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Parallel writing on zirconium nitride thin films by local oxidation nanolithography

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Parallel pattern transfer of submicrometer-scale oxide features onto zirconium nitride thin films is reported. The oxidation reaction was verified by Auger microprobe analysis and secondary ion mass spectrometry. Oxide features of ~70 nm in height can be formed and selectively etched in a dilute aqueous hydrogen fluoride solution. This provides an interesting route to potential new applications for high-melting point, biocompatible surfaces that possess small feature sizes with controlled geometries. © 2004 American Institute of Physics. [DOI: 10.1063/1.1833569]

Nanoimprint technology is being intensively studied as an alternative to traditional optical lithography, especially for new applications outside the microelectronics field such as optoelectronics and biomedical templating. There are a growing number of methods involving pattern transfer by a stamp, template, or master using resist layers, direct mechanical deformation, or electrical transfer methods.1–8

Recently, Cavallini et al.7 and Yokoo8 have proposed a method for parallel writing based on local oxidation nanolithography. The concept emerges from kinetic studies of scanning probe oxidation in which a voltage generates an intense nonuniform electric field between the scanning probe microscope (SPM) tip and a substrate.10,11 This field creates a water meniscus from the ambient water vapor and causes the electrochemical generation of oxyanions, resulting in oxide growth on a scale determined by the size and shape of the meniscus.12 In their generalization of this view of the single-tip case to the nanoimprinting case, which uses a stamp with many morphological features, the water meniscus is a compliant mediating material. Since the meniscus adjusts to varying gaps across the stamp, narrow tolerances and good reproducibility of feature sizes at the nanometer scale can be achieved. This allows patterns to be transferred from the stamp to the substrate simultaneously, or in other words, parallel writing.

These previous demonstrations7,8 used silicon as the substrate onto which oxide pattern transfer occurred. This is largely because most SPM oxidation kinetic studies have been performed using this material. However, almost all materials can be oxidized under the extremely high fields, ~108 V/m, generated by an electrically biased SPM tip. Many metallic, semiconducting, and insulating materials have been patterned by scanning probe oxidation. In particular, the group IV metals and their nitrides exhibit remarkably enhanced kinetics, as first reported by Gwo et al.13 and, more recently, in our work.14 For example, oxide feature heights for silicon tend to self-limit at 10 nm or less, whereas for ZrN films, heights of several hundred nanometers have been obtained. The motivation for the present study is to see if these enhanced feature heights obtained with a single SPM tip can be extended to the parallel writing case on group IV nitride films using a stamp.

Thin films of zirconium nitride were sputter deposited onto silicon substrates by rf-magnetron sputtering with 120 W power and a wide range of N2/Ar mixtures at The University of Akron. N2 flow rates varied from 0 up to 10 sccm, as described previously.14 Film thicknesses were typically 200 nm in the present study. Characterization of the thin films included x-ray diffraction, electrical resistivity, x-ray photoelectron spectroscopy, and SPM oxidation kinetic studies. The films are metallic below about 0.5 sccm flow rates of nitrogen and become increasingly dielectric above this value. In this letter, we describe results for zirconium nitride films with N2 flow rates above 4 sccm.

Master stamps were fabricated on silicon by standard photolithography at NIST15 and coated with an ~100-nm-thick layer of PdAu. The 1 cm × 4 cm stamps consist of sparse and dense arrays of isoareal geometrical features in which the lengths and widths are varied systematically from 5 to 125 µm. Shapes include rectangular features with straight, inward/outward triangular, and inward/outward hemispherical end caps and appear both in positive and negative relief, i.e., as posts and wells. Feature heights for two sets of stamps were 550 and 730 nm, determined by silicon etching and verified by SPM topographic imaging. An optical image of a portion of a stamp consisting of several arrays is shown in Fig. 1(a). These stamps were used to generate oxide patterns on the ZrN films. Pattern transfer was performed with dc voltages between 70 and 300 V in the presence of isopropyl alcohol. An optical image of a ZrN film following pattern transfer is shown in Fig. 1(b).

Consistent with oxidation being the chemical process responsible for the observed pattern transfers, etching studies using a dilute 2%–5% HF solution show that zirconium oxide can be removed with good selectivity relative to zirconium nitride. This leads to the following pattern transfer scheme: A SPM topograph of a portion of a stamp appears in Fig. 2(a). The patterned features in this case are negative relief, i.e., wells. The resulting oxide pattern formed on the surface of a zirconium nitride film is shown in the SPM
image in Fig. 2(b). Here the raised oxide features, appearing bright in the image, correspond to the upper surface plane. After etching in a dilute HF solution, the SPM image appears reversed, as shown in Fig. 2(c). The right-hand side portion of Fig. 2 illustrates each step in the fabrication.

SPM topographic images of more of these oxide patterns are shown in Fig. 3. Rectangular features are shown in the left-hand column, features with inward triangular end caps are shown in the middle column, and those with outward hemispherical end caps are shown in the right-hand column. The top row of images (a) shows posts, with cross sections of these features shown in row (b). Row (c) shows cross sections of corresponding wells formed by the etching procedure, which are taken from the images shown in row (d). The size and shape of the transferred patterns are well-maintained during the etching process. Cross-sectional analysis indicates that the height/depth reversal is close to 70 nm. Secondary ion mass spectrometry (SIMS) depth profiling of the oxygen ion signal (not shown) confirms that the oxide-patterned regions continue well below the surface of the unpatterned films. Our conclusion is that the total oxide thickness is roughly twice the oxide height, in good agreement with our height-to-depth ratios obtained from single-tip SPM oxidation and HF etching studies of ZrN films.

An explanation of our use of isopropyl alcohol is required: In their work with silicon substrates, Cavallini et al. used water as the source of oxidizing species. However, oxygen is present in these ZrN films already, which reduces the need for an external supply of oxidizing species. Nevertheless, a coupling medium capable of ionic breakdown is still necessary. In fact, our initial attempts to use water, while producing the desired patterns, caused considerable damage to the entire film. A search for a less-reactive medium led us to isopropyl alcohol, prompted by the recent work of Tello and Garcia.

FIG. 1. Optical micrographs of (a) feature arrays on the reference stamp and (b) oxide patterns formed by the stamp on a zirconium nitride film. Feature heights of the etched silicon stamp are 550 nm.

FIG. 2. Scanning probe topographic images of (a) a portion of the stamp, (b) oxide features patterned on a zirconium nitride thin film, and (c) features as they appear after etching in dilute HF. A schematic of the sequence is depicted on the right.

FIG. 3. Scanning probe topographic images of three types of oxide features patterned on a zirconium nitride thin film before (a), (b), and after (c), (d), etching. The height difference from dark to bright is ~70 nm, as seen in the cross sections.
Finally, chemical analysis by Auger microprobe of the patterned features and unpatterned areas of the films confirms the conversion of ZrNx → ZrOy at stamp-substrate contact locations, as shown in Fig. 4. These data are important, since they clearly identify the replacement of metal–nitrogen bonds by metal–oxygen bonds, and oxidation as the primary mechanism responsible for these patterns. Previously we have argued that this conversion takes place, enhancing the height of the nanostructures as compared to other materials system.

Group IV metal thin films and their oxides and nitrides have many unique properties including hardness, dielectric constant, corrosion resistance, high melting temperatures, biocompatibility, and biocatalytic activity. Although coating technology for these films is mature, the difficulty of structuring these materials, especially on the nanoscale, has thus far limited their application. The results reported here enable promising applications for patterned group IV films for the fabrication of templates for directed cell growth studies. For example, Galli et al. have investigated protein ordering of actin filaments by SPM oxide lines patterned on titanium films, and we have reported that zirconium oxide layers may mitigate bacterial growth. The ability to produce oxide patterns on ZrN surfaces by local oxidation nanolithography with a stamp will allow us to fabricate large-area biotemplates on the order of 100 cm². In addition, the process reported here is quick, simple and robust. These qualities should dramatically accelerate progress in the bioattachment and biotemplating research areas.

In this work, we have demonstrated an emerging nanoimprint technology that is a promising approach to patterning group IV thin films. Although important issues such as ultimate resolution, alignment method, and exposure uniformity across centimeters remain to be addressed, these are challenges which are largely generic to most nanoimprint schemes. Furthermore, a detailed understanding of local oxidation kinetics has provided considerable guidance in establishing the optimal conditions for parallel writing, as Cavallini has shown for silicon, and as we have shown here for ZrN.

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