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Preparation of Atomically Smooth $SrTiO_3$ Substrates

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Abstract

$SrTiO_3$ has been used as a substrate to grow thin films of materials including high-temperature superconductors such as cuprates, ferromagnetic oxides such as manganites, and ferroelectric oxides such as $BaTiO_3$. The use of $SrTiO_3$ as a substrate for the deposition of manganite thin films provides an excellent template for observing unique effects observed only in ferromagnets, such as the anomalous and planar Hall effects. The as-received $SrTiO_3$ substrates require a process that prepares atomically smooth surfaces for thin film deposition. This study focuses on using ultrasonic cleaning, water annealing, and thermal annealing in air to prepare $SrTiO_3$ substrate surfaces and verifying their smoothness at the atomic scale using atomic force microscopy.

Keywords: thermal annealing, perovskite substrates, atomic force microscopy

Introduction

The perovskite oxide $SrTiO_3$ (STO) can exhibit unique properties, such as superconductivity and quantum paraelectricity, which makes it an interesting material for study. As shown in Figure 1, STO has a three-dimensional perovskite structure, which also makes it a desired candidate as a substrate for thin film deposition. Its cubic structure is particularly desirable because it will influence the deposited thin film to take on a cubic structure as well. This property imposes a biaxial strain on the deposited film and provides an additional tuning parameter for the observation and modification of anomalous, planar, and ordinary Hall effects. In addition, STO can be turned metallic through either niobium doping or vacuum annealing to induce oxygen reduction (Kwak et al., 2017). This behavior allows it to be used for fabrication of device structures, such as field-effect transistors. This project focuses on finding the optimal preparation conditions of STO substrates specifically due to its cubic structure and the fact that its lattice constant matches that of several other oxide materials, such as high-temperature cuprate superconductors like $YBa_2Cu_3O_7$ (YBCO), ferroelectric oxides, and ferromagnetic

oxides (Liu et al., 2006). To use it as such, the material needs to have an atomically smooth, top surface that is optimal for a good quality thin film to deposit.

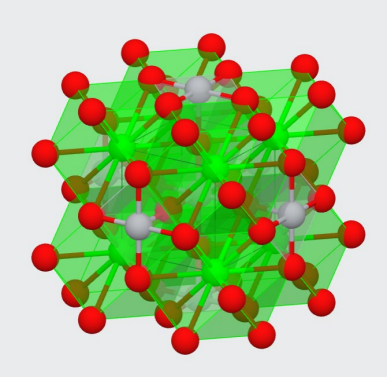

Figure 1. The chemical structure of STO (The Materials Project). The grey and red atoms represent planes of TiO_2 and the green and red atoms represent planes of SrO.

Using techniques of atomic force microscopy (AFM) and lateral force microscopy (LFM), the surface of STO has been observed and studied (Kwak et al., 2017). Our study of this substrate has been aided by previous research done by Kwak et al. and Gellé et al. in 2017 and 2018, respectively. Kwak et al. provide a detailed procedure for the annealing process and experiments performed on the substrate surface. In the work of Gellé et al., the importance and production of a TiO_2-terminated surface of $SrTiO_3$ are described in greater detail. These studies were conducted using techniques such as high-temperature annealing and atomic force microscopy, which are applicable to a variety of long-term research projects.

The annealing of STO substrates is a necessary step for the growth of thin films because it can produce an atomically smooth, singly-terminated surface, which is what the thin film bonds to initially. This determines the bonding sequence and subsequent growth of the film. The unit cell of STO has planes of SrO and planes of TiO_2, and at the surface of the perovskite, either the TiO_2 layer or the SrO layer can be exposed. A singly-terminated surface will either have an exclusively TiO_2-terminated or an SrO-terminated surface. The substrate's termination type is significant because the atoms exposed at the surface will have different microscopic interactions with incoming ions during the film deposition process, which determines the order in which the atoms of thin films are deposited on the substrate and the composition and properties of the film (Gellé et al., 2018). Often, a TiO_2-terminated surface is considered optimal for STO's use as a

substrate, and it can be obtained through a water and thermal annealing process. Under-annealing the substrate will not allow for the surface to become atomically smooth. However, over-annealing the substrate was shown to produce square-shaped holes along the surface, which would leave substrates unfit for thin film deposition (Kwak et al., 2017). After the substrates receive optimal treatment, the desired TiO_2-terminated surface can be verified through the use of atomic force microscopy, revealing a terraced structure with steps that are the same height as the unit cell of STO (i.e. atomically smooth, Kwak et al., 2017). Once the substrate surfaces achieve atomic smoothness, they are ready to undergo thin film deposition.

We seek a method that optimally prepares STO substrates for thin film deposition through a two-step annealing process that avoids using acid etching and over-annealing the substrate. This project has broad significance because it focuses on perfecting the two-dimensional interface between the substrate and thin film. This interface plays an important role in the properties of oxide thin films with applications in oxide electronics, where metal oxides are substituted for traditional silicon. The optimized process developed in this study will increase the efficiency of substrate preparation, allowing more research to be done on the thin films they support.

Methods

To obtain the TiO_2-terminated surface, we use a two-step annealing process. Before being annealed, the substrate undergoes ultrasonic cleaning, first with acetone and then with ethanol, followed by drying with nitrogen gas. This acetone and ethanol cleaning helps to remove impurities, such as dust, from the surface, and drying with nitrogen helps to avoid unnecessary oxidation of the surface. Next, the STO goes through water annealing in a distilled water bath at 51-57°C for 55 minutes (Kwak et al., 2017). Water annealing at this temperature agitates the STO surface, removing some of the SrO terminations as the water reacts with SrO (Gellé et al., 2018). A few of the STO samples were further treated using acid etching after water annealing, where the samples were sonicated in aqua regia for 12 minutes. The *aqua regia* was a mixture of three parts HCl and one-part HNO_3. Acid etching with *aqua regia* is a stronger method for removing SrO terminations, as it acts faster than the water and is more abrasive to the surface due to its increased reactivity.

After ultrasonic cleaning and water annealing, all samples undergo air-annealing, or thermal annealing, at ~1000°C for 30-70 minutes in a box furnace. The ramp rates, set temperatures, and

annealing times were programmed using the front panel of the box furnace. We set the first temperature goal to be 1000°C and the second to be 100°C. We then programmed the furnace to ramp up to 1000°C by 20°C per minute and ramp down to 100°C by 20°C per minute. Between the ramp up and ramp down times, we set a hold time, where the furnace maintains a set temperature for the programmed amount of time. For this experiment, we programmed the furnace to hold the sample at 1000°C for times ranging between 30 and 70 minutes. About every three minutes during the hold time, the temperature fluctuates between 996°C and 1005°C for around 30 seconds, but it remains stable at 1000°C between these times. Thermal annealing allows the terminations of TiO_2 to expand into the regions detached from the SrO terminations through water annealing. After the annealing process, the singly-terminated surface is verified using atomic force microscopy. The atomic force microscope uses a cantilever map the surface features of a sample. As the fine tip of the cantilever scans the surface, it interacts with various microscopic points, and the resulting forces cause the cantilever to deflect. These deflections are measured to provide an image denoting the heights of a sample's surface features. The goal is to get as wide of steps as possible (on the scale of micrometers) and steps with the same height as the unit cell of STO. The resulting image should reveal the unit cell steps as was shown by Kwak et al. in 2017.

Experimental Results and Discussion

We prepared various samples using the described method with slight variations. All STO samples underwent the same ultrasonic cleaning with acetone and ethanol, as well as the water annealing procedure for 55 minutes at 51-57°C. Two samples were additionally etched with aqua regia, however, none of the three samples in Figures 2, 3, or 4 underwent acid etching. The variable that was changed for the various substrates was the annealing time at 1000°C. The first sample was annealed for 30 minutes, the second for 50 minutes, and the third for 70 minutes. The acid-etched samples were annealed for 70 minutes as well. After preparation, we use AFM to scan the surface and verify its atomic smoothness. The sample is first cleaned again with acetone and ethanol and then attached to a magnet with vacuum grease to keep it stationary while scanning. The AFM produces overhead scans of the sample, so to analyze the step height of the terraced surface, we utilize a program in the AFM software that shows the profile of a chosen line across the surface. This allows us to determine whether we have achieved the desired step

height. We also use MATLAB to further analyze the surface by looking at profiles and creating three-dimensional plots of the sample.

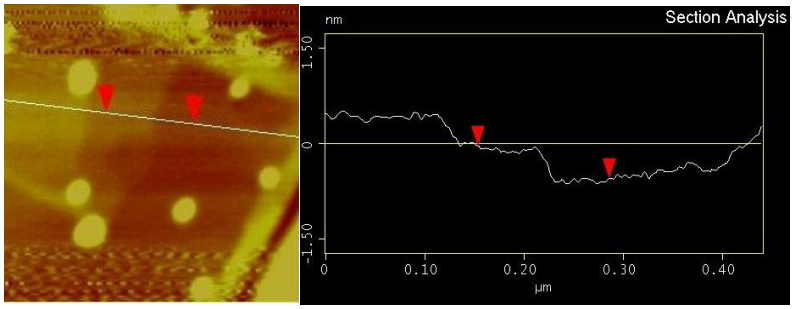

Figure 2. (A, left) A cropped image of a 2x2µm AFM scan of STO Sample 1, which was annealed for 30 minutes. (B, right) The profile of Sample 1 along the line in (A).

For the first sample, which was annealed for 30 minutes, atomic force microscope (AFM) scans showed large dot structures and irregular features across the surface, as can be seen in Figure 2 (A). The surface profile in Figure 2 (B) shows that there were a few confirmed steps measuring 0.432 nm comparable to the unit cell height, but they were rare across the surface. To obtain more consistent steps and reduce the overall roughness, we decided to increase the thermal annealing time from 30 to 50 minutes.

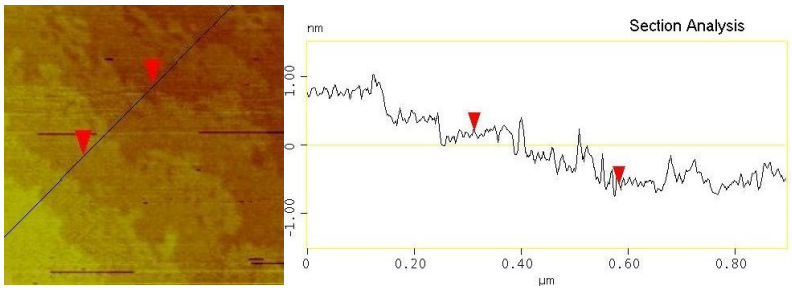

Figure 3. (A, left) A cropped image of a 2x2µm AFM scan of STO Sample 2, which was annealed for 50 minutes. (B, right) The profile of Sample 2 along the line in (A).

Figure 3 (A) shows the AFM scan of the second sample that was annealed for 50 minutes. Various scans showed that there are fewer large dots across the surface, but they are still present. The steps were measured to be around 0.489 nm from Figure 3 (B), which is close to the unit cell height of STO. However, the steps could be more distinct and consistent across the surface, so we increased the thermal annealing time again.

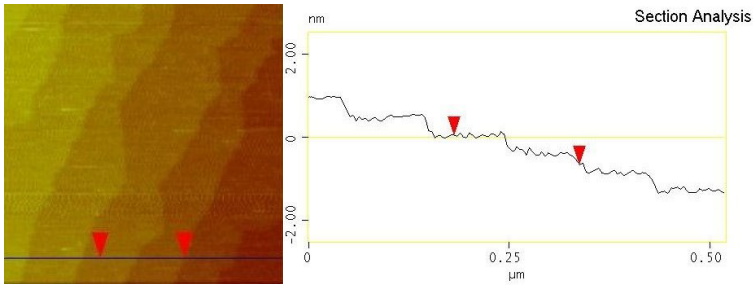

Figure 4. (A, left) A cropped image of a 2x2µm AFM scan of STO Sample 3, which was annealed for 70 minutes. (B, right) The profile of Sample 3 along the line in (A).

Figure 4 (A) shows the AFM scan of the third sample that was annealed for 70 minutes. The amount of dot structures across the surface is significantly reduced, leading us to believe that increasing the time the sample spends in the furnace decreases the frequency of the dots. The steps are consistent across the sample and their height is determined to be 0.493 nm using the profile from Figure 4 (A), so the steps found on the surface are likely unit cells.

We also tried acid etching with *aqua regia* for a few samples separate from samples 1-3. This was completed in accordance with the procedure outlined by Kwak et al. in 2017 with the goal of enhancing the removal of SrO terminations on the substrate surface before thermal annealing. Although the desired steps were achieved with the addition of the acid etching step, there were irregularities still present on the surface, which is inconsistent with the focus of the project. Acid etching also needs to be quickly followed by distilled water cleaning and thermal annealing. Prolonging annealing to the next day gives any leftover acid time to distort the STO surface well beyond the favorable etching. Furthermore, the use of *aqua regia* is a safety risk and is outside the scope of undergraduate experimental research in our research lab. Thus, acid etching requires a strictly timed procedure and enhanced safety precautions. Since the results obtained with acid etching were not as favorable as with the 70-minute annealing without the acid etching, we omitted it from the procedure.

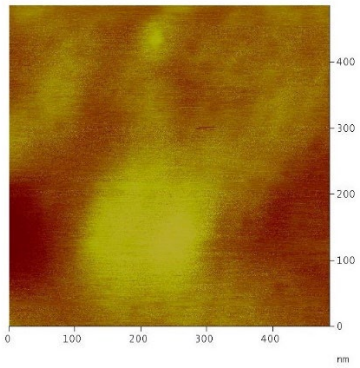

Figure 5. Figure 5 shows a cropped image of a 2x2µm AFM scan of STO Sample 3 three months after the annealing process.

After a few months, we took scans of samples we had made previously that turned out well, such as Sample 3 above, which has been stored in a humidity-controlled box. As Figure 5 shows, the surface is no longer atomically smooth with uniform steps; the distortions on the surface cause AFM scans to have poor quality. The sample seems to have undergone reactions that altered its surface, suggesting that the TiO_2-terminated surface is sensitive to air. This means that after an undefined period of time, samples that have previously been prepared are no longer suitable for thin film deposition. To prevent oxidation of the substrate surface from interfering with thin film deposition and quality, optimally prepared substrates should either be stored in a vacuum desiccator away from ambient air, or thin films should be deposited soon after substrate preparation.

Conclusion

Through our ongoing preparation of $SrTiO_3$ substrates, we learned that creating large steps is possible through a two-step annealing process. This process includes ultrasonic cleaning, low-temperature annealing in a hot water bath, and high-temperature thermal annealing for 70 minutes at 1000°C, and it does not include acid etching. Furthermore, we discovered that the TiO_2 layer might make the substrate more sensitive to air, which means that the substrate surface could oxidize quickly before the film is deposited. Thus, the samples either need to be stored more carefully in vacuum desiccators, or thin films need to be deposited soon after the substrates are prepared. Future work based on this study includes thin film deposition of various perovskite oxides on the STO substrates as they are prepared using the methods developed during this project. Once thin films are deposited, they will experience biaxial strain due to the cubic

structure of STO, which will create an additional handle through which we can control and measure the Hall effects. Another possibility is to further prepare it for use in field-effect transistors by turning it metallic through oxygen reduction or niobium doping.

Acknowledgements

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References

Gellé, F., Chirita, R. Mertz, D., Rastei, M. V., Dinia, A., & Colis, S. (2018). Guideline to atomically flat – terminated (001) surfaces. *Surface Science*, 677, 39-45. https://doi.org/10.1061/j.susc.2018.06.001

Jain, A., Ong, S. P., Hautier, G., Chen, W., Richards, W. D., Dacek, S., Cholia, S., Gunter, D., Skinner, D., Ceder, G., & Persson, K. A. (2013). Materials project: A materials genome approach to accelerating materials innovation. *APL Materials*, 1(1), 011002. https://doi.org/10.1063/1.4812323

Kwak, I., Varnoosfaderani, S. S., Barquist, C. S., Paykar, A., Shakya, A., Lee, Y., Hebard, A. F., & Biswas, A. (2017). Optimization of atomically smooth and metallic surface of $SrTiO_3$. *Journal of Applied Physics*, 121(13), 135305. https://doi.org/10.1063/1.4979967

Liu, X. Z., He, S. M., Wu, D. J., Duan, K. Y., & Li, Y. R. (2006). Heteroepitaxial growth of YBCO/STO thin films for voltage tunable varistors. *Physica C: Superconductivity*, *433*(3–4), 147–153. https://doi.org/10.1016/j.physc.2005.10.011

The Materials Project. *Materials Data on SrTiO3 by Materials Project*. United States. https://doi.org/10.17188/1263154