitutes the fingerprints that can be used to recognize different gases based on the same principle as that of olfactory system. Thus the DPN and sol-gel based nanopatterning approach has great potential for niche technological applications and a scientific basis for further studies.

References

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[2] C. Cobianu et al., Sens. Actuators B 77 (2001) 496.
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FIG. 1

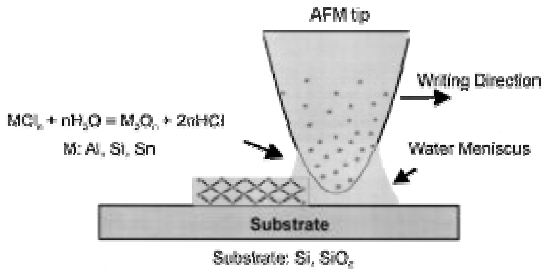

FIG. 2

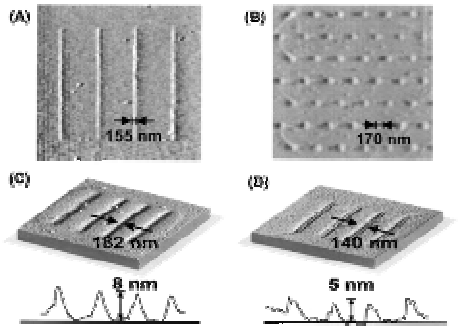

FIG. 3

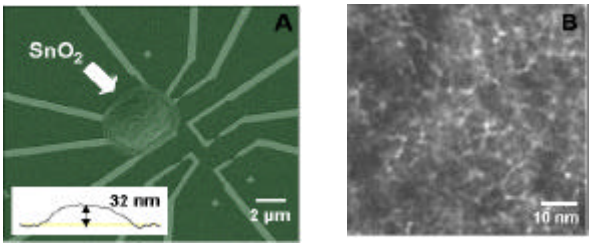

FIG. 4

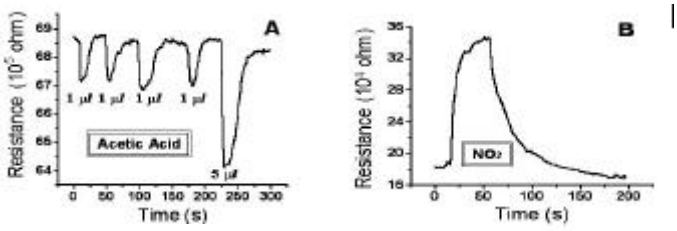

FIG. 1. Scheme of dip pen nanolithography using sol-based inks.
FIG. 2. Nanopatterning of solid materials. SnO_2/polymer nanolines (a), Al_2O_3/polymer nanodots (b), SiO_2/polymer nanolines before (c) and after (d) heat treatment.
FIG. 3. SEM image of a SnO_2 nanodisk sensor on electrodes and a section profile of an AFM image (a), TEM image a bulk SnO_2 sample after heat treatment at 400°C for 2 hours(b).
FIG. 4. Sensing responses to different concentration of acetic acid vapor(A) and 200 ppm NO_2.

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