Laser Annealing Novel Substrates for Rutile Thin Films

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Abstract

Since the discovery of superconducting RuO_2 thin films, the subject of rutile thin films has been under-studied due to a lack of suitable substrates and processes that prepare them for thin films deposition. Commonly available rutile substrates are not stable under the conditions necessary for growing oxide thin films with a rutile crystal structure. This work seeks to identify a set of substrates to be used for rutile thin films and establish optimized processes that prepare them for thin films deposition.

Introduction

For many materials that superconduct, they can do so in both their bulk and thin film forms. Oxides with a rutile crystal structure are not known to superconduct in their bulk states; however, when the rutile RuO_2 was deposited epitaxially as a thin film under large compressive strain, it was capable of superconducting [1]. This raises questions about whether other rutiles could be superconductors when in thin film form. For this, we need to identify and optimally prepare a set of substrates that would best serve as a platform for discovering superconducting rutiles.

To achieve commensurate epitaxial strain in the thin film, it is best to have an atomically smooth substrate, where the surface has terraces with steps of unit cell height. As-received substrates require some sort of preparation process, since the polishing done by the manufacturer can leave residues or amorphous layers at the surface, which would degrade the interface.

To select the substrates of interest, a number of considerations had to be made. Firstly, an ideal substrate would remain stable under both oxidizing and reducing conditions at high temperatures. This rules out most transition metal oxides. Next, we sought materials that are structurally similar to rutiles. Unfortunately, the most commonly available rutile substrates do not fit the previous criteria: TiO_2 is prone to reduction at high temperatures in vacuum, and MgF_2 decomposes at the high temperatures desired for growth. Lastly, we want an oxide with octahedral coordination to ensure a strong oxygen framework throughout the heterostructure. Based on these considerations, the substrates that were chosen are (001) and (010) $BeAl_2O_4$, (010) Mg_2SiO_4, and (001) and (010) $Al_2SiO_4(F,OH)_2$ or topaz, as shown in Figure 1 (a)-(e).

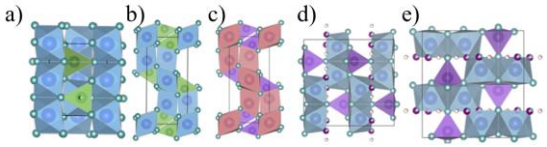

Figure 1. The crystal structures of (a) (001) $BeAl_2O_4$, (b) (010) $BeAl_2O_4$, (c) (010) Mg_2SiO_4, (d) (001) Topaz, and (e) (010) Topaz.

Methods

Our preparation processes focused primarily on annealing, which was supplemented by acid etching in the case of topaz. Supplying thermal energy to the atoms at the substrate surface allows them to redistribute themselves into the configuration with the lowest surface energy [2]. We began with laser annealing under distilled ozone at 10^{-6} Torr, which is advantageous because it takes place within the thin film deposition chamber. This means that substrates can be annealed under the same oxidizing conditions as for the desired growth, immediately prior to deposition. This expands the number of substrates available for thin film deposition to those that are air-sensitive. We also used furnace annealing, which can be a more delicate approach with lower temperatures and longer anneal times. We monitored the annealing *in situ* using reflection high-energy electron diffraction (RHEED) and *ex situ* using atomic force microscopy.

Results and Discussion

The first substrate we studied was $BeAl_2O_4$. No acid etching was attempted due to the material's robust chemical stability. The as-received substrates of the (001) direction in Figure 2 (a) show steps with rough edges. Laser annealing at 1100℃ for 200 seconds (s) left steps that meander quite a bit, so the anneal temperature was increased to 1200℃ to clean these up. Even with the high 0.6° miscut, the steps still appear rough. Annealing at

1250℃ for 200 s produced steps that were rather straight, and the corresponding RHEED pattern had sharp dots instead of streaks, as shown in Figure 2 (b). We also tried annealing at 1300℃ for 200 s, which caused more meandering of the steps, as well as small holes to appear within the terraces. This suggests a longer anneal time is needed, so we increased the hold time to 500 s. Unfortunately, although the steps look cleaner, this caused particles to form across the surface. So, annealing at 1250℃ for 200 s produced the best results for this substrate so far.

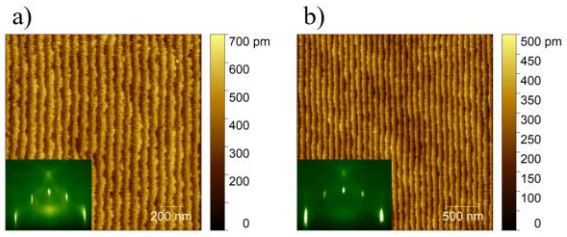

Figure 2. AFM scans and corresponding RHEED patterns of (001) $BeAl_2O_4$ (a) in the as-received state and (b) after laser annealing at 1250℃ for 200 seconds.

Next, we studied the (010) direction of $BeAl_2O_4$. The as-received substrates have rough steps, similar to the (001) direction in Figure 4 (a). Laser annealing at 1100℃ for 200 s (not shown) only smoothed out the edges slightly, so we increased the temperature to 1200℃, where the terraces became rough. At 1300℃ for 200 s, the steps meandered quite a lot, and small holes formed in the terraces. Annealing at 1400℃ and 1450℃ formed deep holes across the surface—the number of which increased with temperature—and many small triangular holes in the terraces. Interestingly, the direction that the triangles faced alternated with the step, suggesting that the (010) orientation becomes doubly terminated. Some of the samples had a step height between 0.35 and 0.4 nm, and others had a step height closer to 0.55 nm. These roughly correspond to two-fifths and three-fifths of the unit cell along the 010 direction. In the crystal structures with 2/5 step height, Figure 3 (a) shows that the beryllium dimers face in two different directions on alternating steps, which creates the double termination. In the crystals with 3/5 step height, Figure 3 (b) shows that the beryllium dimers only appear in every other step surface, also creating a double termination. Having a doubly-terminated surface is not always desirable for thin film growth, as it can contribute to inhomogeneity and twinning in the film.

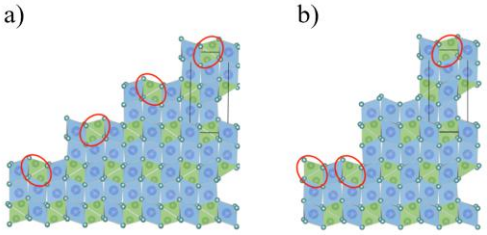

Figure 3. Crystal structures of (010) $BeAl_2O_4$ (a) with 2/5 unit cell step heights and (b) 3/5 unit cell step heights.

Without achieving desirable results within the temperature limits with laser annealing, we tried annealing with the tube furnace. Annealing at 850℃ for 2 hours produced terraces with many holes along the edges, as well as some deep pits starting to form across the surface. We then annealed at 900℃ for 1 hour, as seen in Figure 4 (b). This produced steps with very few small holes along the edges, as well as few pits across the surface, making this the best preparation for growth. We also tried annealing at higher temperatures and found that the deep pits get larger as the anneal temperature is increased. What seems to occur is that small needle-like defects form, pulling surrounding material into it and forming a pit around it.

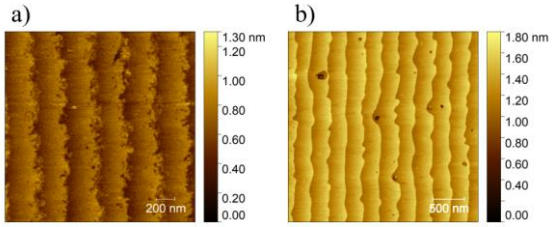

Figure 4. AFM scans of (010) $BeAl_2O_4$ (a) in the as-received state and (b) after furnace annealing at 900℃ for 1 hour.

In addition to $BeAl_2O_4$, we also studied (010) Mg_2SiO_4. From the AFM and RHEED results in Figure 5 (a) and (b), we see that laser annealing at 1300℃ for 200 s leaves the surface best suited for thin film deposition.

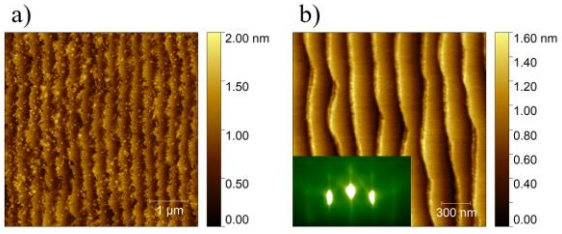

Figure 5. AFM scans of (010) Mg_2SiO_4 (a) in the as-received state and (b) after laser annealing at 1300℃ for 200 seconds.

Next, we studied topaz, both directions of which were etched in a buffered hydrofluoric acid (BHF) solution for 60 s. Beginning with the (001) direction, we could see that laser annealing left the steps similarly rough to the etched state (Figure 6 (a)). We could also see that the RHEED pattern begins to fade at high temperatures, suggesting that something unfavorable may be taking place, such as the fluorine leaving the surface. We also tried furnace annealing, beginning with a lower temperature. The steps are much smoother than those produced by laser annealing, with the best results being produced by annealing at 750 ℃ for an hour, shown in Figure 6 (b). However, more work is being done to investigate lower anneal temperatures to address the patterns in RHEED at high temperatures.

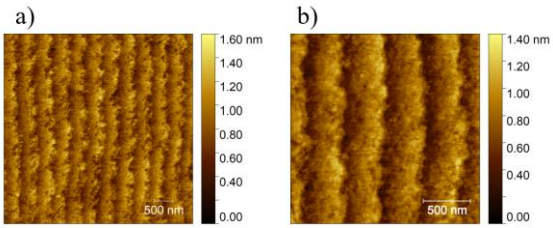

Figure 6. AFM scans of (001) topaz (a) after BHF etching and (b) after furnace annealing at 750 ℃ for 1 hour.

Lastly, we focused on (010) topaz, where BHF etching smoothed out and defined the steps quite a bit. Both laser and furnace annealing, however, did not make much progress beyond this. Laser annealing produced rough steps that meandered, so we tried increasing the temperatures to smooth them out. Although this helped to straighten out the steps some, the RHEED patterns fade in and out above 600 ℃ and do not clear up much during cooldown. So, we attempted the milder approach of furnace annealing. Annealing at lower temperatures for a longer amount of time tends to produce smoother, straighter steps than the as-received state (Figure 7 (a)), with the best results being from annealing at 600 ℃ for an hour (Figure 7 (b)). It is possible that the particles that appear across the surface at lower anneal temperatures could be removed with an additional step of BHF etching. Similar to the (001) topaz, more work is being done to study anneal recipes below 700 ℃. At higher temperatures, the steps are rough and become doubly-terminated. For the doubly-terminated samples, the step heights are around 0.2 nm, which roughly corresponds to one-fourth of the unit cell. As can be seen from the crystal structure in Figure 8, the silicon polyhedra face opposite directions on alternating steps, creating a dual termination.

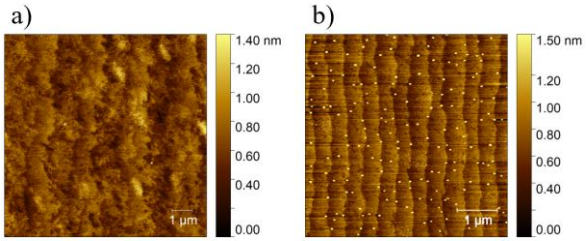

Figure 7. AFM scans of (010) topaz (a) in the as-received state and (b) after furnace annealing at 600 ℃ for 1 hour.

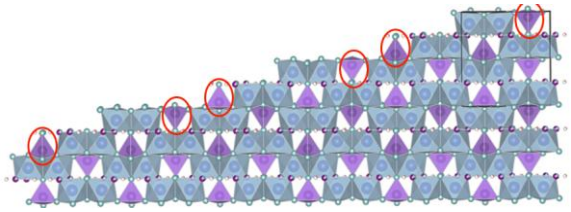

Figure 8. Crystal structures of (010) topaz with 1/4 unit cell step heights.

Conclusion and Future Work

The best recipes we developed include laser annealing (001) $BeAl_2O_4$ at 1250 ℃ for 200 s and furnace annealing (010) $BeAl_2O_4$ at 900 ℃ for 1 hour. For Mg_2SiO_4, the best results were produced by laser annealing at 1300 ℃ for 200 s. The topaz annealing requires further optimization. The best recipes so far include BHF etching for 60 s, then furnace annealing at 750 ℃ for 1 hour of the (001) direction and furnace annealing at 600 ℃ for an hour of the (010) direction. Overall, we successfully developed processes that prepare this set of substrates. These recipes can be used as a starting point for future researchers to grow rutile thin films, possibly revealing ones that superconduct.

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References

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