

ADVANCED MATERIALS

Reprint

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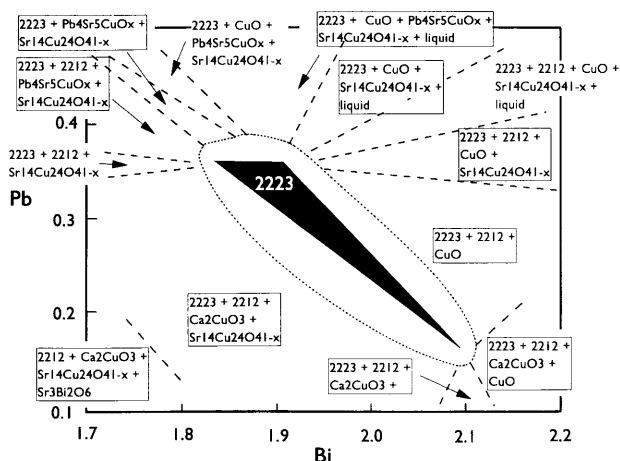


Fig. 5. Schematic section through the 2223 region of homogeneity at 850 °C including surrounding phase regions.

equilibrium with 2212, Ca_2CuO_3 , $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41-x}$, CuO , 451 phase^[19-21] and a liquid, the maximum number of about 56 of two, three, four, and five phase regions are surrounding the 2223. However, the actual number of phase regions is possibly lower than 56, since several four and five phase regions, which theoretically could exist, are not present. However, all two and three phase regions capable of existing are believed to be present, as they can be constructed by considering the observed four and five phase regions. Therefore, by adding together the maximum amount of two and three phase regions and the observed four and five phase regions (Table 2), the minimum number of 37 phase regions are surrounding the 2223 phase within a very narrow concentration range, not considering the phase equilibria of the Ca rich 2223 phase involving Ca_2PbO_4 instead of 451.^[22,23]

Experimental

Samples were prepared by the conventional solid state synthesis route starting from 99.9 % pure oxides (Bi_2O_3 , PbO , CuO) and carbonates (CaCO_3 , SrCO_3). The powders were weighed and intimately mixed in an agate mortar. The calcination was performed in three steps: 12 h at 750 °C, 24 h at 780 °C, and 12 h at 800 °C. This careful calcination is necessary to avoid liquid formation during heating to the sintering temperature, which is due to the eutectic reaction of Bi_2O_3 and CuO at about 706 °C [15]. After calcination, the powders were again ground, pressed into small cylindrical rods and sintered for 60 h in air at 850 °C. The sintering step was repeated after an intermediate grinding and pressing step to assure complete homogenization. In order to determine the extension of the 2223 single phase region, 2223 samples with different compositions which are single phase at 850 °C were annealed at higher and lower temperatures for several days.

Phase identification was performed by optical microscopy using polarized light (Zeiss Axiomat); X-ray diffraction using CuK_α radiation (Siemens D5000) and the JCPDS standard data, or sometimes in-house standards and EDX analyzes (Cambridge S200 operating at 20 kV). Due to the overlap of Bi-M and Pb-M lines in EDX, wavelength dispersive X-ray (WDX) analyzes were necessary for the accurate determination of the Bi and Pb content.

Received: April 1, 1996
Final version: May 10, 1996

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Shadowed Sputtering of Gold on V-Shaped Microtrenches Etched in Silicon and Applications in Microfabrication**

By Younan Xia and George M. Whitesides*

Silicon micromachining has a wide range of applications in microelectronics, integrated optics, and microelectrical mechanical systems.^[1] For example, V-shaped microtrenches etched in single crystal Si(100) have been used as surfaces for topographically controlled growth of cells,^[2] as

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[**] This work was supported in part by ONR and ARPA. This work made use of MRSEC Shared Facilities supported by NSF (DMR-9400396). The SIMS analysis was carried out by Judy Baker at the Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign, which is supported by the U. S. Department of Energy under grant DEFG02-91-ER45439.

capillary channels for capillary electrophoresis (CE on a chip),^[3] and as diffraction gratings or beam splitters.^[4] For the first two applications, chemical modification of the surfaces is usually required in order to control their properties. For the third, microfeatures having more complex relief structures than V-shaped microtrenches are usually desired in order to optimize the efficiency of the device.^[5] Here we describe the use of a combination of several techniques—shadowed sputtering,^[6] microcontact printing (μ CP),^[7] micromolding in capillaries,^[8] and selective wet etching—in modifying the surface properties of V-shaped microtrenches etched in single crystal silicon, and as part of a methodology for fabricating surface relief structures having complex topologies on silicon substrates.

Shadowed sputtering (or angled evaporation) is a widely used technique for fabricating micro- and nano-structures of semiconductors, metals, and superconductors. Microcontact printing is a convenient technique for generating patterned self-assembled monolayers (SAMs)^[9] on the surfaces of Au, Ag, Cu, and Si/SiO₂.^[10–13] Patterned features with sizes of 0.5 μ m and larger can be produced routinely using this technique; with some difficulties, features with sizes of \sim 100 nm have also been fabricated.^[14] Two configurations have been used in μ CP. In one, an elastomeric stamp (usually made from poly(dimethyl)siloxane, PDMS) whose surface has been patterned with a relief structure is used to form patterned SAMs on a planar surface.^[10] In the second, a flat PDMS stamp is used to derivatize the raised areas of a non-planar surface with SAMs.^[15]

Figure 1 outlines schematically the procedure we have developed. A combination of μ CP with hexadecanethiol and selective wet etching in aqueous ferricyanide solutions and aqueous KOH/2-propanol produced V-shaped microtrenches on Si(100) wafers, using patterned gold or silver films as resists.^[12,16] After etching the silicon, the metal films were removed by immersing the substrates in aqua regia for \sim 1 min. The shadow masks have usually been fabricated using procedures such as under-cutting and lift-off.^[6] No separate shadow masks were used in this work. The step edges of the V-shaped microtrenches acted as shadow masks when the sputtering angle (θ) was less than 54°. The dimensions of gold features on the sides of microtrenches were controlled by using different etching times for silicon and/or different sputtering angles.

The gold patterns prepared using this method can be used in several different ways. As shown in Fig. 1A, these gold patterns can be used as substrates for the formation of patterned SAMs. In this particular case, three different SAMs were formed on these contoured surfaces using a combination of μ CP and orthogonal self-assembly.^[17] The surfaces of the plateaus were derivatized with hexadecanethiol by printing with a flat PDMS stamp; the remaining regions of gold (that is, those on the sides of the microtrenches) were covered by a second SAM (C₆F₁₃C₂H₄S[⊖]) by immersing the patterned samples in the alkanethiol solution; finally, the bare surfaces of silicon in

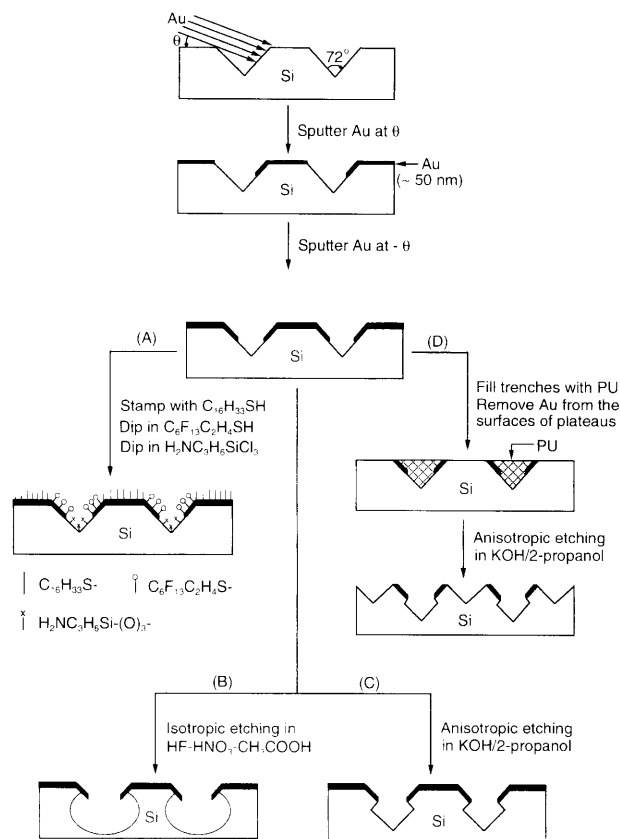


Fig. 1. Schematic outline of the experimental procedure. (A) Evaporated films of gold were patterned with SAMs using μ CP and orthogonal self-assembly. (B, C, D) The patterned features of gold were used as resists in the isotropic or anisotropic etching of silicon.

the microtrenches were derivatized with a third SAM (H₂NC₃H₆SiO₃[⊖]) by immersing the samples, in which the gold was completely covered with alkanethiolate SAMs, in a hexane solution containing the trichlorosilane. These patterned features of gold can also be used directly as resists in the further etching of silicon (anisotropic or isotropic) to produce more complex topologies on the silicon surfaces (Fig. 1B–C). In Fig. 1D, the gold films on the plateaus were selectively removed first, and the remaining films on the sides were then used as resists in silicon etching (see Experimental section for details).

Figure 2 shows scanning electron microscope (SEM) images of silicon microtrenches at different steps of gold evaporation. The edge resolution of the gold features was \leq 100 nm (Fig. 2D), although our evaporation was carried out at room temperature.^[18] When carried out at cryogenic temperatures, the edge resolution of features fabricated using this technique can be as high as 20 nm.^[6]

Figure 3 shows secondary ion mass spectrometry (SIMS) ion maps of SAMs that have been put on the surfaces of V-shaped microtrenches. These SIMS images are consistent with the SEM images shown in Fig. 2. By using molecules with different terminal groups, this procedure should be able to form numerous different combinations of SAMs on the surfaces of microtrenches. This figure shows only one

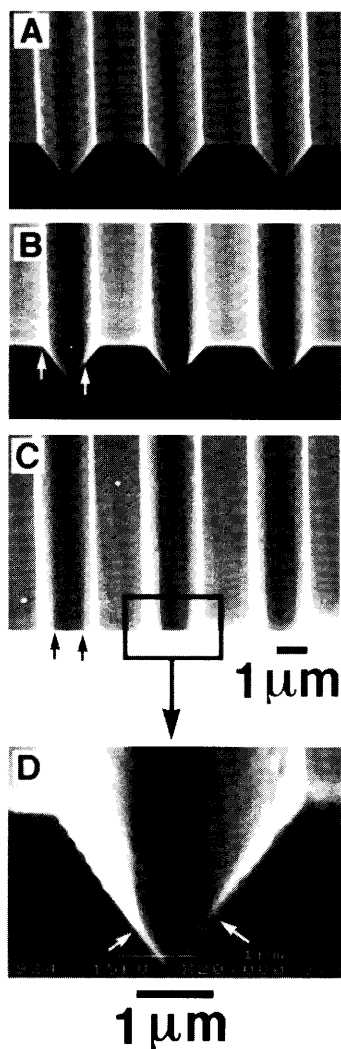


Fig. 2. SEM micrographs of silicon microtrenches at different steps of gold evaporation (500 Å thick Au, primed with 50 Å thick Ti, prepared by e-beam evaporation). (A) Before Au sputtering; (B) after Au sputtering from angle θ ; (C) after Au sputtering from both θ and $-\theta$; (D) a blow-up of (C) to show the edge resolution. The edges of gold features in the trench are indicated by arrows.

of these combinations: the three different SAMs shown here were chosen to be easily characterized by SIMS.

Figure 4 shows four examples of complex topologies that can be easily generated on the surfaces of silicon using anisotropic and/or isotropic etching, with the shadow-evaporated features of gold as resists. In principle, we can repeat the procedure of shadowed sputtering (at different angles) and etching of silicon to produce even more complex topologies.

There are several potential applications for the micropatterns and microstructures prepared in this paper. The patterned SAMs formed on the contoured surfaces of silicon can be used for templated cell attachment. The complex microstructures of silicon fabricated and described in this paper could serve as novel diffraction gratings. Microstruc-

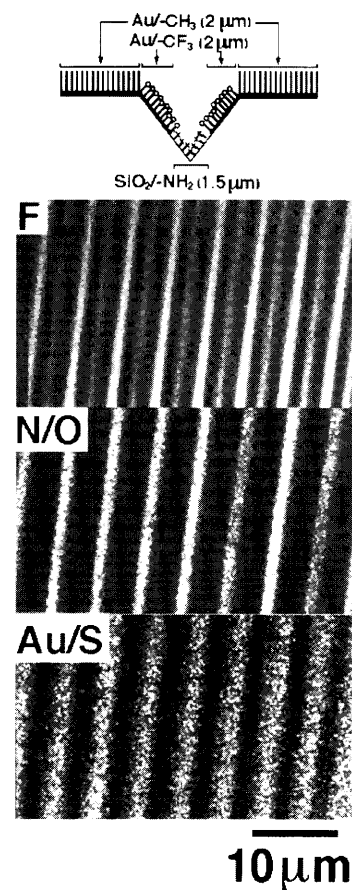


Fig. 3. SIMS ion maps of microtrenches that have been derivatized with three different SAMs formed using μ CP and orthogonal assembly (see Fig. 1A).

tures such as those of Fig. 4B and D might be used as micromechanical Velcro for the bonding of substrates in microelectronics.^[19]

Experimental

For the patterns shown in Fig. 1D, the gold films on the plateaus were selectively removed first, and the remaining films on the sides were then used as resists in silicon etching. In doing so, the microtrenches were covered with a flat PDMS stamp, and filled with a liquid polyurethane prepolymer (PU, NOA-73, Norland Products) using capillary filling [8]; the prepolymer was cured into a cross-linked solid material, and the gold films on the plateaus were then removed by immersing in aqua regia for ~1 m. The PU polymer was dissolved or lifted-off in the etching bath used for silicon, leaving the microtrenches open for further etching.

The complex topologies that can be easily generated on the surfaces of silicon using anisotropic and/or isotropic etching (see Fig. 4) with the shadow-evaporated features of gold as resists were generated using an anisotropic etchant of aqueous KOH/2-propanol solution (400 mL of H₂O, 92 g of KOH and 136 mL of 2-propanol); the isotropic etchant was an aqueous HF/HNO₃/CH₃COOH solution (10 mL of 48 % HF, 150 mL of 63 % HNO₃, and 50 mL of glacial CH₃COOH).

The wafers used in this study were Si(100) (Cz. N/Phosphor-doped, 1–10 Ω cm, test grade, SEMI Std. flats) and were obtained from Silicon Sense (Nashua, New Hampshire, USA).

Received: March 26, 1996
Final version: May 29, 1996

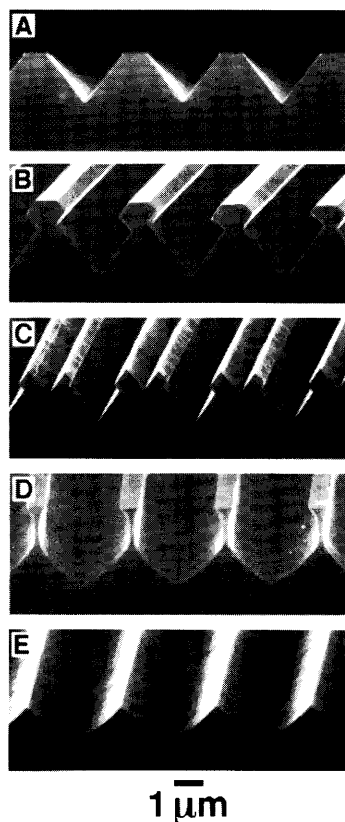


Fig. 4. SEM micrographs of complex microstructures etched in silicon, using shadow-sputtered patterns of Au as resists. (A) V-shaped microtrenches in Si(100) formed by anisotropic etching for ~15 min at 65 °C. These substrates were then used for shadowed evaporation of Au (500 Å thick Au, primed with 50 Å thick Ti), and further etching of silicon. (B) Anisotropic etching in an aqueous KOH/2-propanol solution for ~10 min at 65 °C (see Fig. 1C). (C) Anisotropic etching in an aqueous KOH/2-propanol solution for ~6 min at 65 °C (see Fig. 1D). (D) Isotropic etching for ~0.5 min at room temperature (see Fig. 1B). (E) Isotropic etching for ~3 min at room temperature (undercutting has removed the gold mask). After Si etching the gold masks were removed by immersing the samples in aqua regia for ~1 m.

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Phosphorescent Oxygen Sensors Utilizing Sulfur–Nitrogen–Phosphorus Polymer Matrices**

By Zhen Pang, Xijia Gu,* Ahmad Yekta, Zahra Masoumi, John B. Coll,* Mitchell A. Winnik,* and Ian Manners*

As a consequence of their considerable fabrication advantages, the use of polymeric materials for the construction of sensing devices is a current area of intense interest.^[1–3] Luminescent sensors based on composites comprising transition metal complexes immobilized in polymer matrices have attracted attention as oxygen sensors for both biomedical and barometric applications.^[4–8] Typically, phosphorescent dyes such as Pt octaethylporphyrin (OEP), Ru^{II} bipyridyl (bipy), or phenanthroline (phen) derivatives with oxygen quenchable excited states dispersed in a polymer matrix of high gas permeability, such as a crosslinked poly(-dimethylsiloxane), have been used.^[4–8] However, attempts to develop a fundamental understanding of the issues which influence the sensitivity of such composites have only recently been initiated and this has limited the optimization of sensors of this type.

In this paper we report that poly(thionylphosphazenes) (PTPs),^[9,10] a novel class of sulfur–nitrogen–phosphorus polymer, form promising polymer matrices in such devices.

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[**] This research was supported by the Ontario Center for Materials Research (OCMR), the Natural Science and Engineering Research Council of Canada (NSERC), and de Havilland Inc. In addition, I. M. is grateful to the Alfred P. Sloan Foundation for a Research Fellowship (1994–1996).