Synthesis of a $SrCoO_{2.5}$ Thin-Film by Pulsed Laser Deposition

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1 Introduction

The goal of this project is to create thin-film heterostructures. This will be done by using pulse laser deposition (PLD). A thin-film can range in different thicknesses. This range can be from nanometers to several micrometers. An example of a thin-film that is more commonly known includes soap bubbles and a type of anti-reflection coating on eyeglasses. [3]

The properties of thin-films can change based on the amount of oxygen in the structure. Some thin-film heterostructures have semiconductive behaviors. [6] Semiconductors are very common today because they can be found in many electronic devices. This includes phones, laptops, tablets, calculators, game systems, Televisions, radios, smart devices, and more. It is important for these semiconductors to be thin in size. The reasoning behind this is that our technology today continues to get thinner and thinner in size. If smart devices and technology continue to get thinner, the materials that make up these devices would also need to get smaller and thinner. This is why thin-film heterostructures are so important. The crystal structure of Strontium Cobaltite (SCO) is important because of its semiconductive behaviors. There is a lot of interest in the field of thin-film heterostructures because of its potential of outperforming conventional semiconductors. [5] The thin-film of Strontium Carbonate is also an antiferromagnetic insulator. [10] There is currently a major interest in antiferromagnetic insulators due to its abilities of storing information on these thin films. This new discovery helps with our current technology advancements. As devices continue to get smaller and smaller, these thin-films can help keep up with this trend since they can store information and are very thin and small. [7]

This experiment will focus on creating thin-film $SrCoO_{2.5}$ by using pulse laser deposition. The powdered substances Strontium Carbonate, $SrCO_3$, and Cobalt (II, III) Oxide, Co_3O_4, will be used to create Strontium Cobaltite, $SrCoO_{2.5}$. The crystal systems for the different powders are orthorhombic for the $SrCO_3$ and tetragonal for the Co_3O_4. The crystal system for the product, $SrCoO_{2.5}$, is orthorhombic. Using the Strontium Carbonate and Cobalt (II, III) Oxide in the correct ratios, conditions, and equipment, Strontium Cobaltite will form.

The correct ratios can be determined by balancing a chemical equation and the mixture of the Strontium Carbonate and Cobalt (II, III) Oxide to create the Strontium Cobaltite. The ratio of what is needed to create the Strontium Cobaltite from the Strontium Carbonate and the Cobalt (II, III) Oxide is 3:1 which is three parts Strontium Carbonate and one part Cobalt (II, III) Oxide. The $SrCoO_{2.5}$ becomes a polycrystalline after the use of PLD.

A method being used in this experiment is X-ray Diffraction, XRD. X-ray diffraction can find the crystallographic structure of a crystal. It can also determine any impurities in a material. This includes its crystal structure, size, and type of crystals present. This method can be done by using incident X-rays and measuring the waves present and the different scattering angles of the X-rays that leave the material. The XRD will also be used to check the properties and changes of the powdered sample when calcined and sintered. It will then be compared with theoretical XRD graphs using a program called VESTA.

After the Strontium Cobaltite crystal is formed using PLD, another technique will be used called Atomic Force Microscopy, AFM. This is used to measure the surface topology of a substance or material and view how the surface looks, or its topology. For example, the AFM can determine if the surface of a material is hilly, smooth, etc. This allows imaging of many different types of surfaces. It can do this by using three methods. The methods are contact mode, non-contact mode, and tapping mode. Contact mode is done when the tip of the cantilever makes very close contact with the surface. This method is used when measuring surface force. Non-contact mode is done by keeping the probe several nanometers away from the surface in a spot with interaction forces. The last method and the method that will be done for this project is tapping mode. This method is done by vibrating near the fundamental resonance frequency and the tip of the probe moves up and down. The tip only sometimes comes into close contact with the surface.

There is a lot of interest and research in the field of semiconductors and thin-film heterostructures. The formations, physical properties, and structural properties of these crystals and their potential applications as solid-state fuel cells. [6]

2 Procedure

2.1 Creating the Target

The method of creating the strontium cobaltite starts with the powders Strontium Carbonate ($SrCO_3$) and Cobalt (II, III) Oxide (Co_3O_4). The balanced equation for this reaction is as follows:

$$12SrCO_3 + 4Co_3O_4 \longrightarrow 12SrCoO_{2.5} + 11CO_2 + 1C$$

Now that the equation is balanced, stoichiometry can be used to find out how much of each powdered reactant is needed to create the target amount of grams of the product, $SrCoO_{2.5}$. For this experiment, two grams of the product

is being created. This means that 1.5827 grams of SrCO3 and 0.8605 grams of Co_3O_4 will be used to create two grams of $SrCoO_{2.5}$.

Next, X-ray diffraction is used to confirm that the powdered reactants are free of impurities. The XRD will be used twice during this step. Once to test the $SrCO_3$ and again to test the Co_3O_4. After the use of the XRD, the data and peaks from the machine need to be compared with the theoretical XRD data. If the peaks do not match or there are extra peaks, then the powder is impure. The conditions for the XRD were set with a start angle of 10^{o} and an end angle of 100^{o}. The step size is 0.02^{o}. The speed was set to 1.0^{o}/min.

When the powders are proven to be pure and free of impurities, the next step is to mix and grind the powders together. This is done by putting the powders in a mortar and grinding it with a pestle. Grind the powders together until fully mixed and finely grounded. The mixture should stick to the walls of the mortar, mixed, and become a fine powder when completely grounded. For this project, the powders were mixed for 40 minutes using the mortar and pestle.

After the powders are finely grounded, the mixture should be placed in a crucible to be placed in a furnace. The $SrCO_3$ + Co_3O_4 should be calcined in a furnace for 900^{o}C for six hours. This process helps remove possible volatile substances and it can oxidize a portion of the mass. This step is a method of purification. [2]

The pellet can be molded by putting the calcined powder into a dry pellet pressing die. This pellet die helps the powder get formed into a pellet. The powder should get grounded again for 40 minutes using the mortar and pestle and then put into the pellet die. After that, the pellet die should be put into a hydraulic press using 20,000 pounds of pressure for 60 minutes. The pellet should not break apart and it should have enough strength to it to where you can put a little force on it without breaking it. Next, the pellet should be carefully taken out of the die and then placed into a crucible.

Finally, the pellet that was placed in the crucible should then be placed in the furnace at 1100^{o}C for 24 hours (1440 minutes). Check the structure of the pellet by using an XRD machine.

The pellet was then placed in the mortar and grounded using the pestle. The pellet gets grounded, placed in a pellet pressing die and hydraulic press, sintered, and then the structure gets checked when using the XRD. This repeats until the pellet gets sintered for the third time.

2.2 Preparing the Substrate

The substrate being used is strontium titanate, $SrTiO_3$ (001). The substrate needs to be prepared and have many steps to ensure that the target gets deposited onto it accurately. The substrate needs to be checked using the AFM. If there are a lot of impurities and different height levels on the substrate after using the AFM, the substrate needs to be water leached and then annealed.

When water leaching the substrate, stir the substrate in deionized water for 30 seconds and then dry it using an air gun. Then, put the prepared substrate

into a crucible. After that, the substrate needs to be annealed. Place the crucible with the substrates inside into a furnace for 60 minutes at 1000^{o}C.

After the substrate is annealed, check to see if it has the different stair step levels in the sample. If not, the sample needs to be annealed again.

2.3 Preparing the Substrate and the Target for the Pulsed Laser Deposition Chamber

Choose the best substrates with fewer or no impurities and the best stair steps after annealing. Water leach the substrate in deionized water for 30 seconds then attach to the heating stage part of the PLD chamber. Place silver paste on the heating stage and then place the $SrTiO_3$ (001) substrate on top of the paste. To help the silver paste hold the substrate, use a heating lamp over the stage and substrate for ten minutes. Once done, place the substrate is ready to be placed into the PLD chamber.

To prepare the target, $SrCoO_{2.5}$, gently sand the front side of the pellet using sandpaper. Also, use a bit of methanol on the sandpaper when sanding the pellet. Sand the pellet until it appears smooth on the front side. The back side does not need to get sanded.

After sanding the pellet, place the smooth side faced up and place the pellet on a hot plate for five minutes to help rid of any trapped gasses and water vapor that might be in the pellet. Then, place the target into the PLD chamber.

2.4 Conditions for the Pulsed Laser Deposition Chamber

The thin-films were grown on a $SrTiO_3$ (001) single crystal substrate using KrF pulsed laser. The background pressure was measured to be 7.2X10^{-7} Torr. The temperature was set to 700^{o}C inside the chamber. The repetition time was 10 Hz. The voltage was set to 27 kV. The aperture was set to 3. The PO_2 level was set to 10MT.

3 Discussion

3.1 Analysing the Powdered Reactions

The XRD graph for Co_3O_4 was shifted a bit to the right more and more after each peak when compared to the theoretical XRD graphs. This error could be due to the XRD machine not being calibrated accurately when scanning the powder.

Figure 1 shows the theoretical XRD data for Co_3O_4. As the x-axis continued to increase, the shift also increased between the peaks.

The $SrCO_3$ powdered reactant seems to be free of impurities when compared to the research from Zahra Asgari-Fard et al. [1] Figure 3 shows the data from Zahra Asgari-Fard et al. [1] and Figure 4 shows the XRD data that was collected for this research.

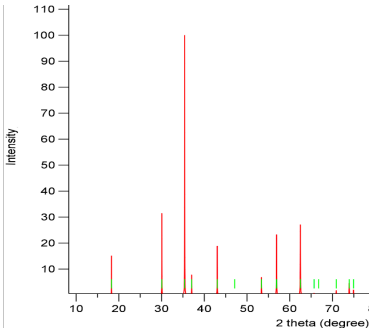

Figure 1: Theoretical XRD of Cobalt (II, III) Oxide (Co_3O_4)

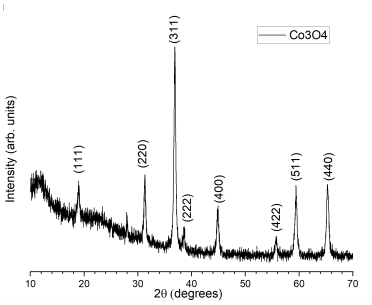

Figure 2: XRD of Cobalt (II, III) Oxide

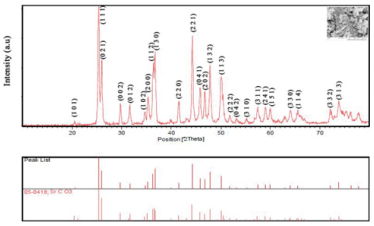

Figure 3: XRD of $SrCO_3$ from Zahra Asgari-Fard et al. [1])

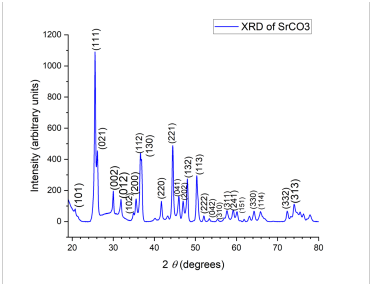

Figure 4: XRD of $SrCO_3$

This can be seen in Figure 2 with the data from the XRD and comparing it with Figure 1 that has the theoretical XRD for Co_3O_4. The XRD for Co_3O_4 also found a possible impurity that can be seen in Figure 2. There is a peak that should not be there. This is the peak between the 111 and 220 miller indices just before 30 degrees.

After the pellet was calcinated at 900^{o}C for six hours, there did not appear to be a color difference when compared to before calcination. Figure 5 shows the mixed reactants before calcination and Figure 6

Figure 5: $SrCO_3$ + Co_3O_4 Before Calcination

Figure 6: $SrCO_3$ + Co_3O_4 After Calcination

3.2 Finding the Right Pressure for the Pellet

When using putting the powders in the pellet die and then under the hydraulic press, the pressure was set to 36,000 lbs. This made the sample very fragile and made it not hold its shape as seen in Figure 8For the second attempt, 20,000lbs. of pressure was used using a different hydraulic press. The press might have a leak because the pressure decreased during the duration of the 60 minutes according to the pressure gauge. This made the pellet less fragile and it still

Figure 7: Pellet of $SrCO_3$ + Co_3O_4 after in press at 20,000lbs. for 60 minutes.

Figure 8: Broken Pellet of $SrCO_3$ + Co_3O_4 pressed at 36,000lbs. for 60 minutes.

kept its shape as seen in Figure 7. The pellet was sintered to help make it denser while maintaining its properties.

3.3 Sintering the Pellet

The pellet was sintered three times. After the first sintering, the pellet was split in half. This was not desired, so the pellet was grounded, pressed in the pellet die, and sintered once again. Figure 9 shows the XRD scan after the first sintering and Figure 14 shows the orthorhombic XRD data from is from A. Muñoz et al. [8]

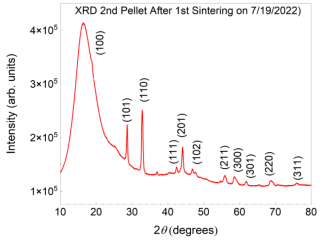

Figure 9: XRD After first Sintering

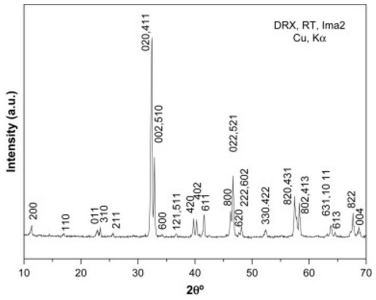

Figure 10: XRD of Orthorhombic $SrCoO_{2.5}$ from A. Muñoz et al.[8]

After the second sintering, the pellet appeared to have more hexagonal properties when checked using the XRD. This was also not desired because, for PLD, the target needs to have an orthorhombic crystal structure. Figure 11 is the data collected from the XRD after the second sintering and Figure 12 is the hexagonal $SrCoO_{2.5}$ data from L. Xie et al. [9]

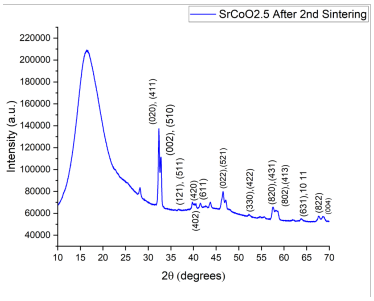

Figure 11: XRD After Second Sintering

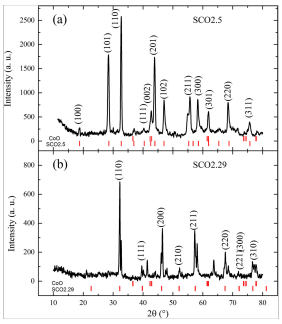

Figure 12: XRD of Hexagonal SCO2.5 from L. Xie et al.[9]

Due to this, the pellet was reground, pressed in a pellet die, and sintered a third time. This time, the pellet appeared to have no hexagonal properties and all orthorhombic proprieties when checked using the XRD.

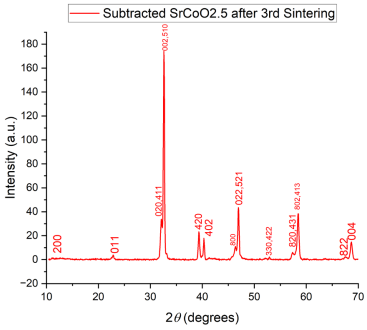

Figure 13: XRD After Third Sintering

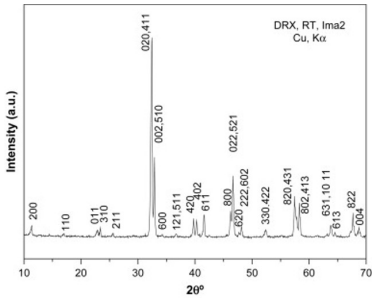

Figure 14: XRD of Orthorhombic $SrCoO_{2.5}$ from A. Muñoz et al.[8]

After each sintering, the pellet appeared more metallic and shiny as shown in Figure 15, Figure 16, and Figure 17.

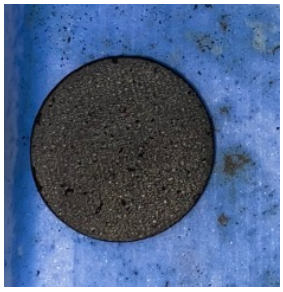

Figure 15: Pellet After First Sintering

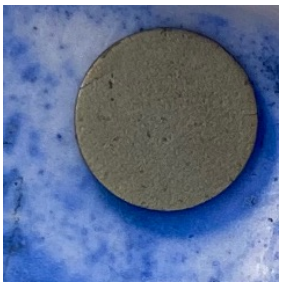

Figure 16: Pellet After Second Sintering

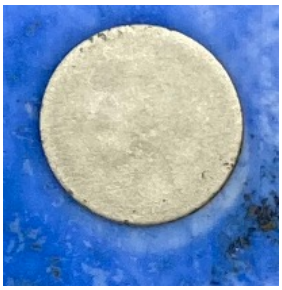

Figure 17: Pellet After Third Sintering

3.4 Using Pulse Laser Deposition

There were not any problems when using PLD. The laser caused engravings in the target. The loss of some of the target traveled in the plasma plume. The target on the plasma plume was then deposited onto the $SrTiO_3$ (001) substrate to create the thin film. The pellet before the use of PLD can be found in Figure 18 and the pellet after the use of PLD can be found in Figure 19. An image of the plasma plume deposition can be found in Figure 20. A thin-film was created as seen in Figure 21

Figure 18: Pellet in PLD Chamber

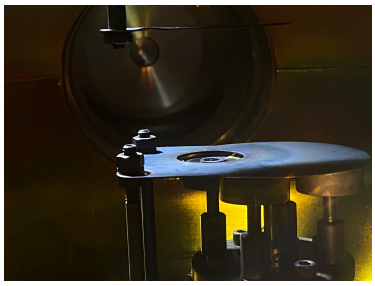

Figure 19: Engraved Pellet After the Deposition of the Thin Film

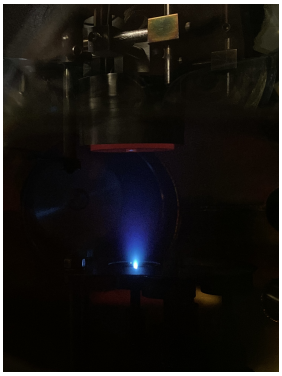

Figure 20: Plasma Plume Depositing the Target $SrCoO_{2.5}$ onto the $SrTiO_3$ (001) substrate.

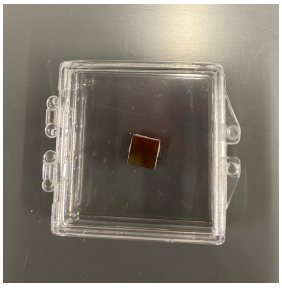

Figure 21: $SrCoO_{2.5}$ Thin-film on the $SrTiO_3$ (001) substrate.

The XRD graph as seen in Figure 22 showed (0 0 1) peaks of $SrCoO_{2.5}$ that matched with the results from other experiments. [4] There was also one impurity peak seen in the XRD graph labeled with a + sign above the peak.

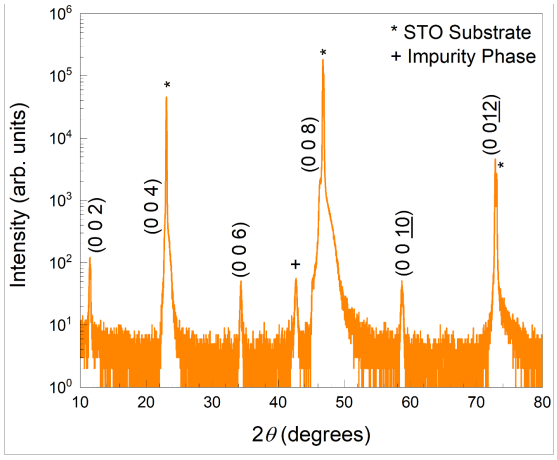

Figure 22: XRD of $SrCoO_{2.5}$ Thin-film on the $SrTiO_3$ (001) substrate.

4 Conclusion

For future work the growth condition of the deposition should be optimized to deposit better quality $SrCoO_{2.5}$ thin-films.

As we continue going to make technology thinner and thinner, the materials inside of these gadgets need to also get smaller and thinner. The use of thin-films can help keep up with this demand for thinner devices. $SrCoO_{2.5}$ has been proven in research to have superconductive properties that can help power these

devices and it can also store a lot of information on them while still maintaining its small and thin size. [7]

There continues to be a lot of interest in thin-films in physics research because of their different properties and different possible uses in the modern world and everyday life. This method has the possibility of changing technology and our lives as we know it.

References

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