Surface Modification of Perovskite Manganite Thin Films using Atomic Force Microscopy

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ABSTRACT

Nanoscale surface modifications have been produced on single crystal silicon and $La0_{0.7}Ba_{0.3}MnO_3$ thin films. Feature heights and widths were found to increase linearly with increasing tip bias voltage, humidity, and decreasing tip speed. Heights of the features on silicon ranged from 1-5 nm with widths of 200 – 500 nm. These results are consistent with results found in previous studies. Structures produced on MnO_3 films also show a linear dependence of height and width as a function of tip voltage and speed. Heights ranged from 10 – 70 nm and widths from 400 – 2000 nm. In addition to the larger surface features, it was found that write speeds were much greater on the MnO_3 films than on silicon.

Keywords: nanolithography, afm, oxidation, manganite, thin films

1 INTRODUCTION

Atomic Force Microscopy (AFM) is now an established technology for studying and modifying surfaces on a nanometer length scale. Surface modification using an AFM nano-oxidation technique has been an active area of research for the past several years. This technique involves bringing a sharp conducting probe in close proximity to a surface in a humid environment. When a voltage is placed onto the tip, strong electric fields are produced under the probe which act to disassociate the water molecules on the surface of the sample. The oxygen and hydrogen ions react with the substrate to form an oxide layer. This process has yielded results on a variety of structures such as silicon[1], silicon nitride[2], GaAs[3], titanium[4], niobium[5], carbonaceous films[6], and organic monolayers[7].

Colossal Magneto Resistance (CMR) manganite materials have been demonstrated to be useful for a variety of technological applications including magnetic sensors and bolometric infrared detectors. Little work has been done to apply the nano-oxidation technique to pattern structures onto these materials [8]. AFM induced surface modifications would enable the realization of such sensors in nanotechnology applications. Here we report results on $La0_{0.7}Ba_{0.3}MnO_x$ thin films and compare these features with those produced on silicon.

2 EXPERIMENTAL

In this work, p-type single crystal silicon wafers (100) were cut into segments approximately 1 cm x 1cm in size. They were cleaned in 50% hydrofluoric acid for approximately 1 minute and rinsed in de-ionized water for 30 seconds. $La_{0.7}Ba_{0.3}MnO_3$ thin films were grown on (100) oriented $SrTiO_3$ substrates by Pulsed Laser Deposition (PLD) technique using a KrF excimer laser with a pulse repetition rate 5 Hz- 10 Hz. Film thickness was in the range of 100 to 200 nm. Growth conditions such as laser pulse energy density and substrate temperature were optimized to replicate the cationic composition of the bulk target. Films were grown under varying oxygen partial pressures to control the film surface roughness which increases as the oxygen partial pressure is varied.

Data was collected by first placing the sample in a Nanoscope E atomic force microscope equipped with a custom-made environmental housing in order to control the sample humidity. An initial image was taken in contact mode (constant height with feedback) of the surface to determine if it was suitable for writing. After imaging, the scan size was set to zero. The sample was then moved under the tip in a prescribed pattern by outputting voltages from a second computer to the x and y piezotube connections. Voltages were controlled via a LabView program. The LabView program also applied voltages to the tip (Asylum Research Cantilevers) at the appropriate times to perform the lithography. Experiments were performed to determine the effects of tip voltage, writing speed, and humidity on the surface features.

3 RESULTS ON SILICON

The LabView program was designed to produce a set of parallel lines on the surface. Figure 1 shows an example of 20 lines produced on silicon. Each line was produced using the same conditions, but with incrementally increasing tip voltage. Cross sectional analysis of the image provides the data represented in this paper.

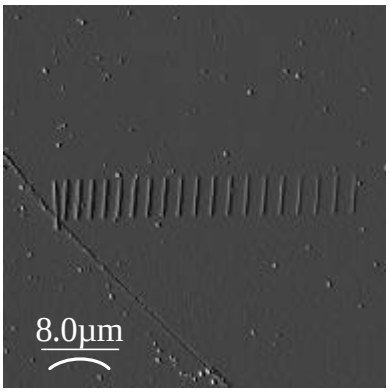

Figure 1: AFM image of parallel lines drawn on a MnO_3.

3.1 Line Size vs. Tip Voltage

Data was collected on silicon to determine the effect of the bias tip voltage on the oxide grown. Figure 2 shows the width and height data for voltages ranging from -5 to -14 V. No lines were observed using positive tip bias voltages. Data was obtained at 80% humidity with a tip speed of 0.4 µm/s. The structures were found to increase in size (both height and width) linearly with voltage. This dependence and the rate of increase is consistent with those reported by Debois et. al. [9].

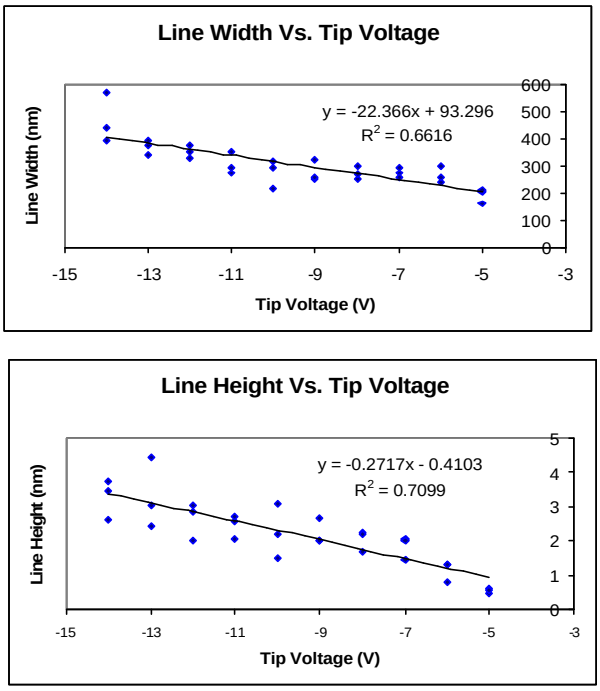

Figure 2: Dependence of surface features on silicon with tip bias voltage.

3.2 Line Size vs. Tip Speed

The effect of the tip speed on the oxide grown is shown in Figure 3. Data was obtained at 80% humidity with a tip bias of -13 V for velocities ranging from .01 µm/s to approximately 4.5 µm/s . The structures were found to decrease in size (both height and width) linearly with increasing tip speed. This data is consistent with published results by Tello et. al. [10] which shows that feature dimensions increase in size for longer voltage pulse times.

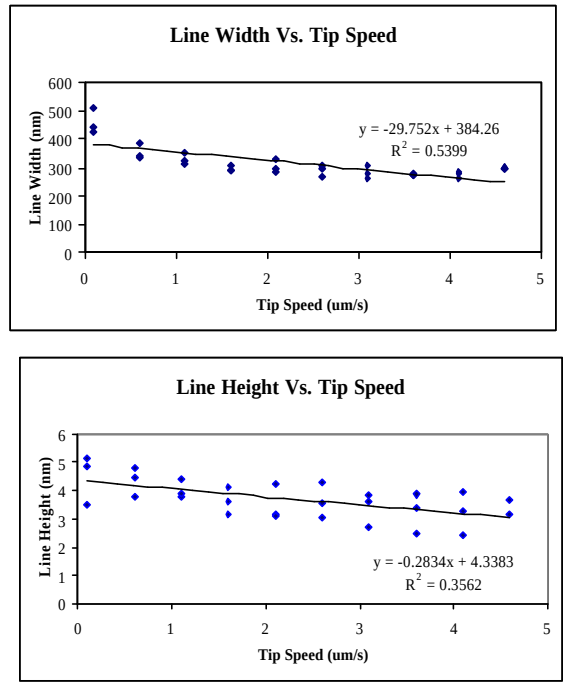

Figure 3: Dependence of surface features on silicon with tip bias voltage.

3.3 Line Size vs. Humidity

The effect of humidity on the oxide grown is shown in Figure 4. Data was obtained at a tip speed of 0.4 µm/s with a tip bias of -13 V. The relative humidity was varied from 45 % - approximately 90%. The structures were found to increase in size (both height and width) linearly with increasing relative humidity. This data is consistent with published results by Jungblut et. al. [11] which shows that feature dimensions increase in size for longer voltage pulse times.

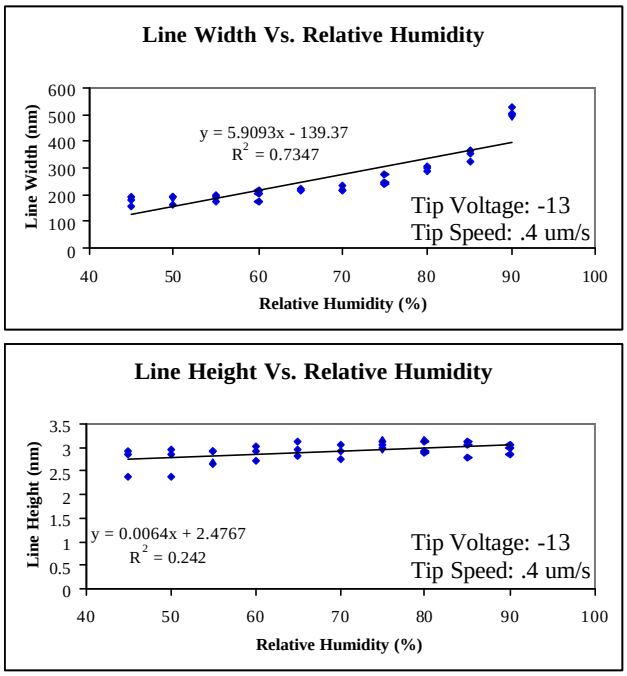

Figure 4: Dependence of surface features on silicon with humidity

4 RESULTS: $La_{0.7}Ba_{0.3}MnO_X$ THIN FILMS

4.1 Line Size vs. Tip Voltage

Similar experiments were performed on $La_{0.7}Ba_{0.3}MnO_X$ thin films. Experiments were performed to study the dependence of tip voltage on surface structures. Data was collected at 85% relative humidity with tip speeds of 0.2 µm/s. Figures 5 and 6 show the results for positive and negative tip voltages. It should first be noted that reproducible structures were obtained with both polarities, indicating a different mechanism for generating the surface features than that responsible on silicon. This was also observed by Li et. al. [8]. Heights on the MnOx films ranged 10 nm to 170 nm, a factor of 10 increase in size compared to features produced on silicon under similar conditions. The widths for positive tip biases were also observed to be considerably larger than that of negative bias voltages (larger by a factor of 3). It appears that a different mechanism is responsible for the surface modifications for different polarities.

4.2 Line Size vs. Tip Speed

The effect of the tip speed on the oxide grown is shown in Figure 7. Data was obtained at 85% humidity with a tip bias of +15 V for velocities ranging from .01 µm/s to approximately 10 µm/s . The structures were found to decrease in size (both height and width) with increasing tip speed. The data shows that writing sizable features can be performed at much higher speeds on these manganite films.

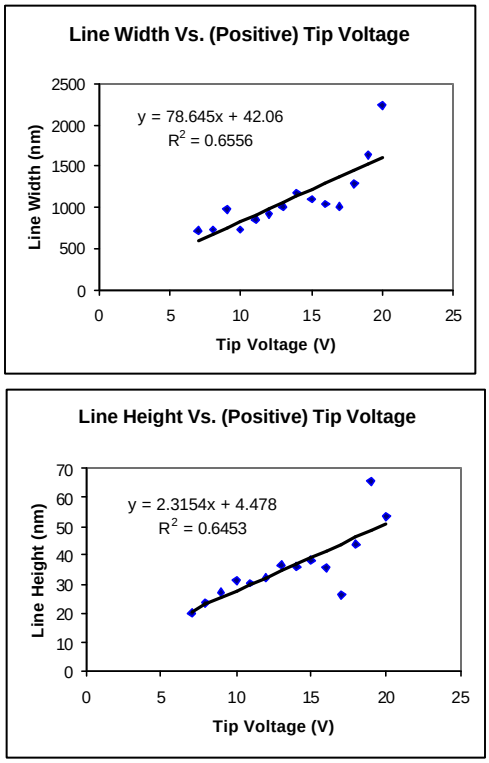

Figure 5: Dependence of surface features on silicon with humidity

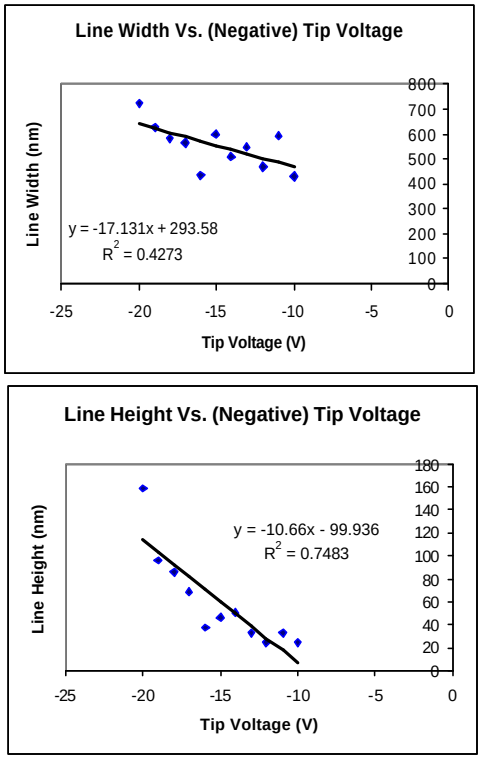

Figure 6: Dependence of surface features on silicon with humidity

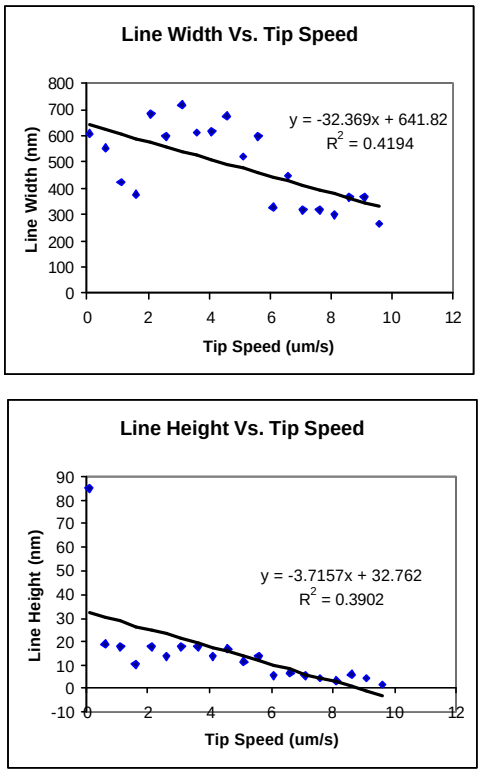

Figure 6: Dependence of surface features on silicon with humidity

4 CONCLUSIONS

Nanometer size surface modification have been performed on silicon and $La_{0.7}Ba_{0.3}MnO_3$ substrates. The dependence on tip voltage, speed, and humidity for silicon is consistent with previous results, indicating a nano-oxidation mechanism. The manganite thin films demonstrate surface modification for both positive and negative polarities, larger surface features, and the ability to produce surface modification at higher speeds. More experiments are necessary in order to study the mechanism of this process.

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