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Physical Characteristics and Morphology of Platinum Nanocrystals on Single Crystal Strontium Titanate

Joshua Gild

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Physical Characteristics and Morphology of Platinum Nanocrystals on Single Crystal Strontium Titanate

by

Joshua Gild

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Science in Material Science & Engineering

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Physical Characteristics and Morphology of Platinum Nanocrystals on Strontium Titanate

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ABSTRACT

Eight nanometer platinum films were fabricated via electron beam deposition upon (001) strontium titanate (STO) substrates at ambient temperature then annealed at a range of temperatures in a reducing, oxidizing, or neutral environment. The evolution of platinum film dewetting and forming distinct nanocrystals was examined with XRD, AFM, and SEM. The initial deposition showed no crystallinity for the film. Upon annealing, a (001) cube on cube epitaxy was expected due to similar lattice parameters. However, an initial weak polycrystalline Pt (111) peak formed, which then transformed into (111) texture and eventually epitaxy. This (111) epitaxial relationship was observed in all annealing environments. The oxidizing environment suffered from significant platinum loss due to the sublimation of PtO$_2$ at high temperatures, which as not seen in other environments. Secondary crystal growth from the STO substrate was seen in oxidizing and reducing environments and possibly indicated the in-plane epitaxy of the particles. Surface terminations of SrO$_x$ were found via AES despite etching to ensure a TiO$_2$ termination, indicating migration of Ti atoms, most likely into the bulk platinum. The formation of (111) platinum epitaxy along with an SrO$_x$ termination in various environments indicates the substrate-platinum interactions are the predominant factor in determining platinum crystallinity and other features of the system.
1 Introduction

1.1 Thesis Statement

The production of more efficient and selective catalysts is of utmost importance. They provide new and unique methods to more sustainable energy production as well as the purification of air and water. Many of these reactions occur on heterogeneous catalysts, which are typically in a solid phase, while the reactants and products are in a gas or liquid phase. Of heterogeneous catalysts, platinum is one of the most prevalent throughout industry; it is used in processes varying from oxidization reactions of carbon monoxide and nitrogen oxides to more complex petrochemical reactions.\textsuperscript{1,2} In order to maximize the efficacy of the catalysts, the surface area of the metal will have to maximized as well as configured in certain shapes in order to prefer certain reactions.\textsuperscript{3} One of the most promising current methods for achieving this is via the fabrication of metallic nanoparticles from deposited thin films on a support.

This thesis investigates the behavior of platinum metal on (001) single crystal strontium titanate, $SrTiO_3$, with respect to the crystalline structure and size of the particles, as to give information for future catalytic studies. The platinum films were deposited at room temperature, annealed, and examined ex-situ. A combination of x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and Auger electron spectroscopy (AES) will be utilized to examine films created by electron beam deposition, a kind of physical vapor deposition (PVD).

1.2 Platinum Nanocrystals

Platinum films have traditionally been made in a variety of ways, varying from physical vapor deposition, to the decomposition of platinum acids, to various chemical vapor deposition methods such as atomic layer deposition (ALD).\textsuperscript{4,5} Utilizing electron beam deposition allows one to avoid the plethora of contaminants associated with chemical vapor
deposition, though the residual gases in the deposition chamber can be problematic. Physical vapor deposition does allow, however, for the gases during deposition to be specialized, especially in the case of reactive ion sputtering. Multiple studies have examined the characteristics of platinum nanoparticles created via sputtering with partial oxygen pressures. The reproducibility of PVD techniques offers valuable knowledge for the fields of surface and catalytic sciences.

2 Background

2.1 Properties of STO

2.1.1 STO in Bulk

Strontium Titanate (STO) is a perovskite of the $ABO_3$ group, with A typically being an alkali or alkali earth metal and B being a metal which can occupy the octahedral site. The (001) facet of STO consists of alternating layers of $TiO_2$ and $SrO$ and the crystal has a bulk lattice parameter of 3.905 Å. An example of the STO unit cell is shown in figure 1. A platinum unit cell, for contrast, is seen in figure 2

![Figure 1: STO unit cell, centered on the Sr atom.](image1.png)

![Figure 2: Single Pt unit cell.](image2.png)

The crystal substrates were provided by the MTI Corporation and created via a modified
Verneuil method, which involves feeding purified powders into open hydroxy flames and allowing the molten $SrTiO_3$ to drop onto a rotating disk beneath to slowly cool, creating a single crystal.

### 2.1.2 STO 100 lattice and surface

As was previously mentioned, the (001) facet of STO can terminate in either $SrO$ or $TiO_2$. It has been seen experimentally that the surface termination of the crystal has a strong affect upon the physical characteristics of the platinum nanoparticles created. Polli et. al observed only (111) nanocrystals when a STO (100) crystal was terminated in $SrO$ but a mixture of (100) and (111) when terminated in $TiO_2$. The bond length between platinum and $TiO_2$ is shorter and stronger than that between platinum and $SrO$ as well, helping adherence to the surface and epitaxial growth. It was found by Kawasaki that buffered hydrofluoric acid preferentially etches $SrO$ off of the surface, leaving a pristine surface termination of $TiO_2$. Aqua regia has also been found to leave a uniform $TiO_2$ surface as well. Further annealing removes carbon contamination and creates atomically flat terraces on the surface. The samples in this experiment were prepared via aqua regia and annealing.

### 2.1.3 Strontium Titanate in Catalysis

N-type strontium titanate, typically doped with niobium, has been shown to be capable of photoelectrolysis without an applied external potential. While it was seen to be superior to $TiO_2$ and $SnO_2$, it nonetheless suffers from poor efficiency and it has not seen any widespread use for that purpose. Carbon dioxide and water have been reduced on $SrTiO_3$ powder into methanol and formaldehyde while under a mercury lamp with an efficiency of six percent as well. Naturally, due to this low efficiency, this is not a common usage of strontium titanate either. Strontium titanate remains as a model metal-oxide interface, however.
2.2 Properties of Pt

2.2.1 Pt Bulk

Platinum is an FCC noble metal with a lattice constant of 3.924 Å, causing an approximately 0.5% lattice mismatch between it and SrTiO$_3$. A platinum unit cell is seen in figure 2. While SrTiO$_3$ has all diffraction peaks present, platinum will omit all mixed peaks in x-ray diffraction. The similarity in lattice parameter makes it difficult to differentiate the two lattices in diffraction scans, since the peaks will overlap. For instance, the location of the (002) peaks of both substances is as follows (using $K\alpha_1$ radiation from Cu):

\[
\theta_{STO} = \arcsin \sqrt{\frac{[h^2 + k^2 + l^2]\lambda^2}{4a^2}} = \arcsin \sqrt{\frac{[0^2 + 0^2 + 2^2](1.54\text{Å})^2}{(4)(3.905\text{Å})^2}} = 23.23^\circ
\]

\[
\theta_{Pt} = \arcsin \sqrt{\frac{[0^2 + 0^2 + 2^2](1.54\text{Å})^2}{(4)(3.924\text{Å})^2}} = 23.11^\circ
\]

Since two theta is what is observed in XRD, the angles will be 46.46° and 46.11°- a difference of only 0.35°. The methodology utilized to discern between (002) Pt and (002) STO will be discussed at greater length in the appropriate section.

While platinum is a noble metal, it forms a strong oxide layer easily at room temperature and pressure, similar to ruthenium and palladium. Platinum can form PtO, PtO$_2$, Pt$_3$O$_4$, though PtO$_2$ is by far the most prevalent. PtO$_2$ has heat of formation at 25°C of -32 kcal per mol; the negative heat of formation allows for its existence at room temperature; however, since it is fairly small value, it will lead to a very thin native oxide layer. PtO$_2$ decomposes at 570°C, with it forming and decomposing increasingly fast at higher temperatures. Since one of the samples will be annealed in Airgas “Ultra Zero Grade Air”, which is approximately 21% oxygen, the loss of platinum at high annealing temperatures must taken into consideration.$^{16,17}$
2.2.2 Pt Catalysis

Not only is platinum known as an excellent catalyst for a plethora of reactions, there are a multitude of studies showing crystalline platinum to be more reactive than its amorphous form. Distinct crystalline faces are known to be more selective and active than others for certain reactions. Komanicky et al. found that (100) facets had a higher affinity for oxygen than (111), while (111) is more active at reducing it in oxygen reduction reactions.\textsuperscript{1,2} Somorjai et al. found that (111) Pt is five fold more reactive than the (100) face for the dehydrocyclization of n-heptane but for the isomerization of isobutane, the (100) was more reactive. In a later study with Bartlie et al., they found that cubic and octahedral platinum nanoparticles had different levels of selectivity in benzene hydrogenation reactions.\textsuperscript{3,18} Hence, control over the shape and size of the platinum nanocrystals is very useful in catalytic applications.

Not only has dependence upon the exposed facets been found but the activity of the platinum catalysts has also been found to be dependent upon size. Somorjai et al. found that for dehydrocyclization of n-heptane that (111) terraces five atoms wide were optimal for the reaction. Smaller sizes were seen to lower adsorption rate and larger created excess open space.\textsuperscript{3} The dehydrogenation of cyclohexane was found to be particle size dependent at certain temperatures due to the varying amount of hydrogen that can saturate upon the platinum surface.\textsuperscript{19} Similar effects were seen for the photocatalytic production of hydrogen on platinum nanoparticles.\textsuperscript{20} Glycerol oxidization was found to be dependent on the particle size as well; if the particles were too small, the carbonyl group was unable to attach efficiently and it lowered reaction rates.\textsuperscript{21} Size has also been seen to affect the stability of platinum nanoparticles, with crystals below 5 nm found to be unstable in acidic solutions for PEMFC uses.\textsuperscript{22}

2.3 Pt/STO (001)

A large amount of studies have been preformed examining the epitaxy of platinum films on single crystal strontium titanate. Since platinum is an excellent candidate for a bottom
electrode for transistors in microfabrication, the studies are split between focusing on catal-
ysis and general epitaxy of relatively thick films. Deposition has been done in a variety of
methods, varying from electron beam deposition and sputtering to atomic layer deposition
and finally the decomposition of platinic acids. The majority of the studies of interest in-
volve deposition via PVD or ALD. Not only are a variety of deposition techniques used, the
temperatures at which deposition occurs (in-situ crystal temperature is the value referred to
in these studies) and the thickness of the films varies greatly and their results vary corre-
spondingly.

As previously mentioned, Polli et al. observed a mixture of (111) and (100) crystalline
islands after depositing 20 nm of platinum on varying levels of $\text{SrO}$ terminated strontium
titanate via electron beam deposition at 850°C. A study by Chen et al. observed (100)
platinum epitaxy when depositing at 750°C, but only if they included 10 % oxygen in their
sputtering gas mixture; it should be noted that they did not clean the substrate with hydroflu-
oric acid, only alcohol and acetone. Likewise, Xu et al. fabricated epitaxial films using an
oxygen-argon sputtering blend, up to 20% oxygen, and depositing at 750 to 800°C. They
pre-cleaned the target with oxygen as well; both Xu et al. and Chen et al. theorized that the
presence of oxygen helps remove sulfur and other impurities that can act as seeds for (111)
crystal formation.

Kahsay et al. fabricated epitaxial Pt films of 10 and 50 nm thickness at 750°C or above
utilizing rf-sputtering techniques. They observed (111) or (022) platinum crystallinity at
lower temperatures, though both of these disappeared at the higher temperatures. Further-
more, they noted that increased thickness only reduced crystal quality but did not affect
the overall crystallinity of the film. At all the thicknesses they noted nucleation by using
atomic force microscopy, though the thicker films merely formed valleys and not distinct
islands.

Aditya et al. deposited 10nm, 50nm, and 100nm Pt films on (100) STO at room tem-
perature via electron-beam deposition. They then annealed the sample at 1150°C for 10
hours in an argon/hydrogen environment. All of their films took on (111) crystallinity and hexagonal crystals were seen with electron microscopy. The thicker films formed an interfacial phase between the platinum crystals and the strontium titanate as well, comprised of SrO$_x$. The titanium concentration was measured to be deficient in this layer, having migrated into the Pt crystals.$^{24}$ Altberg et al. observed similar results in their study, with 50nm films obtaining mostly (111) crystallinity after annealing at 1050°C for 10 hours in a 2% oxygen atmosphere. The platinum crystal (111) facets were seen to be significantly offset from (100) of the substrate and, similar to Aditya’s findings, SrO terminations were found despite BHF etching.$^{25}$

The Pt/STO interface as been examined in multiple studies with Auger Electron Spectroscopy as well. It was found that SrTiO$_3$ transfers electrons to the platinum film, creating Ti$^{4+}$ ions as well as creating a 0.4 eV Schottky Barrier. In a vacuum, the concentration of strontium at the sample surface decreased with temperature. The creation of this barrier as well as the change in strontium concentration necessitates a high temperature or an external potential to be present in order for proper interface bonding to occur.$^{26,27}$ It is important to note that the samples were heated in high vacuum for a long period prior to to measurement. This was done to cause oxygen deficiencies, which allows the sample to become more conductive as STO is an insulator. The effect that the oxygen vacancies has upon the interface or spectroscopy is not mentioned.

2.4 Catalytic Properties of Pt/STO (001)

Platinum on strontium titanate for the purpose of hydrogen production is a fairly well studied field, with a large amount of the research happening the 1970’s and 1980’s. A study by Carr and Somorjai show that platinized strontium titanate, doped and undoped, can preform electrolysis on water at sufficiently high pressures and temperatures, given the incoming light exceeded the bandgap of STO, 3.1 eV. Interestingly, the efficiency was highest when the platinum only partially covered the surface, insinuating the strontium titanate
partakes in the photolysis. Wagner et al. found that both bare and platinized Ta doped $SrTiO_3$ produced hydrogen in aqueous NaOH solutions when exposed to light, though the bare crystal did require high concentrations of hydroxide. A film of only platinum did not, however, show any hydrogen production in similar conditions nor did a platinum film in pressure contact with STO; the interface between strontium titanate and platinum was responsible for the increased efficiency. Zhong et al. utilized a STO crystal with Pt on one side and Au on the other to simultaneously produce hydrogen and oxygen with success as well.

3 Experimental Design

Since the goal of this thesis is to examine the morphology and crystallinity of platinum nanoparticles after annealing in different environments, multiple instruments will be needed in order to characterize the evolution of the platinum thin film into supported nanostructures. Crystallography, spectroscopy, and imaging will be utilized to determine changes in physical and chemical properties of the sample. Changes in the crystallinity and epitaxy of the film and later the nanoparticles is examined via x-ray diffraction. Furthermore, x-ray diffraction will yield useful information about the stress of the film and possible changes in lattice parameters caused by contaminants as well. Atomic force microscopy will give a three dimensional topographical image of the sample surface, yielding information about the height and size of the individual particles. This is of great importance to catalytic experiments, since the size of the nanoparticles can affect the activity of the platinum in various reactions. Auger electron spectroscopy is utilized to examine the elemental composition of the sample surface. Since previous studies have seen a change in the concentration of Sr or Ti on the surface of the sample, it is important to see if the data is in agreement with their past results.
3.1 Deposition Techniques

There are a large variety of techniques currently available for platinum deposition. They vary from the decomposition of platinic acids, chemical vapor deposition (CVD)/atomic layer deposition (ALD), to various methods of physical vapor deposition, including but not limited to, magnetron sputtering and electron-beam deposition.\textsuperscript{5,25,32,33} In this study, electron beam deposition was utilized for the deposition of the thin film. This method utilizes a tungsten filament under high voltage in a vacuum system, which causes an electron beam to form. This beam then follows a circular path due to an external magnetic field and the electrons hit the sample surface. The impinging electrons cause a rapid heating of the surface, which then allows for sublimation into the vacuum chamber. A shutter is utilized to catch contaminates while this electron beam is active initially in order to ensure the purity of the deposited film.

Since the thickness is measured by the change in the resonance frequency of a quartz crystal as deposition occurs inside of the chamber, the thickness is not always commensurate with the measurement of the apparatus. Hence, x-ray reflectivity (XRR) is often utilized post-deposition as a non-destructive way to more precisely measure the thickness of the film.

Electron beam deposition has a few advantages over other deposition systems that are available. CVD and ALD require reactive gases to be pumped into the chamber, allowing for contamination from these gaseous residues. Deposition via platinic acids has the same possible source of contamination. In contrast to sputtering forms of PVD, the electron beam deposition minimizes the possibility of back-sputtering onto the sample surface, possibly causing defects to form on the surface. Another distinct advantage of electron beam deposition is the very localized heating of the sample. Since the electron beam is quite small and easily controlled via magnetic fields, one can very precisely heat the area where the sample is while keeping the rest of the chamber cool. This helps minimize contamination from the walls or other sources in the chamber. While the electron beam deposition method does
still have possibly contamination from residual gases within the chamber, it is a relatively ideal way to proceed.

3.2 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a tool that allows for imaging down to the Ångstrom scale. It utilizes a force probe that either contacts or measures deviations in location at points on a two dimensional array, allowing for a topographical 3D image to be created. The force probe works by either “dragging” a tip on the end of a cantilever across a surface or by resonating a tip with a cantilever above the surface and measuring Van der Waal or Colomb forces. In either case, a laser is reflected off the top of the cantilever and deviations in location are noted by the laser moving on a detector. The reflection data is then interpreted and transformed into topographical and phase data for the user. The two methods aforementioned are typically referred to as contact and tapping modes, respectively. Tapping mode is usually preferred, since it operates above the sample surface, minimizing damage of the sample and tip-surface interference, which can lead to poor image quality.34

Utilization of an AFM will allow for the topography of the sample to be measured at various annealing conditions. This yields useful information such as as average crystal size and height, spacing between the crystals, and allows for the various facets of the platinum crystals to be seen. For instance, figure 3 is platinum on single crystal strontium titanate fabricated by Dr. Vladmir Komanicky of Pavol Jozef Šafárik University. Figure 4 is epitaxial Au on TiO₂ fabricated at RIT by Professor Michael Pierce. Both images were taken using a Bruker Innova AFM at RIT.
In figure 3, the flat surface on the top of the crystals can clearly be seen and corresponds to the (001) face of the metal, hence the square shape. On the sides of the crystals, the (111) and (110) crystal faces can be seen, giving a clear image of the cuboctahedra that is likely to form with epitaxial platinum on STO. Any extra objects are due to the image being taken ex-situ in the open atmosphere; the microscope will image any debris as well as the surface. In figure 4, epitaxial (111) Au crystals are seen as hexagonal shapes, with the sides of the crystals being too steep for the AFM to yield good resolution. SEM imaging, on the other hand, can easily see the topography better but requires a high vacuum while these images were taken in ambient air.

3.3 X-Ray Diffraction

X-ray diffraction (XRD) is a tool utilized to examine the atomic structure of a crystal by utilizing the diffraction of x-rays from the crystal lattices. XRD can yield information concerning the lattice parameters, crystal structure, and uniformity of the film and substrate being examined. An example of this is epitaxial Au on a single crystal (110) $TiO_2$ substrate. Au is an FCC metal, while the $TiO_2$ in this case is rutile, a tetragonal body centered crystal.
These scan can be seen in figures 5 and 6.

Figure 5: A specular scan of epitaxial Au on TiO$_2$.

Figure 6: In-plane epitaxy of (111) Au on TiO$_2$.

One can see the strong (111) Au peak with respect to the TiO$_2$ peaks present in figure 5, which correlates to out-of-plane epitaxy. In figure 6, the scans are oriented with respect to Au (111) being the surface normal. The scan is then oriented so that reflections of the side (100) faces are being examined. The scan is then done in reciprocal space, not real space, showing (200) and (020). The two peaks that are 90$^\circ$ from each other correspond to the sides of the crystals that have a (200) and (020) face present, which is expected for (111) hexagonal particles - an image of these particles is figure 4. The peaks have a 90$^\circ$ separation due to the scan being in reciprocal space instead of real space; in real space, there are 120$^\circ$ between the (200) and (020) facets of a hexagonal crystal. If the scan were
continued in reciprocal space, (200) and (020) would be seen at 180° and 270°. A real-space illustration of this crystal faces is seen in figure 7.

The other method to search for in-plane epitaxy is to do a large in-plane circle scan, which will show either the (111) family or the (110) family of peaks identified in figure 7. For a hexagon on cube arrangement, as is the case for Au (111) on $TiO_2$ (110), there is only one way to symmetrically overlap the two, meaning six distinct peaks will appear in the circle scan. These peaks correspond to all of the peaks in the (100) family, including the negative indices set. For a hexagon on cube arrangement, however, twelve peaks will appear since there are two symmetric ways to overlap a hexagon and a cube. Examples of this will be seen in the results section.

### 3.3.1 X-Ray Reflectivity

As was mentioned in the previous electron-beam deposition section, x-ray reflectivity (XRR) is a method by which the thickness of thin films can be ascertained. At sufficiently
low angles, x-rays can be reflected from the sample surface and a fringe pattern can be seen in the detector. Not only can the thickness of the film be calculated from these fringes but the overall roughness can be as well, given the scan has enough precision. A diagram showing the reflection of x-rays from the sample surface is seen in figure 8 and the equation 3 is utilized to compute film thickness.

![Figure 8: X-Ray Reflectivity schematic.](image)

\[
t = \frac{\lambda}{2 \sin(\Delta \theta)}
\]  

(3)

Where \( \Delta \theta \) is the distance between adjacent fringes. An example of an ideal XRR scan is seen in figure 9 for 10 nm of Au on MgO, via the Center for X-Ray Optics.\(^{35} \)
3.4 Auger Electron Spectrometry

Auger Electron Spectroscopy is a method by which electrons emitted via the Auger effect in an ultra high vacuum are measured and their kinetic energy data is graphed, which can be analyzed to yield elemental data. The Auger effect occurs when an atom is bombarded with high energy electrons, causing a core shell electron to be ejected. A higher orbital electron then relaxes down into the core shell and that energy ejects another outer shell electron, known as the Auger electron. Since the energy level of the Auger electron will be unique for each element, it is an excellent method for elemental analysis on the surface. Auger spectrometry cannot examine more than a few monolayers into the surface of the sample since the incoming electrons will fail to penetrate deeper. The limited mobility of electrons in gases and solids is the rationale for utilizing AES in an ultra high vacuum system of at least $10^{-7}$ Torr. If the pressure is appreciably higher, insufficient amounts of the electrons will reach the sample for measurement. Ideally, AES is performed at even lower pressures, in the range of $10^{-9}$ to $10^{-10}$ Torr, to maximize the signal and minimize surface contamination. Since there is a large amount of backscattering causing a conti-
uously large amount of background noise, $\frac{dN(e)}{dE}$ is typically analyzed in order to see the energy peaks more distinctly.

Despite Pierre Victor Auger explaining the experimental and theoretical basis of Auger electrons in his doctoral thesis in 1926 and Lise Meitner discovering it in 1923, Auger electrons were not used for analysis until the 1950’s and fully until the 1960’s. While x-ray photoelectron spectroscopy is now a more common method than AES, it is still very useful for depth profiling and diffusion experiments.\textsuperscript{36} Since previous research of platinum on strontium titanate has suggested an interfacial layer forms that modifies the surface stoichiometry, AES will be useful in seeing if any such deficiencies are present in the samples.\textsuperscript{24,26,27}

Due to AES having a historical relationship to x-ray science, traditional x-ray notation, KLM, is used to define the transition states of the Auger electron. The first letter refers to the core level hole initially emitted, the second letter refers to the relaxing electron’s initial state, and the third the emitted Auger electron initial state. Hence, the Auger electrons are referred to as KLL, LMM, or MNN transitions. For instance, KLL refers to an electron being emitted from the s-shell and two p-shell atoms being involved, one relaxing and one being emitted. KLL is the most common for light elements ($Z<30$), LMM is used until high atomic numbers, over $Z = 65$, are present. Since platinum has an atomic number of 78, a mixture of LMM and MNN Auger electrons are used. The transitions can be further defined by subscripts on the letters, defining the distinct orbitals that the electrons move from and into.\textsuperscript{36,37}

Since Auger spectroscopy is based upon utilizing an electron gun in an ultra high vacuum system, the scans are described by the voltage the electron gun is utilized at, the current through the filament, and the sensitivity of the measurement. Figures 10 & 11 shows example scans of $TiO_2$ and $MgO$, with settings of 3 kV, 2 mA, and 1-2 eV peak to peak allowance, meaning that values $\pm 1$ or 2 eV are considered within the peak as well. Lower peak to peak allowances will lead to sharper images at the cost of intensity or increased
scanning times, the latter of which can be problematic for non-conductive samples - similar
to a SEM, the sample surface can easily be charged by incoming electrons if it is an insu-
lator. Once the sample becomes charged, the precision becomes too poor to read bonding
states and chemical shifts properly.

![Auger spectra of TiO$_2$.](image1)

**Figure 10:** Auger spectra of TiO$_2$.

![Auger spectra of MgO.](image2)

**Figure 11:** Auger spectra of MgO.

Auger spectroscopy becomes more complicated as atomic weights increase, as there are
an increasing number of allowed LMM and MNN peaks appearing. For instance, Mg and
O have only KLL peaks, creating a fairly simple peak set and Ti has LMM peaks, creating a more complicated peak set, as is seen in figures 10 & 11. Platinum, on the other hand, utilizes MNN peaks and has at least 25 known energy peaks, though the peak at 1967 eV is used for identification and analysis. Since it is inevitable that some of the platinum peaks overlap with other primary or secondary peaks for other elements, great care must be taken in order to properly identify and measure the peaks in a sample with multiple elements.

AES is typically a destructive process due to the utilization of an ion sputtering gun to clean the surface of debris accumulated while exposed to air. Therefore, it was only used on the samples once all of the annealing, AFM, and XRD measurements had taken place.

3.5 Scanning Electron Microscopy & Energy Dispersive Electron Spectroscopy

Scanning Electron Microscopy(SEM) is an imaging method that works, in principle, fairly similarly to light microscopy. Instead of using photons, however, it utilizes high energy electrons to image the surface. Most commonly, the high energy electrons are projected onto the sample surface, which creates secondary electrons after colliding with surface atoms. These secondary atoms are collected to give topographical information. Utilizing these methods, a SEM can give resolution down to 1 nm and maintain a fairly large depth of field, which is ideal for three dimensional samples - especially when compared to AFM, in which this is a more difficult accomplishment. Another advantage of the SEM is its relative speediness - the microscopes can raster images over a relatively large sample in a short period of time, while other methods can take longer.

While SEM has many advantages, it does have a major disadvantage over some other methods in that it requires the surface of the sample to be conductive. Since the imaging is based upon utilizing high energy electrons impinging upon the surface, the surface will quickly become locally charged if it is an insulator. The local charging, in turn, drastically reduces the resolution and clarity of the images created. Therefore, for an insulator to be
examined in a SEM, it must first be sputter-coated with a conductive film, typically Au or a Au/Pd alloy. Strontium titanate is a insulator, so it will require a Au/Pd coating in order to be imaged in the SEM.

Energy Dispersive Electron Spectroscopy (EDX), is an elemental spectroscopy method that utilizes high energy electrons to excite core-shell electrons in the sample, which then in turn create x-rays when they relax. Unlike AES, EDX penetrates deep into a sample, giving the elemental composition of the bulk and the surface, instead of only the surface. Like Auger electrons, the x-rays created by excited electrons is elementally unique and are denoted by KLM notation as well as $\alpha$ and $\beta$ to distinguish between the energy transitions further.

### 3.6 Residual Gas Analyzer

A residual gas analyzer (RGA) is a small mass-spectroscopy device most commonly utilized in UHV or other surface science systems to measure the elemental composition of gases within the system. It utilizes a high voltage set-up to ionize gases near the analyzer and the partial pressures for various respective mass to charge ratios are recorded. While this does just give a spectrum of weights for the gases instead of identifying the gases specifically, it should not be difficult to identify which gases are present in a clean chamber. One of the very useful applications of a RGA in a vacuum system is for measuring reduction and oxidization reactions of gases within the chamber. For instance, carbon monoxide and oxygen can be purposefully inserted into the chamber in the presence of a platinum catalyst and the amount of carbon dioxide present after a set amount of time can be measured. This can give useful information about the efficacy of a catalyst since RGA’s can typically measure partial pressures down to $10^{-14}$ Torr, meaning that even small amounts of converted gases are detectable. Such a set-up can test the catalytic activity of the platinum nanoparticles in this experiment as well.
4 Results and Analysis

4.1 Platinum Deposition

The platinum films were grown upon 1 $cm^2$ (001) $SrTiO_3$ single crystals with a mis-cut angle of $<2^\circ$ and surface roughness $<5$ Å provided by the MTI Corporation. The crystals were etched in aqua regia to ensure a uniform $TiO_2$ surface termination and subsequently annealed to ensure atomically flat terraces at 1100°C for approximately 2 hours. An electron-beam deposition chamber was then utilized to deposit nominally 8 nm of platinum at a pressure of $10^{-6}$ Torr and at a rate of $0.5 \AA/s$ with the crystals at ambient temperature.

X-ray reflection scans confirmed the average film thickness upon the crystals to be $8.34 \pm 0.15$ nm, as is seen in figure 12 with the ideal simulation of said XRR scan via CXRO(Center for X-Ray Optics) seen in figure 13. The difference between the actual scan and CXRO scan are due to lack of intensity, which will cause higher $2\theta$ peaks to be smaller, and the non-ideal bandwidth that x-rays from a copper source intrinsically have. Atomic force microscopy confirmed the films to be atomically flat at multiple locations on each surface with figure 14 as an example. X-ray diffraction scans showed no crystallinity for the platinum film after deposition., as is seen in figure 15.

![Figure 12: XRR scan of Pt film after deposition.](image1)

![Figure 13: A simulation of the XRR via CRXO.](image2)
Figure 14: AFM image of surface post-deposition. RMS roughness was >1Å.

Figure 15: XRD scan of platinum film post-deposition. Note the lack of any platinum crystal peaks.

With the goal of examining the effects of the temperature and atmosphere upon platinum crystal formation, two crystals were separately annealed in a quartz furnace in steps of 50°C or 100°C in flowing Ultra Zero Grade Air (Airgas) or a reducing atmosphere (Ar/0.5%H₂) for 30 minutes. At each temperature step, the crystallinity of the films was examined via x-ray diffraction and their morphology was examined via atomic force microscopy in both tapping and contact modes ex-situ.
4.2 Annealing in Oxidizing Environment

Annealing of the sample was performed in a Lindberg/Blue quartz tube furnace. Ultra-high purity dry air from AirGas was used as an oxygen source for annealing. The sample was annealed in an alumina boat for 30 minutes at each temperature step, with 100°C steps occurring until 700°C, where steps were reduced to 50°C. The reduced temperature steps was due to the formation of crystalline islands on the surface starting at 700°C.

4.2.1 XRD

Figure 16: A (111) and (022) peak of Pt can be seen at high temperatures, while (002) Pt does not appear. The gap between 62° and 65° at 100°C is due to avoiding a possible λ/2 peak.

The film reoriented itself to become increasingly crystalline with (111) specular epitaxy as annealing temperatures increased. A platinum (111) peak appeared at 200°C, albeit very weakly. The (111) peak increased in magnitude at each annealing step until a temperature of 1050°C, as is seen in figure 17. The plateau in the magnitude of the (111) Pt peak is likely due to loss of platinum during the annealing process - since the film was originally 8.34 nm thick, the loss of even a few monolayers of platinum is significant with respect to diffraction peaks. The effect of a flowing oxygen environment upon platinum loss is unknown as well, making a quantitative measurement of the amount of Pt loss difficult. At 1000°C, a platinum (022) peak appeared as well; the peak was unaffected by further annealing both in shape and
in magnitude, seen in figure 19. Theta scans showed that the (022) crystals were textured, though fully epitaxy is quite doubtful. Evidence of this at 1150°C can be seen in figure 84 in Appendix A. This is in contrast to results by Kahsay, who reported the peak disappearing by 750°C, but in agreement with Altberg, who observed it at 1050°C.\textsuperscript{23,25}

![Figure 17: (111) Peak of platinum at various annealing temperatures.](image)

Throughout the entire experiment no discernible change was observed at the (002) peak, as is seen in figures 16 & 18. While the (002) of Pt and (002) of STO are approximately 0.3° apart, causing a meld of the majority of their intensity, a discernible (002) platinum peak can easily be observed via XRD.\textsuperscript{33} Furthermore, scans with theta offset by 0.3° in each direction were performed at the (002) peak to check for epitaxial platinum. The rationale for the theta offset scans are that the peak for (002), like most single crystal metal oxide peaks, is very narrow compared to the platinum (002) peak. Hence, a small offset in theta will not strongly effect the platinum (002) peak but drastically decrease the intensity of STO (002), helping compensate for the two peaks overlapping. None of these scans indicated
any presence (002) platinum in any form. Therefore, formation of epitaxial (002) platinum is very unlikely. It is important to note the studies that observed (002) platinum were all preformed in a high vacuum, not ex-situ.

Table 1 is the values of the full-width half max (FWHM) of the (111) platinum peak in $2\theta$ and $\theta$ with respect to annealing temperatures. The data shows a steady decline in the width
of the (111) peak in $\theta$ and $2\theta$. The final width of $2\theta \approx 0.35^\circ$ is limited by the width of the opening in the slits, which was predetermined before crystal formation. The increasingly narrow $\theta$ peak suggests a strong uniformity amongst the platinum particles concerning the location and direction of the (111) planes specularly. A graph displaying this relationship can be found in the appendix. Utilizing the location of the (111) and (002) peaks, the offset of (111) Pt with respect to (002) can be found - since ideally they should be parallel. This offset was found to be less than $0.7^\circ$ for all temperatures, which is most likely within error for the measurements.

With the FWHM data, the integrated intensity values of the (111) platinum peak can be found via numerical integration. These values give an excellent measurement of the volume of crystals that are pointing in the (111) direction specularly. While the absolute values of the intensities is not meaningful, their relative strengths compared to one another is. The values are seen in figure 20. Once again, the values at high temperatures has lowered due to platinum loss. The (022) intensities are shown as an inset in the figure. Due to the weak intensity of the (022) peaks, they need to be shown on a different scale in figure 21.

Figure 20: Integrated values of (111) Peaks with respect to temperature.  
Figure 21: Integrated values of (022) Peaks with respect to temperature.

Due to the magnitude of (111) at 1000°C, XRD scans concerning in-plane epitaxy of the
crystals were preformed. The methodology to check for in-plane epitaxy assumed that (111) of the platinum crystals were parallel to (001) of the STO substrate. When this is sound, the (111) of the substrate will be in the same direction as the (100) faces of the platinum crystals. Therefore, the (111) peak of STO was found, then the $\theta$-$2\theta$ values were changed to satisfy the conditions for (002) faces of platinum. By doing such, the (001) faces of the platinum nanocrystals were examined. The sample was then rotated in a circle around the (001) surface normal. This rotation occurs via movement of the angle henceforth known as “phi”. The circle this scan creates in reciprocal space is also known as the (002) powder ring before the full formation of epitaxial crystals; it then becomes the off-specular (002) ring. The relationship between the (111) and (100) faces of the crystal and substrate are shown in figure 22, with the white arrows signifying directions with respect to the platinum crystal and the green with respect to the STO substrate.

![Figure 22: Miller indices with respect to both the crystal(white) and the substrate(green).](image)

Scanning along the (002) off specular ring of platinum showed sharp peaks every 30°, with smaller peaks on both sides. Furthermore, fifteen degrees away from these sharp peaks there were five broader peaks agglomerated together.
Since there are two symmetrical ways to project a hexagon onto a square substrate, in this case the STO, there are twelve clusters corresponding to the twelve sides of the hexagons present on the sample surface. Not only will there be twelve peaks due to this, there are also particles rotated slightly to each side of these alignments; hence, the broader set of peaks having three principal orientations. The sharp, narrow peaks appearing at 50°, 80°, and every additional step in figure 23 are in alignment with (11) of the strontium titanate substrate. Note that the unequal intensities of sharp peaks are likely due to non-ideal position of the crystal during scanning. A pictorial representation peak alignment is seen in figure 24.
Figure 24: A pictorial representation of a hexagonal (111) crystal in alignment with (11) of the STO substrate.

To better view the overall shape and nature of the peaks on the (002) platinum ring, two dimensional scans in hk-space were taken of the sharp peak and its two satellites, in figure 25, and of the set of five peaks in figure 26. Figure 25 shows that there was no longer a powder ring of platinum (002) at 1000°C.

Figure 25: A wide reciprocal space map of the sharp epitaxial peak and its satellites.
Continued annealing showed the sharp peaks decrease in intensity slightly at 1050°C and 1100°C and dramatically at 1150°C. However, all of the peaks, including specular (111), decreased in intensity after annealing at 1150°C, likely to the aforementioned platinum loss at these high temperatures. Interestingly, the five peaks changed at every temperature step after 1000°C. The center peak of the five grew and then returned to its original intensity while the outer twin peaks eventually melded into a single one of greater intensity. The change can be seen in figures 27 and 28. The weak ring in the upper right of figure 28 is due to scattering from the aluminum post that the sample is on during scans. Any rings of that nature in later scans are also due to aluminum.
Figure 27: The auxiliary peaks in the (002) powder ring melding together for a total of three peaks after annealing at 1100°C.

Figure 28: The previously five peaks have melded into three distinct ones after annealing at 1150°C.

A comparison of the HK circle scans for temperatures from 1000°C to 1150°C is shown in figure 29:
In an attempt to achieve uniform in-plane epitaxy of the (111) crystals, the sample was annealed again at 900°C for three hours, in order to eliminate possible time constraints for the movement of platinum on the sample surface. Unfortunately, no change was seen in the sample in specular or off-specular scans. Therefore, it was attempted again at 1050°C for three hours. While it did not change the location of peaks or the amount of them in XRD scans, it did greatly diminish the intensity of all of the peaks. Approximately two orders of magnitude were lost at the platinum (111) peak and off-specular epitaxy was barely visible. This is most likely due to significant platinum loss in the oxygen atmosphere.

4.2.2 AFM

Atomic Force Microscopy was utilized to gain information concerning the topography of the sample surface. Images were taken from 100°C to 1150°C at various steps to observe the creation of the crystals and give information about their average height and widths. The temperature vs the RMS roughness of the surface sample, averaged over multiple surface locations, versus temperature is as follows:
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>RMS surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.80</td>
</tr>
<tr>
<td>200</td>
<td>0.90</td>
</tr>
<tr>
<td>300</td>
<td>2.13</td>
</tr>
<tr>
<td>400</td>
<td>2.62</td>
</tr>
<tr>
<td>500</td>
<td>2.55</td>
</tr>
<tr>
<td>600</td>
<td>3.02</td>
</tr>
<tr>
<td>700</td>
<td>8.42</td>
</tr>
<tr>
<td>750</td>
<td>12.8</td>
</tr>
<tr>
<td>800</td>
<td>15.4</td>
</tr>
<tr>
<td>850</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Table 2: RMS Surface Roughness v. Annealing Temperature

As can be seen from Table 2, the surface did not change very significantly until 700°C, though roughening of the film was observed. While the values for RMS roughness at these low temperatures is useful in seeing the overall change in the film, it is increasingly misleading as the particles agglomerate into large, distinct particles due to the amount of bare substrate skewing the values.

The topographical changes that occurred before 700°C primarily comprised of a small amount of the platinum dewetting and forming into bead droplets on the surface; these shapes illustrated no morphology that would indicate their crystallinity. Example images from 100°C to 600°C are seen in figures 30 - 33.
At 700°C, significant amounts of dewetting started to occur as well as the formation of distinct triangular (111) crystals. This behavior continued at higher temperatures, creating taller triangular crystals until they transformed into hexagonal crystals. The hexagonal crystals are caused by two overlapping (111) triangles facing in opposite directions. Due to the nature of self-attraction, the crystals will look akin to a stretched regular hexagon rather than a six-pointed star. Triangular (111) crystals are visible in figures 34 - 37:
Another significant change occurred at 700°C: dark spots started to appear throughout the sample surface. The majority of these dots were large enough to be easily visible with a light microscope as well, hence the “dark” nomenclature. This is visible in figure 38:

Figure 38: Light microscope image of platinum surface after annealing at 850°C.

Inside of these darker areas, the platinum nucleated into more distinct (111) crystals than on the general surface. That is, they formed into hexagonal shapes well before other areas did. These circles are likely points of crystal defects, either in the crystal surface or the metal, which encouraged (111) growth. While previous literature suggests the presence of sulfur or other impurities could be the root cause of these issues, this is very unlikely for
distinct nanocrystals unlike for a uniform film. If the cause of (111) nucleation of platinum was an impurity, it would cause a single (111) crystal to form but not change its surrounding neighborhood of crystals. This is in contrast to a film, where a single nucleation point would cause a cascading effect throughout the film. In other words, if the impurities were the root cause there would be single, randomly dispersed (111) hexagonal crystals instead of well defined circle orientations. These darker circles increased in size and amount at higher annealing temperatures. Representative pictures are seen in figures 39 - 44.

Figure 39: 10x10, 700°C.

Figure 40: 5x5, dark area, 750°C

Figure 41: 20x20, 750°C.

Figure 42: 50x50, 750°C
In figure 39, a mixture of the “dark” and light areas are visible as hexagonal vs triangular crystal formation, respectively. The dark areas saw increased dewetting of the platinum from the STO surface, causing the hexagonal crystals to be taller than the associated triangular crystals. Figure 41 gives an excellent contrast between the dark circle containing hexagonal crystals and the rest of the surface still containing triangular ones. At 1000°C, the crystals had transformed into a purely hexagonal shapes, as is visible in figures 45 and 46.
In figure 45, the primary platinum crystals have shorter crystals adjacent to at least one of their faces. In the reducing atmosphere, these crystals were not found to contain platinum and similar composition is expected here. The formation of these secondary crystals are likely to have a significant effect upon the epitaxy of the particles.

After the final annealing, another set of AFM pictures was taken via contact mode. They showed appreciably smaller and shorter particles than was seen at 850°C. This was due to the aforementioned platinum loss due to high temperatures in the oxygen atmosphere. They did maintain hexagonal shape and exhibited epitaxial direction. This is visible in figure 47. SEM pictures confirm the loss of platinum as well, as seen in figure 48.

![Figure 47: 15x15 micron](image1)

![Figure 48: SEM of sample after substantial platinum loss.](image2)

The small crystals seen in the SEM picture are the small remnants of platinum nanocrystals still existing, as well as possible secondary crystals that formed out of the SrTiO$_3$ substrate; this will be elaborated on more in a later section.
4.2.3 Auger Electron Spectroscopy

After the final annealing, the sample was examined with Auger electron spectroscopy to check for any changes in surface concentration of strontium or titanium. A blank \( SrTiO_3 \) substrate was examined as well, in order to compare the relative compositions of \( SrTiO_3 \) prior and post platinization and annealing. A 3 kV electron beam with a current of 0.2 mA was utilized in all measurements. The lower energy scans utilized 4 eV peak to peak while the higher energy accepted 10 eV. The base pressure of the chamber was approximately \( 5 \times 10^{-10} \) Torr. Argon ion sputtering was utilized on the annealed and blank samples to minimize carbon and other impurities that may have been present on the sample surface. To confirm the cleanliness of the chamber, a SRS 100 RGA was utilized to measure the partial pressure of gases in the chamber, as is seen in figure 49.

![RGA Elemental Analysis of AES UHV Chamber](image)

Figure 49: RGA spectra showing residual gases in UHV chamber.

Figures 50 and 51 show the low and high energy spectra for the samples, respectively. Oxygen has its principal KLL peak at 503 eV, Ti has a principal LMM peak at 418 eV, Strontium has a principal LMM peak at 1649 eV, and Pt has its MNN peak at 1967 eV.\(^{37}\) All of these peaks, save the principal Pt peak, can be identified in these figures.
As can be seen in figure 50, the titanium peak significantly diminished after platinization and annealing. Furthermore, in figure 51, the strontium peak can be seen to have stayed more or less constant. This indicates a titanium deficiency in the surface termination.

Nominally, the composition of \( \text{SrTiO}_3 \) in an Auger scan will be seen as 20% Sr, 20% Ti, and 60% O. Analysis of the Auger data of the sample post-annealing yielded a composition of 37 ± 4% Sr, 8 ± 1% Ti, and 54 ± 4% O. Considering the sample surface was etched with aqua regia to ensure a \( \text{TiO}_2 \) termination, this indicates that nearly all of the titanium on the surface has either diffused deeper into the substrate or into the platinum nanoparticles themselves.
4.3 Annealing in Reducing Environment

4.3.1 XRD

Figure 52: A (111) peak of Pt can be seen at high temperatures, while (002) Pt does not appear. No Pt(022) (not shown) is present.

Since there was little film reorientation in the oxidizing film until 300°C, XRD analysis was omitted at the annealing steps of 100°C and 200°C. The same process of annealing, cooling down to 50°C or lower, then annealing once again was followed in the same fashion as it was for the oxidizing environment to ensure comparability of the data. Table 3 shows the full width half maximum data for the $2\theta$ and $\theta$ peaks, similarly to Table 1. A graph displaying the temperature and FWHM in $\theta$ relationship can be found in the appendix. Utilizing the location of the (111) and (002) peaks, the offset of (111) Pt with respect to (002) can be found - since ideally they should be parallel. This offset was found to be less than 1.0° for all temperatures.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pt (111) Location (deg)</th>
<th>FWHM 2θ (deg)</th>
<th>FWHM θ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>39.75</td>
<td>1.24</td>
<td>1.37</td>
</tr>
<tr>
<td>600</td>
<td>39.75</td>
<td>0.67</td>
<td>0.75</td>
</tr>
<tr>
<td>800</td>
<td>39.80</td>
<td>0.61</td>
<td>0.50</td>
</tr>
<tr>
<td>900</td>
<td>39.74</td>
<td>0.65</td>
<td>0.49</td>
</tr>
<tr>
<td>1000</td>
<td>37.85</td>
<td>0.51</td>
<td>0.29</td>
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<tr>
<td>1100</td>
<td>39.80</td>
<td>0.37</td>
<td>0.17</td>
</tr>
<tr>
<td>1150</td>
<td>39.80</td>
<td>0.41</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 3: Location of (111) Pt peaks in 2θ and their FWHM at various temperatures.

At 300°C, the sample possessed a significant (111) specular peak that was equivalent in intensity to the 600°C sample in the oxidizing sample, as shown in figure 54. No (002), (022), or (311) peaks of platinum were observed. However, three fringes were seen left to the primary (002) peak caused by the substrate when the sample was examined immediately after annealing. These fringes were likely caused by a high amount of tensile stress of platinum film on the surface. This is supported by the lack of two of these peaks the next day; the film allowed itself to find a more stable, less stressed configuration overnight. It is surprising that this occurred in less than 24 hours at room temperature. The fringes can be seen in figure 53 and correspond to lattice parameters of 4.07 Å, 4.01 Å, and 3.97 Å immediately after annealing.

![Pt Fringes at 300°C](image)

Figure 53: Pt fringes next to (002) STO immediately and post 24 hours from annealing at 300°C.
X-ray analysis was once again skipped at 400°C and at 500°C, since that is where the most significant change occurred in the oxidizing sample. The (111) peak of the platinum grew drastically once again; it was equivalent in intensity to the 850°C annealing for the oxidizing sample, as can be seen in figure 54. This increase in intensity was not accompanied by (002), (022), or (311) specular platinum peaks.

At 800°C, the (111) peak strengthened and scans were performed to check for in-plane epitaxy. While not very intense, small peaks began to appear indicating (002) off-specular peaks, confirming the start of epitaxy for the sample. This peak can be seen in fig 55.
The next annealing step, 900°C, yielded a strong increase in off-specular epitaxy of the (111) crystals, as well as a small increase in specular (111) peak intensity. Unlike the oxidizing sample, sets of five peaks were not observed in the (002) platinum ring at this temperature. However, the sharp peaks were in alignment with (11) of the STO substrate. A pictorial representation is seen in figure 24.

Two sets of peaks did exist, however, indicating there was once again two orientations that the hexagons can partake in on the cubic STO. Figures 56 and 57 show the off-specular peak aligned with (111) of STO and the peak that is 15° offset from it. Both of these images are in reciprocal space. Note that both of these images have intensities on a log scale, to allow the 15° offset peak to be more distinct.

![Figure 56](image-url)

Figure 56: A (002) off-specular peak in alignment with (111) of the substrate.
Figure 57: A (002) off-specular peak offset by 15° with respect to (111) of the substrate.

Note that the (002) powder ring is still present in significant strength. This signifies a substantial portion of the (111) crystals are not aligned epitaxially with respect to the substrate.

At 1000°C, the (111) peak increased in intensity while no other changes were seen speculately. The off-specular (002) peak in alignment with (11) of the $SrTiO_3$ substrate narrowed but did not grow significantly in intensity, while the peak offset by 15° was mostly unchanged. The narrowing of the peak in reciprocal space indicates that the particles are more uniformly pointing in the same direction with respect to (11) of STO. Figure 58 shows the peak in alignment with (11) of the substrate.
Figure 58: A (002) off-specular peak in with alignment with (11) of the substrate.

After annealing at 1150°C, the (111) peak not only grew significantly in intensity, it narrowed in $\theta$ by nearly 50%. (values can be seen in table 3) This indicates a strong agreement amongst the particles concerning the (111) platinum plane being parallel to the substrate (001). A comparison of the (111) peak on this sample are seen in figure 59.

Figure 59: The (111) peaks of platinum nanocrystals after multiple annealing steps in a reducing atmosphere.

Figure 60: Note the lack of any Pt epitaxy.

Similar to the oxidizing sample, no change was seen in the (002) peak for platinum at any temperature as well. This is visible in figure 60. One of the major differences between
the oxidizing environment and reducing environment is seen in comparing figures 17 & 59 as well as figures 20 & 61. In comparing the figures, one can see that there was little to no platinum loss at high temperatures in the reducing environment unlike in the oxidizing.

Figure 61: The integrated intensity of the (111) peaks of platinum nanocrystals at various temperatures.

The most significant change at 1100°C occurred at the (002) off-specular ring. While up to this temperature, peaks existed on the (002) ring at 30° intervals, corresponding to the two allowed hexagonal arrangements on the cubic substrate. After this annealing, a set of five peaks appeared at the 15° point between these two peaks, akin to the oxidizing sample. It is important to note that these five peaks lie directly on top of the platinum powder ring, indicating that they share the same lattice parameter. If it was caused by STO, overlap with the platinum powder ring would be observed but its primary intensity would be offset. The peak change can be seen in figure 62.
Figure 62: A set of five peaks in the off-specular (002) platinum ring.

These five peaks quickly melded into three peaks at 1150°C, as is seen in figure 63. It is interesting to note this change was much slower at for the oxidizing sample.

Figure 63: A set of three peaks in the off-specular (002) platinum ring.

The sharper peaks continued to grow at 1100°C and 1150°C without significant change in their topography in reciprocal space, as can be seen in 64 & 65.
A straightforward comparison of the changes in the (002) off-specular ring at various temperatures are most clearly seen in figure 66:

Figure 64: Sharp peak on the (002) ring, 1100°C.  Figure 65: Sharp peak on the (002) ring, 1150°C.

Figure 66: (002) Off-Specular Ring of (111) Platinum Nanocrystals.
4.3.2 SEM/AFM

Images were taken with a JOEL SEM of the sample after annealing at 1150°C. The sample was covered in a thin Au/Pd film to ensure proper conductivity, since STO is an insulator. While the SEM does not yield useful information concerning the height of the platinum nanocrystals, it does yield a plethora of useful information. The platinum crystals had spacing similar to that seen in the oxygen atmosphere sample at 1000°C. A scan at 7000x magnification is seen as figure 67.

![SEM image at 7000x magnification.](image)

The most interesting development, however, is the appearance of small crystals attached to the sides of the platinum hexagonal crystals. While this is difficult to see clearly in figure 67, it is very easy to see in figures 68 & 69:
Upon examining figures 68 & 69, it can be seen the extraneous crystals do not attach to adjacent edges of the platinum crystals. This indicates that these crystals have a preference for the (100) or (110) faces of platinum, causing them to only form on certain sides of the platinum crystals. Using the methods currently available to the author, there is not a method by which the individual facets of the platinum crystals can be identified to indicate the preference. Furthermore, utilizing energy dispersive electron spectroscopy (EDX), the crystals were not seen to contain any platinum but still contained strontium, titanium, and oxygen. Since EDX penetrates deep into the sample, it cannot be concluded if the particles are composed of an interstitial layer such as $SrO_x$, only that platinum is not present.

Imaging the sample at an angle of 70° with respect to the normal shows the platinum particles have steep sides and confirms the extra crystals are shorter than the main platinum crystal. Since the non-platinum particles are shorter than the platinum ones, there is a possibility that they extend underneath the platinum ones, which would have a strong effect upon epitaxy. The sample surface imaged at the 70° angle can be seen in figure 70.
To better measure the heights of the particles, as well as determine how steep their sides were, atomic force microscopy pictures were taken in tapping mode of a non-coated surface. The images determined that the mean height of the particles was in the 40-60 nm range, with a fair amount of particles in the 80-100 nm range as well. The AFM showed very steep sides to the platinum crystals and the secondary crystals attached to the platinum crystals were evident once again. These images can be seen in figures 71 & 72.
Figure 71: 5x5 micron image, showing the secondary crystals attached to the platinum ones.
4.3.3 Auger Electron Spectroscopy

After the final annealing, the sample was examined with Auger electron spectroscopy to check for any changes in surface concentration of strontium or titanium. A blank $\text{SrTiO}_3$ substrate was examined as well, in order to compare the relative compositions of $\text{SrTiO}_3$ prior and post platinization and annealing. A 3 kV electron beam with a current of 0.2 mA was utilized in all measurements. The lower energy scans utilized 4 eV peak to peak while the higher energy accepted 10 eV. The base pressure of the chamber was approximately $5 \times 10^{-10}$ Torr. Argon ion sputtering was utilized on the annealed and blank samples to
minimize carbon and other impurities that may have been present on the sample surface.

Figures 73 and 74 show the low and high energy spectra for the samples, respectively. Oxygen has its principal KLL peak at 503 eV, Ti has a principal LMM peak at 418 eV, Strontium has a principal LMM peak at 1649 eV, and Pt has its MNN peak at 1967 eV. All of these peaks, save the principal Pt peak, can be identified in these figures.

![Figure 73: Auger spectra containing Ti and O peaks before and after platinization.](image1)

![Figure 74: Auger spectra containing Sr and Pt peaks before and after platinization.](image2)

As can be seen in figure 73, the titanium peak significantly diminished after platinization and annealing. Furthermore, in figure 74, the strontium peak can be seen to have stayed more or less constant. This indicates a titanium deficiency in the surface termination.
Nominally, the composition of $SrTiO_3$ in an Auger scan will be seen as 20% Sr, 20% Ti, and 60% O. Analysis of the Auger data of the sample post-annealing yielded a composition of $35 \pm 5$ % Sr, $12 \pm 2$ % Ti, and $52 \pm 5$ % O. Considering the sample surface was etched with aqua regia to ensure a $TiO_2$ termination, this indicates that a significant amount of the titanium on the surface has either diffused deeper into the substrate or into the platinum nanoparticles themselves.

### 4.4 Nitrogen Atmosphere

A sample fabricated and annealed by Vladmir Komanicky of Pavol Jozef Šafárik University was briefly examined with XRD and AFM. The strontium titanate substrate was prepared in the same fashion as the previous two samples. The platinum was nominally 8nm thick and deposited at room temperature. It was then annealed at 1100°C for one hour. XRD analysis of the sample showed strong (111) specular epitaxy as well as off-specular epitaxy at the (002) ring. No (022) peak was observed on the sample. The specular and off-specular epitaxy can be seen in figures 75 & 76:

![Figure 75](image-url)

Figure 75: Wide 2θ scan of nitrogen annealed sample. Pt (111) is present but (002) and (022) are not.
Interestingly, no secondary crystals appeared nearby the platinum (111) crystals, while they did appear in the reducing environment very clearly in the SEM and AFM images near this temperature. The average height being in the range of 60-80 nm, however, did match. The topography of the surface can be seen in figures 77 & 78:
Figure 77: 5x5 micron image, showing no secondary crystals attached to the platinum ones.
4.5 Surface Terminations Post-Annealing

Multiple studies have examined the possibility of the surface termination of strontium titanate modifying after the deposition of platinum. AES studies have reported a lowering of the Sr concentration in the top few layers, which disagrees with later high-angle annular dark-field imaging preformed by Altberg et al. on the surface near the Pt crystals showing a $SrO_x$ termination.\textsuperscript{24-27}

What has not been addressed in much detail, however, is whether is it is possible for Pt/Ti or Pt/Sr eutectics to form at these various concentrations and if it is favorable to do so. Platinum and titanium can form an alloy of $Pt_8Ti$ at low concentrations of Pt but even being overly generous concerning the amount of Ti that could migrate into the platinum crystal, this alloy will not exist above 1000°C. Furthermore, this phase will not exist above 1080°C,
even at higher concentrations. At temperatures exceeding 1000°C, the platinum will not form any known alloy; any remaining titanium will be present in the form of defects.\textsuperscript{38} It is unreasonable to assume the atomic percent of Ti exceeds 1-2%, since only the top layer and possible the second $TiO_2$ layer will be able to diffuse into the nanocrystal without significant substrate deformation. The $Pt_8Ti$ phase does take on a tetragonal phase and could account for some of the stress fringes seen by (002) peak at temperatures 300°C but overall that is fairly unlikely.

Strontium and platinum are not known to form any specific phase until a substantial atomic percentage, >15%, is comprised of strontium. Until that concentration is reached, only interstitial and replacement defects are likely to be present. This makes an alloy of platinum and strontium to be very unlikely to form in this situation.\textsuperscript{39}

Since the sample surfaces were seen to be titanium deficient, the titanium likely moved upwards into the platinum, creating an $SrO_x$ layer. The $SrO_x$ layer, unsurprisingly, caused (111) platinum crystals to form. This is in agreement with Polli et al. and other studies that showed strontium oxide terminations encourage (111) growth.\textsuperscript{8-10}

4.6 Secondary Crystal Formation

In both the AFM and SEM images at high temperature, secondary crystals attached to the larger platinum crystals were observed. Since EDX confirmed that these crystals do not contain platinum, they are composed of a mixture of Sr, Ti, and O. Supporting EDX data is shown in Appendix B. Coupling the EDX data with the AES surface analysis, it is most likely that these crystals are some form of strontium oxide. The lack of crystals not attached to the platinum ones directly supports the theory that the titanium migrates into the bulk of the platinum. If the titanium migration was deeper into the crystal substrate, the crystals should form fairly uniformly throughout the surface instead. While strontium oxide has a rock salt structure, the lattice constant is approximately 5.1 Ångstroms, causing cubic platinum epitaxy to be unlikely (though the $SrO_x$ is by no means required to have
this lattice constant).\textsuperscript{40} Due to the sharp sides of the crystals and lack of access to TEM imaging, it is difficult to determine the (hkl) that is normal to these crystals.

These crystals have a stronger effect upon the epitaxy of the platinum nanocrystals that just in the specular direction, however. The formation of highly epitaxial platinum nanocrystals in-plane requires a substrate to give a sense of direction. Therefore, these secondary crystals still have their hkl directions determined by the substrate. This gives rationale to the triple set of peaks seen on the (002) off-specular ring at high temperatures on both samples; they were caused by the formation of the $SrO_x$ on the surface. It is important to note that the 15° offset peaks are not due to the secondary crystals themselves; that would require them to have the same lattice parameter as platinum. If they were merely overlapping with the (002) platinum ring, they would be seen in the reciprocal space scans. Instead, the secondary crystals force the platinum to arrange in certain configurations with respect to the substrate. These forced configurations are the cause of the set of five or three peaks. This is supported by the growth of the three peaks on the oxidizing sample at 1100°C and 1150°C despite the loss of platinum, evident by the weakening of the (111) specular platinum peak. While these three peaks appeared in both environments, it is interesting to note that they did not appear until 1100°C in the reducing environment while they were quite strong at 1000°C in the oxidizing. The strengthening of the three peaks due to the secondary crystal formation indicates that the platinum-surface interface near these crystals impedes the loss of platinum in oxygen atmosphere. Future research into these crystals and their interface with platinum should help illuminate the rationale for this relationship.

Interestingly, the epitaxial particles seen in the nitrogen atmosphere do not show any secondary crystal formation. Since the sample was annealed in a different fashion than the other two, it is not possible to pinpoint a single reason for this. Both the oxidizing and reducing samples were annealed for short periods of time but repeatedly and exposed to atmosphere between annealing steps. The nitrogen sample, on the other hand, was annealed at 1100°C for one hour. The difference between the amount of time and energy given to...
the platinum and substrate to reconfigure and form crystals is profoundly different due to these conditions. Another reason for the difference between the samples could be attributed to oxygen and hydrogen interacting with impurities in the platinum or the substrate itself, while the nitrogen interacts with neither. The lack of secondary crystals does not preclude the creation of a $SrO_x$ interstitial layer. The $SrO_x$ layer observed by Atiya et al. was only 10 nm thick.$^{24}$ Therefore, an unseen interstitial layer between the platinum and strontium titanate could be present, causing (111) platinum epitaxy.

5 Concluding Remarks

5.1 Conclusion

The purpose of this thesis was to examine the relationship between platinum crystal formation on strontium titanate (001) at various temperatures and the annealing environment. Overall, the annealing environment had a surprisingly small effect upon the crystallinity, shape, and size of the platinum nanocrystals. Despite the very close lattice parameters of strontium titanate and platinum, cube on cube epitaxy was not observed at any temperature in any environment. While the formation of (111) platinum at lower temperatures was expected, due the FCC structure of Pt, the increasing texture then epitaxy of (111) hexagonal crystals at higher temperatures is a very interesting result. Furthermore, the formation of the secondary crystals from the (001) strontium titanate substrate was interesting as well. With the exception of the Atiya et al. literature previously mentioned, there is no previous literature mentioning the formation of these crystallites. Similarly, there is no previous literature to the author’s knowledge that examines the temperature dependence of formation of textured and epitaxial platinum nanocrystals in a high level of detail. The information gleaned from the XRD specular and off-specular scans indicate a correlation between the secondary crystal formation and the set of five/three peaks in the off-specular platinum (002) scans. The XRD information, along with the AES information showing a $SrO_x$ surface termi-
nation, can imply that the secondary crystals are related to the migration of Ti atoms from the substrate surface. Furthermore, it shows a relationship between the overall annealing time and the formation of these secondary crystals. Since Atiya et al. annealed only at 1050°C with no intermediate steps, their 10 nm platinum film did not have as much time to interact with the STO substrate to cause the migration of titanium atoms. On the contrary, these films were annealed in a large number of lower temperature steps for shorter periods, which allowed for the Ti surface atoms to migrate well before the platinum had completely dewet from the sample surface. This is of interest for catalysis, since many reactions occur at elevated temperatures. If the secondary crystals will grow from the substrate after prolonged annealing in multiple environments, then the catalytic properties could change while reactions are taking place, changing the selectivity and reactivity of the substrate-metal system significantly.

Overall, as for the discernible differences between the annealing environments, the only definite conclusion that is made is the significant platinum loss at high temperatures in an oxidizing environment. The oxidizing environment was found to have the negative effect of significant platinum loss, since $PtO_2$ was likely forming and sublimating continuously in the flowing oxygen environment at high temperatures. The lack of secondary crystals in the nitrogen environment is inconclusive at this time, since the annealing conditions differed significantly from the other environments. While there were differences in the intermediate steps as to the rate of increase of the (111) platinum peak and the possible formation of (022) textured platinum, the former averaged out at high temperatures and the latter was a very weak intensity peak compared to (111) platinum. Furthermore, since both the reducing and oxidizing environments had $SrO_x$ terminations, the substrate-metal interactions seem to be the predominant factor in the formation of (111) platinum crystals and their corresponding epitaxy.
5.2 Future Research

Moving this work forward contains two separate avenues of research. As was mentioned in the introduction, the characterization of the sample surface with respect to catalytic activity is of great interest. Strontium titanate alone is already known to have catalytic promise, as does the $STO - Pt$ interface. The highly crystalline particles fabricated in this study contain the potential to be highly active and selective in certain reactions, which is of utmost appeal. Furthermore, the activity may be enhanced or diminished by the $SrO_x$ termination seen, as the $STO - Pt$ interface is doubtless distinct chemically from the $SrO_x - Pt$ interface. It is possible that platinum on strontium titanate will only be fit for lower temperature catalytic reactions in order to prevent the formation of an undesirable termination layer.

The other venue of research is the continued investigation of the $STO - Pt$ interface with respect to dewetting, crystal orientation, and secondary information. The research preformed here shows that oxidizing and reducing environments have little effect upon these properties but it is still inconclusive as to the effect of a neutral or other more complex atmospheres. It is also of interest to see if short periods of annealing at low temperatures create a $SrO_x$ termination layer as well while merely omitting the formation of fully fledged secondary crystals. If not, the classic $STO - Pt$ interface could be preserved while still obtaining a highly crystalline sample surface. In a similar vein, platinum on strontium titanate (111) and (110) merit further research to investigate the metal-substrate interactions on these facets and if similar properties appeal post-annealing.
References


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[29] F. T. Wagner and G. A. Somorjai. “Photocatalytic and photoelectrochemical hydrogen production on strontium titanate single crystals”. In: *Journal of the Ameri-


Appendices

Appendix A - Additional XRD Data

Oxidizing Sample

Figure 79: Wide 2\(\theta\) scans of oxidizing sample from 100\(^\circ\)C to 400\(^\circ\)C.

Figure 80: Wide 2\(\theta\) scans of oxidizing sample from 500\(^\circ\)C to 750\(^\circ\)C.
Figure 81: Wide $2\theta$ scans of oxidizing sample from 800°C to 950°C.

Figure 82: Wide $2\theta$ scans of oxidizing sample from 1000°C to 1150°C.
Figure 83: $2\theta$ scan of (022) Platinum at 1150°C

Figure 84: $\theta$ scan of (022) Platinum at 1150°C. The sharp peak indicates (022) texture.

Figure 85: Relationship of the FWHM of (111) Pt in $\theta$ with respect to temperature
Reducing Sample

Figure 86: Wide 2θ scans of reducing sample from 300°C to 900°C.

Figure 87: Wide 2θ scans of reducing sample from 1000°C to 1150°C.
Figure 88: Relationship of the FWHM of (111) Pt in $\theta$ with respect to temperature
Appendix B - EDX Data of Reducing Sample

Figure 89: EDX data of multiple locations on sample surface

Figure 90: EDX data of multiple locations on sample surface
Appendix C - Atomic Force Microscopy Images of Oxidizing Sample

Figure 91: 5x5 micron image, 100°C

Figure 92: 10x10, 100 °C

Figure 93: 5x5 micron image, 200°C

Figure 94: 10x10, 200°C
Figure 95: 5x5, 300°C

Figure 96: 10x10, 300°C

Figure 97: 20x20, 300°C
Figure 98: 5x5, 400°C

Figure 99: 10x10, 400°C

Figure 100: 50x50, 400°C
Figure 101: 5x5 micron, 500°C

Figure 102: 10x10, 500°C

Figure 103: 5x5 micron, 600°C

Figure 104: 10x10, 600°C
Figure 105: 20x20 micron, 600°C

Figure 106: 50x50, 600°C

Figure 107: 5x5 micron, 700°C

Figure 108: 10x10, 700°C
Figure 109: 5x5 image, light area, 750°C

Figure 110: 5x5, darker area, 750°C

Figure 111: 10x10, light area, 750°C
Figure 112: 20x20, including a darkened spot area, 750°C

Figure 113: 50x50, including a darkened spot areas, 750°C

Figure 114: 5x5 image, 800°C
Figure 115: 10x10, 800°C

Figure 116: 20x20, 800°C

Figure 117: 5x5 image, 850°C
Figure 118: 10x10, 850°C

Figure 119: 20x20, 850°C