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Maskless Microetching of Transparent Conductive Oxides (ITO and ZnO) and Semiconductors (GaAs) Based on Reaction-Diffusion

Stoyan K. Smoukov and Bartosz A. Grzybowski*

Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208

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This paper describes a chemical, maskless-but-parallel method of etching micropatterns in transparent conducting oxides (here, ITO and ZnO) and semiconductors (GaAs) with lateral resolution down to 200 nm. Both types of materials are of great importance in modern technology and are used in optoelectronic devices (ITO electrodes[1]), sensors, and prototype on-chip UV lasers (ZnO[2,3]), as well as in integrated circuits, high-efficiency solar cells, and optical switches (GaAs[4]). Because all of these applications rely on the ability to define pertinent microscopic architectures, a variety of methods have been developed to micropattern these materials. Serial methods based on laser scanning or focused ion beam (FIB) techniques offer direct maskless and resistless patterning, but require expensive equipment and are relatively slow, especially at high resolutions.[5] On the other hand, parallel etching techniques (wet etching, RIE) are usually more rapid and less expensive but give rise to pattern underetching,[6] and the solvents they use to remove the masking photoresist place severe compatibility restrictions on the possible plastic/flexible substrate materials.

Here, we describe how a combination of reaction and diffusion (RD) processes initiating from hydrogel stamps[7,8] can circumvent these limitations and allow for direct imprinting of microscopic reliefs into ITO, ZnO, and GaAs films with submicrometer resolution. Our technique is general in nature and opens a new chemical route to benchtop structuring of hard materials using easily moldable, soft masters.

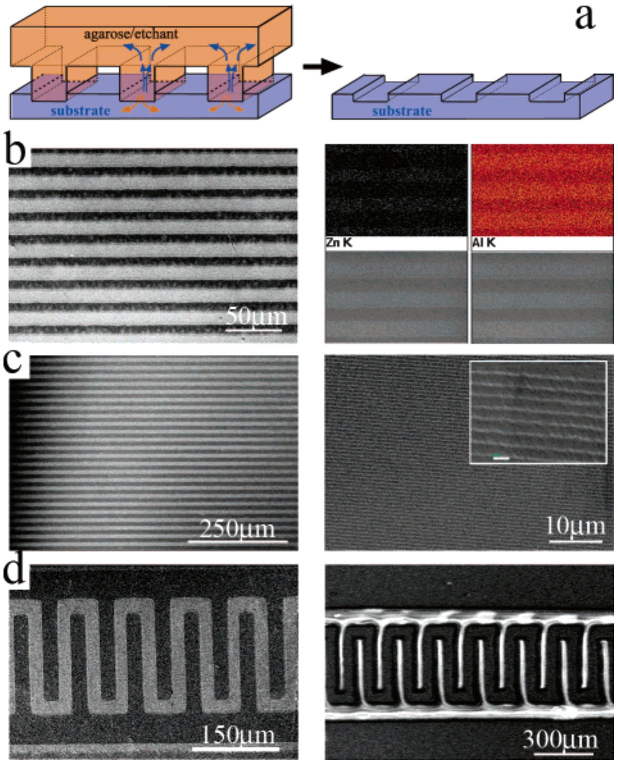

Figure 1. (a) Scheme of the experimental procedure for reaction-diffusion microetching of ZnO and GaAs. Arrows illustrate the two-way RD mechanism (etchant, red; reaction products, blue). (b) SEM images, sharp 10 μm lines etched into ZnO supported on sapphire (left); energy dispersive X-ray (EDX) maps (right) show element-specific X-ray emission intensities from the same region as the SEM images below them. The dark lines in the Zn map show complete removal of the ZnO (light lines in the SEM), which also correspond to the bright lines in the Al-map revealing the substrate. (c) SEM of large areas of 25 μm wide/50 μm pitch (left) and 200 nm wide/700 nm pitch lines (right) etched into GaAs. Scale bar in the inset corresponds to 1 μm. (d) SEM of interdigitated electrodes etched into ITO on glass (left) and ITO on PET (right).

Stamps micropatterned in bas-relief were prepared according to a published procedure[7,8] by casting a hot 1:9 w/w solution of high-gel-strength agarose (American Bioanalytical, AB00979) against PDMS masters. The stamps were soaked in an appropriate etchant for 60 min and then dried by placing on filter paper for 5 min and under a nitrogen stream for 10−15 s. To etch the ZnO and GaAs films, the stamps were simply placed on the substrate, pattern-side-down (Figure 1a); for ITO films, this was done under oil to minimize lateral spreading and vapor content of the etchant.

Regardless of the substrate type, the mechanism of localized microetching relied on diffusive transport of chemicals within a stamp (Figure 1a). The stamp's bulk acted as a two-way chemical "pump", simultaneously supplying fresh etchant onto the gel−solid interface while removing reaction products along the concentration gradient − that is, into the stamp. The removal of products circumvented diffusional limitations and allowed for constant etching rates.[9] Overall, the reaction-diffusion process allowed the gel to cut

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(5) Typical speeds range from as fast as to ∼1 m/s for 20−50 μm resolution laser patterning (Yavas, O.; Takai, M. *Appl. Phys. Lett.* **1998**, *73*, 2558) to as slow as 30 min to pattern 60 μm^2 ($\sim 8 \times 8$ μm) with FIB at 15 nm resolution (see ref 3).

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(9) This observation is corroborated by a theoretical model in which the stamp is approximated as a semi-infinite slab and the diffusion equation of the etchant, $\partial C/\partial t = D\partial^2 C/\partial x^2$, is solved subject to the conditions that (i) the concentration of the etchant far from the interface is constant and (ii) the reaction (etching) rate at the interface is proportional to the flux of etchant therein. In the reaction-controlled regime, the solution to this problem gives a constant etch rate.

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into the solid substrate and imprint into it the topography of the stamp's microfeatures.

Patterns in thin films of ZnO (100−300 nm thick; Figure 1b) were etched using a 1:1:300 (v/v/v) mixture of acetic acid, phosphoric acid, and water. Etching was complete within 30−60 s and was uniform over large areas (up to ∼1 cm^2). Because agarose stamps tolerate the dilute acid etchant well, they could be reused multiple times (>20 and even after prolonged soaking in the etchant solution) without noticeable reduction in patterning quality. Similarly, wafers of GaAs were readily patterned with a 1:1:20 v/v/v H_2SO_4:H_2O_2:H_2O solution over large areas (up to ∼1 cm^2), at etching rates of ∼30 μm/h and depths up to 20 μm (Figure 1c, right). Because of a higher acid content, the stamps could be reused only a few times. The smallest features that could be patterned into both types of substrates were of submicrometer dimensions and remained uniform and continuous down to ∼200 nm (Figure 1c). Below this limit, effects associated with the porosity of the agarose matrix became dominant, and the features were ill-defined.

Microetching of polycrystalline ITO films (Figure 1d) required harsher conditions and careful optimization of the etchant to make it compatible with agarose stamps. Because ITO is degraded mostly by undissociated halogen acids,[10] procedures using HCl usually require high etchant concentrations and elevated temperatures − under these conditions, however, agarose loses its structural integrity and even dissolves. We found that 2 M HCl (17% of assay)/0.2 M $FeCl_3$ solutions and room temperature presented the best compromise between stamp rigidity and the etching rate. Because this formulation was compatible with glass substrates (i.e., it did not degrade them), we used it to pattern thin (100−200 nm) ITO/glass substrates at etch rates of ∼30 nm/h. For ITO supported on polymeric substrates (e.g., poly(ethylene terephthalate), PET), it was possible to use more powerful HF etchants, such as 2:1:100 HF:H_2O_2: H_2O, which gave etch rates of ∼600 nm/h. (***Caution:*** *HF is able to painlessly penetrate skin, extract calcium from bones, and destroy soft tissues. Working with it requires special Norfoil gloves, antidote calcium gluconate next to the hood, and familiarity with exposure symptoms and emergency response procedures.*)

Water-based etchants spread readily on hydrophilic ITO substrates and reduced lateral resolution of the etching process to ∼50 μm. To minimize these untoward effects, we performed ITO structuring, under light mineral oil containing 1:1000 v/v Triton X-100 surfactant, as previously for glass.[8] The surfactant helped the oil penetrate in between the features of the agarose stamp, thus limiting etching to the areas of contact between the stamp's microfeatures and the substrate.[11] In this way, the resolution was improved to ∼10 μm, adequate for rapid prototyping and low-end/niche industrial applications[12] (e.g., microelectrode systems for flexible electronics, RFID tags, or displays).

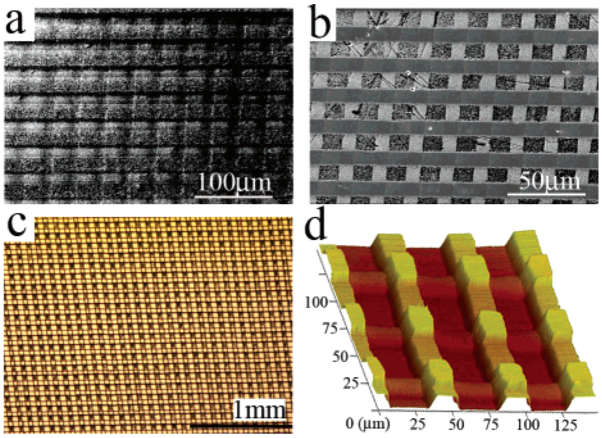

Figure 2. Three-dimensional architectures fabricated by sequential application of arrays of parallel lines along perpendicular directions. Patterns in (a) ITO (SEM image) and GaAs (b) SEM image; (c) large-area optical micrograph and (d) AFM image of 3D structure showing trenches 0.7 and 0.4 μm deep (y-, x-direction, respectively).

The knowledge of etching rates allowed for facile fabrication of three-dimensional surface reliefs by applying stamps sequentially for desired periods of time. This capability is illustrated in Figure 2, showing crossed-line structures prepared in ITO (Figure 2a) and GaAs (Figure 2b−d) by etching the same array of parallel lines at mutually perpendicular directions. Multilevel structures of this type can be useful in wavefront engineering[13] and in making corrective/diffractive optical elements without the need for multiple mask/deposit procedures.[14]

In summary, we have demonstrated a non-lithographic technique for direct microstructuring of transparent metal-oxides and semiconductors. We believe the easy-to-make hydrogel "sponges" can personalize microstructuring of solid materials much in the same way that microcontact printing based on elastomeric stamps personalized surface patterning. The simplicity and low cost of our technique make it especially suitable for benchtop, rapid prototyping applications. The approach is general in nature and should be easy to extend to other types of materials, for which wet chemical etchants are known (e.g., InGaAsP, InP, etc.).

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