

## High Resolution Assembly of Patterned Metal Oxide Thin Films via Microtransfer Molding and Electrochemical Deposition Techniques

Keith J. Stevenson,\* Greta J. Hurtt, and Joseph T. Hupp<sup>z</sup>

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60208, USA

A versatile method for preparing patterned thin films of metal oxides ( $\text{MoO}_3$  and  $\text{WO}_3$ ) and related materials on transparent, conductive indium-tin oxide (ITO) glass platforms is reported. Micrometer-sized features are formed by microtransfer molding of an optically transparent, thermally curable epoxy on ITO substrates followed by cathodic electrodeposition of the metal oxide from aqueous metal-hydrogen peroxide solutions. Atomic force microscopy was used to characterize the resulting microstructure and to examine effects of sintering on the patterned thin films.

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Redox-active metal oxide materials have shown considerable promise for application in the areas of electrochromics, photocatalysis, photovoltaics, and batteries.<sup>1</sup> Central to the development and fabrication of technologically useful devices is the ability to control the uniform deposition and patterning of metal oxide thin films. Recently, advances in a range of nonphotolithographic patterning techniques, known as soft lithography,<sup>2</sup> have begun to attract significant attention for the fabrication of microstructures. Soft lithography is a collective name for a range of techniques that use an elastomeric stamp for the printing and molding of organic monolayers or polymers.

Although soft lithographic techniques have been previously employed for preparing patterned thin films, most efforts have focused on microcontact printing ( $\mu\text{CP}$ )<sup>3</sup> of self-assembled monolayers.<sup>4</sup> For instance, in investigations most relevant to our report, Nuzzo and co-workers have used  $\mu\text{CP}$  of octadecyltrichlorosilane monolayers on various substrates [sapphire,  $\text{Si-SiO}_2$ , glass, and indium-tin oxide (ITO)] for the directed patterning of metal,<sup>5,6</sup> and ceramic oxide thin films.<sup>7,8</sup> While these advances clearly are significant, these methods typically entail several lengthy processing steps (e.g., mechanical polishing and spin casting) and/or require use of capital-intensive film deposition techniques (i.e., chemical vapor deposition).

In this paper, we describe an alternative fabrication procedure for preparing patterned metal oxide thin films on transparent, conductive substrates. The new procedure relies upon a different and arguably underutilized form of soft lithography, known as microtransfer molding ( $\mu\text{TM}$ ).<sup>9</sup> By employing  $\mu\text{TM}$  in concert with electrochemical deposition techniques, we have developed a simple and versatile method of preparing patterned substrates in ambient, liquid environments with unprecedented control over the film deposition conditions. The methodology reported here offers several potential advantages over existing techniques in that thicker films can be prepared, less costly instrumentation is employed, and fewer processing steps are required.

### Experimental

Using a previously described method,<sup>6</sup> polydimethylsiloxane (PDMS) stamps for microtransfer molding were fabricated by curing a 10:1 mixture of elastomer-hardener (Sylgard Silicone 184, Dow Corning) over commercially obtained lithographic master templates. The templates used in this study were either a Planotec Si calibration specimen (Ted Pella, Inc.) or an atomic force microscopy (AFM) calibration grating (Digital Instruments) having etched features  $\sim 185$  nm deep and patterned lateral dimensions of  $8 \times 10$  and  $5 \times 5$   $\mu\text{m}$ , respectively. The PDMS was cured at room temperature for 1 h, followed by additional curing at  $60^\circ\text{C}$  for 1 h.

Transparent, conductive ITO substrates (Delta Technologies, Ltd.,  $10 \Omega/\square$ ) were cleaned by immersion for 15 min in a heated ( $80^\circ\text{C}$ ) aqueous solution of ethanolamine (Aldrich, 20 wt %). The substrates were then rinsed several times with deionized water and dried under a stream of nitrogen. The PDMS stamp was filled with

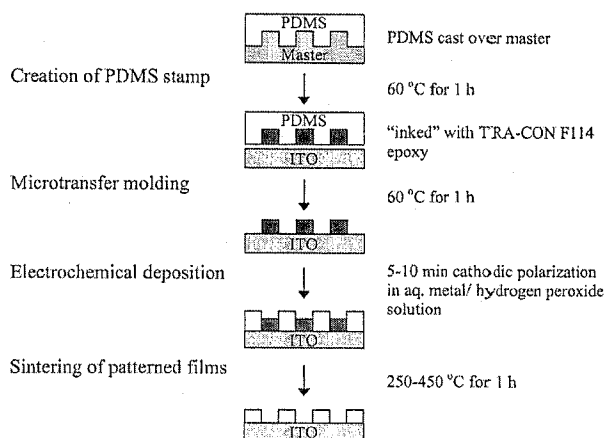


Figure 1. Schematic illustration of the microtransfer molding and electrodeposition process for patterning of metal oxide thin films.

a thermally curable epoxy (TRA-CON F114) and the excess was removed by brushing the surface lightly with a soft, lint-free cloth. The inked PDMS stamp was then placed on a clean ITO substrate and a light weight ( $\sim 10 \text{ g/cm}^2$ ) was applied to the top of the stamp to ensure conformal contact. The ITO-epoxy-PDMS mold was cured at  $60^\circ\text{C}$  for 1 h. The mold was then allowed to cool to room temperature and the PDMS stamp was then peeled away from the substrate.

Following the procedure described by Guerfi et al.,<sup>10,11</sup> aqueous molybdenum and tungsten deposition solutions were prepared by dissolving 1 g of the respective metal (either in powder or solid form, Alfa Aesar) in 6 mL of 30% (v/v) aqueous hydrogen peroxide solution (Fisher). When the metal was completely dissolved and the exothermic reaction had ended, platinum black, prepared by a previously published procedure,<sup>12</sup> was added to reduce the excess peroxide. The solutions were then diluted to 100 mL volume with deionized water. The patterned ITO substrates, acting as the working electrode, were then placed in the respective deposition solution along with a Ag-AgCl (3 M NaCl) reference electrode and a platinum wire counter electrode. Blue-colored thin films were obtained after  $\sim 10$  min by applying a fixed potential ( $-0.2 \text{ V}$  for tungsten oxide and  $-0.02 \text{ V}$  for molybdenum oxide).

AFM was performed using a Digital Instruments Multimode Nanoscope IIIa. All measurements were obtained in tapping mode with single etched silicon (TESP) Nanoprobe SPM tips (cantilever length 125 mm and resonance frequency 307-367 Hz, Digital Instruments).

### Results and Discussion

The overall strategy for patterning of metal oxide thin films on transparent, conductive substrates is shown in Fig. 1. A PDMS stamp created from a lithographic master was used to pattern a thermally

\* Electrochemical Society Student Member.

<sup>z</sup> E-mail: kjsteve@chem.nwu.edu

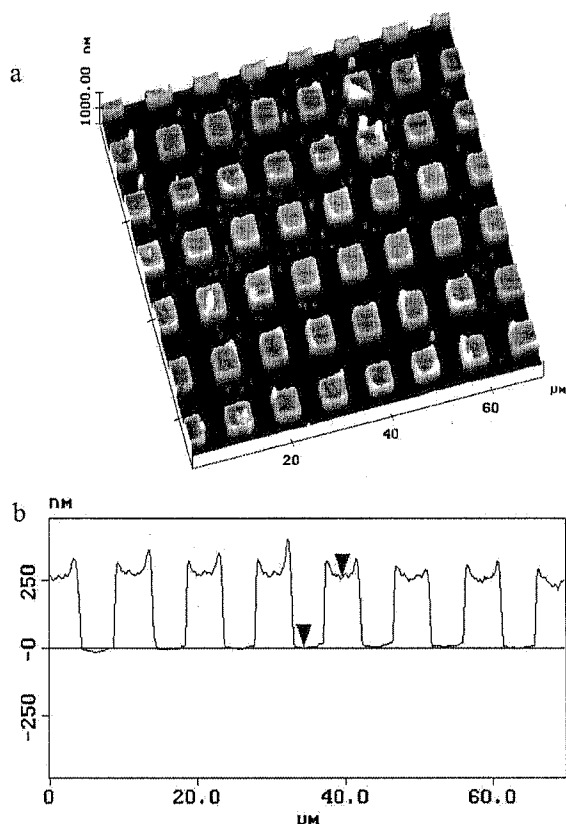


Figure 2. (a) A 70 x 70 μm AFM image of a patterned  $\text{WO}_3$  thin film on ITO from 10 min cathodic polarization and sintering at 250°C for 1 h; (b) height vs. distance profile showing uniformity and thickness of patterned features.

curable epoxy on ITO. A metal oxide negative of the pattern was then generated via electrodeposition, as described above. Subsequent oxide sintering in air at 250°C for 1 h produced nearly translucent, strongly adherent films. Due to the higher volatility of the epoxy (~130°C) most, if not all, was effectively burned off in the sintering process. Although we report specific experimental conditions, these electrochemical and sintering conditions can be varied to control film thickness and composition.

Figure 2 shows a representative, large-scale 70 x 70 μm AFM image of a patterned  $\text{WO}_3$  thin film formed from PDMS stamps made from a 5 x 5 μm lithographic master. Excellent array replication with limited pattern distortion is observed and the regularity of this array was maintained over ~5 mm<sup>2</sup>. Figure 2b shows a cross-sectional height vs. distance plot, indicating that 10 min cathodic polarization followed by sintering at 250°C for 1 h produces ~250 nm thick films. Patterned depositions of  $\text{MoO}_3$  and polyaniline<sup>13</sup> thin films were also successfully performed with similar results.

The templating of thin films is also extremely useful for examining structural and chemical changes induced by physical or chemical exposure. For instance, AFM analysis of the  $\text{WO}_3$  films shown in Fig. 2, before and after sintering, indicates that film dehydration and densification results in an approximately 10% decrease in film thickness. In addition, the measured root-mean-square (rms) surface roughness for these films was observed to decrease by ~30%. A higher resolution AFM image of the sintered  $\text{WO}_3$  microstructure is shown in Fig. 3, revealing the formation of an amorphous structure consisting of smaller, spherical particles ranging from 60 to 180 nm.

A more noticeable dependence of film structure and crystallinity on heat-treatment is observed for patterned  $\text{MoO}_3$  thin films. Figure 4 shows the surface of a patterned 8 x 10 μm array for an as-deposited film (Fig. 4a) and the same film after heat-treatment at 250°C for

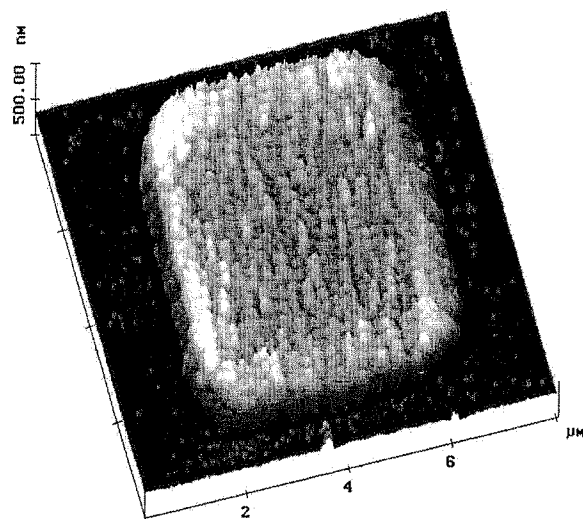


Figure 3. A 8 x 8 μm AFM image showing the microstructure of a single  $\text{WO}_3$  square.

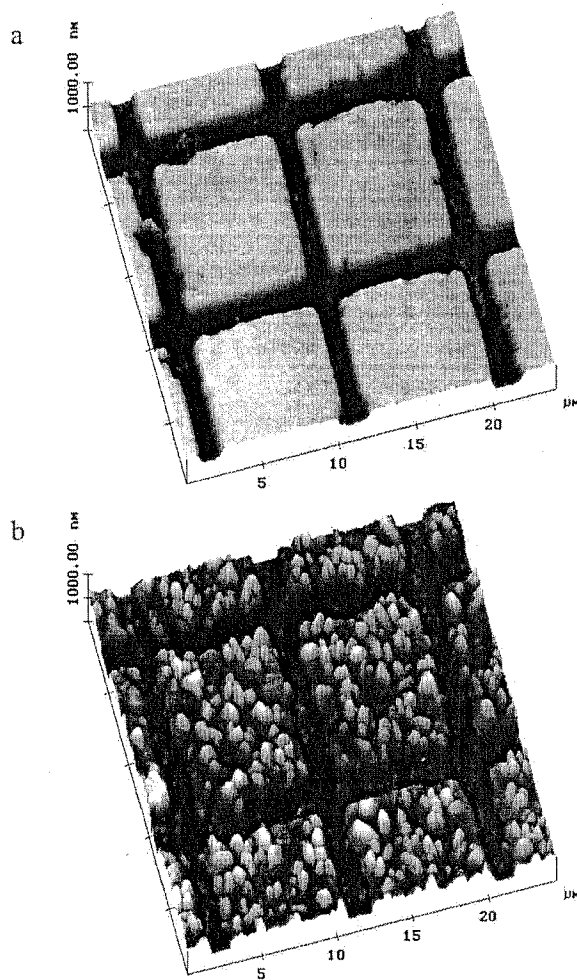


Figure 4. A 24 x 24 μm AFM image of a patterned  $\text{MoO}_3$  thin film on ITO from 10 min cathodic polarization (a) before and (b) after sintering at 250°C for 1 h.

1 h (Fig. 4b). The AFM images indicate that the surface of the as-deposited film consists of smooth grains ranging from ~40 to 100 nm in diam, while those for the sintered films comprise a two-phase

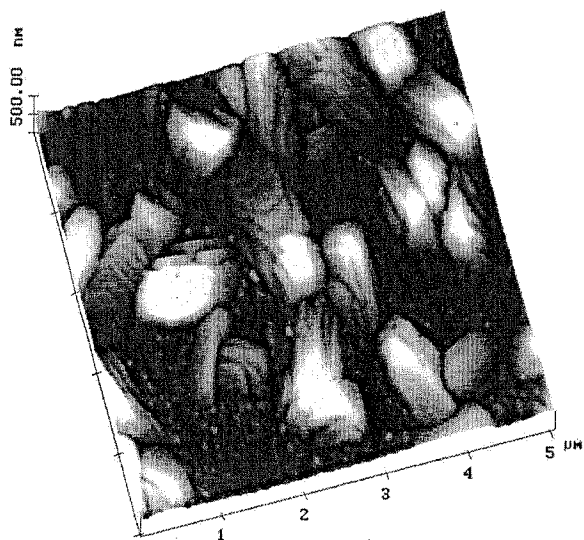


Figure 5. A higher resolution  $5 \times 5 \mu\text{m}^2$  AFM image of the patterned  $\text{MoO}_3$  thin film shown in Fig. 4b.

mixture of amorphous and layered crystalline domains of increased size ( $\sim 200$ – $600$  nm). A higher resolution  $5 \times 5 \mu\text{m}^2$  AFM image demonstrating the formation of the layered phase is shown in Fig. 5. Additionally, AFM analysis of films before and after sintering indicates that film dehydration and densification results in an approximate 35% decrease in film thickness and a  $\sim 24\%$  increase in (rms) surface roughness. These morphological changes were confirmed by X-ray diffraction measurements<sup>14</sup> and are consistent with previously published reports,<sup>11,15</sup> which indicate that extended heat-treatment at  $250^\circ\text{C}$  and above can induce a phase transition from an amorphous structure to a more thermodynamically stable, layered orthorhombic structure.

#### Conclusion

We have demonstrated a convenient approach for fabrication of metal oxide thin films with micrometer-sized features on transpar-

ent, conductive substrates. AFM measurements of templated films allowed for high-resolution characterization of microstructural changes associated with extended heat treatment. The capability of this method to produce patterned thin films with precise electrochemical control and very few processing steps offers distinct advantages over existing techniques. In addition, this methodology can be easily modified to incorporate the directed templating of a broader spectrum of materials (e.g., organic and metallopolymeric films), including materials not easily accessed by otherwise versatile sol-gel processing or vapor deposition techniques.

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