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Growth of uniform cobalt nano magnetic dots on titanium dioxide surface

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

GROWTH OF UNIFORM COBALT NANO MAGNETIC DOTS ON TITANUM
DIOXIDE SURFACE

A thesis submitted in partial fulfillment of the
requirements for the degree of
MASTER OF SCIENCE

in
PHYSICS

by
En Cai

2008

To: Dean Kenneth Furton
College of Arts and Sciences

This thesis, written by En Cai, and entitled Growth of Uniform Cobalt Nano Magnetic Dots on Titanium Dioxide Surface, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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Dean Kenneth Furton
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Florida International University, 2008

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ABSTRACT OF THE THESIS

GROWTH OF UNIFORM COBALT NANO MAGNETIC DOTS ON TITANIUM
DIOXIDE SURFACE

by

En Cai

Florida International University, 2008

Miami, Florida

Professor Jiandi Zhang, Major Professor

This research investigated the growth of cobalt magnetic nanodots on the rutile TiO_2 (110) surface. Well ordered TiO_2 (110) surface was prepared in the Ultra High Vacuum (UHV) via Ar^+ sputtering and annealing. Co was deposited in-situ by Molecular Beam Epitaxy (MBE). Characterization of the growth was performed in-situ by a Variable Temperature Scanning Tunneling Microscope (VT-STM). The TiO_2 (110) surface was proven to promote the Volmer-Weber growth of Co nanodots. The cobalt atoms formed small clusters at the stage of initial growth. As the coverage increased, the size and density of clusters increased. It was discovered that there existed a stable dot size, especially after a delicate post-annealing. Statistical analysis showed the stable size of nanodots was 4.0 ± 0.5 nm. The existence of the stable dot size was supported theoretically based on jellium model. An optimal set of fabrication parameters was established for the uniform magnetic nanodot growth.

TABLE OF CONTENTS

CHAPTER	PAGE
1 INTRODUCTION	1
1.1 The nanoscale world	1
1.2 Nanomagnetism	3
1.3 Magnetic nanodots	4
2 SURFACE INVESTIGATION TECHNIQUES.....	7
2.1 Scanning Tunneling Microscopy	7
2.2 Low Energy Electron Diffraction	11
2.3 E-beam Molecular Beam Epitaxy (MBE).....	13
3 EXPERIMENT	14
3.1 The Ultra High Vacuum (UHV) Experiment System.....	14
3.2 Setup and Procedures	17
4 TITANIUM DIOXIDE SURFACE PREPARATION.....	21
4.1 The TiO ₂ (110) surface.....	21
4.2 Treatment effect on the TiO ₂ surface morphology.....	26
4.3 Discussions.....	32
5 COBALT DEPOSITION	33
5.1 Quantum Dot Growth Mechanism.....	33
5.2 Control of cobalt nanodot morphology.....	34
5.3 Statistics Analysis	35
5.3.1 Flooding	36
5.3.2 Coverage	38
5.3.3 Size distribution	38
5.3.4 Height Vs Diameter	42
5.4 Results of the nanodot growth	42
5.4.1 Morphology.....	43
5.4.2 Statistics	45
5.5 Discussions.....	47
6 CONCLUSIONS.....	51
6.1 TiO ₂ as a substrate for quantum dot growth	51
6.2 Co dots with a uniform size	52
6.3 Future work	54
6.3.1 The role of surface defects	54
6.3.2 The internal structure of Co dots.....	54
6.3.3 The scaling behavior of Magnetic properties.....	55
REFERENCES.....	56

LIST OF FIGURES

FIGURE	PAGE
Fig. 1.1 Bulk energy band vs. quantum dot energy band.....	2
Fig. 2.1 Schematic demonstration of Scanning Tunneling Microscope.	8
Fig. 2.2 The STM image of a circular corral of Fe atoms on Cu (111) surface.....	9
Fig. 2.3 The schematic view of LEED.....	11
Fig. 2.4 Illustration of Bragg diffraction.....	12
Fig. 2.5 Picture of an e-beam evaporator.	13
Fig. 3.1 A photo of the UHV system.	16
Fig. 3.2 Sample mounting procedure.	17
Fig. 3.3 Schematic view of surface preparation and Co dot deposition.....	18
Fig. 3.4 A schematic illustration of experimental procedure.	19
Fig. 4.1 The rutile TiO ₂ unit cell.	22
Fig. 4.2 Ball and stick model of rutile TiO ₂ truncation creating (110) (1×1) surface.....	23
Fig. 4.3 Schematic ball model of TiO ₂ (110) surface.	24
Fig. 4.4 STM image and LEED pattern of the TiO ₂ (110) 1 × 1 surface.....	24
Fig. 4.5 Charge density contours for the (001) surface of TiO ₂	25
Fig. 4.6 STM image of the TiO ₂ (110) surface	27
Fig. 4.7 STM image and LEED pattern of the reconstructed 1×2 structure.	27
Fig. 4.8 Large terraces with atomic resolution.....	28
Fig. 4.9 Surface defect concentrations corresponding to different treatments.....	30
Fig. 4.10 Flow chart of the substrate characterization procedure.	31
Fig. 5.1 Schematic view of three growth modes.....	34

Fig. 5.2 An example of STM image for observing the cobalt nanodot morphology.	36
Fig. 5.3 Compares of the image before and after apply the flood function.	37
Fig. 5.4 Perimeter histogram of the nanodots.	38
Fig. 5.5 Connected nanodots cannot be distinguished in the flood function.	39
Fig. 5.6 The nanodots morphology before and after Laplace transformation.	40
Fig. 5.7 The data analysis procedure.	41
Fig. 5.8 Height vs. diameter.	42
Fig. 5.9 STM investigation of the initial stages of the cobalt nanodots growth.	43
Fig. 5.10 Nanodots morphology at a higher coverage and after post-annealing	44
Fig. 5.11 Size of cobalt nanodots as a function of coverage.	45
Fig. 5.12 Post annealing effects on the dot size.	46
Fig. 5.13 Theoretical calculation of energy per electron of a jellium cluster.	48

CHAPTER 1 INTRODUCTION

Nanoscience has been thriving for the past decade. Many fascinating new physical properties and functionalities were observed from materials in nanometer scale, some of which have greatly challenged the previous understandings of condensed matter physics; while many have evolved into potential applications that may significantly change people's lives.

In a great variety of nanomaterials, nanomagnetic materials have their unique attraction. Combination of quantum electronic structure and magnetism in nanomagnetic materials embraces great attention in fundamental condensed matter physics and new technology revolution such as “spintronics” [1,2] ---- an emerging technology which exploits the quantum spin states of electrons as well as making use of their charge states. One challenging issue in the study of nanomagnetism and nano-spintronics is the synthesis /fabrication of nanomagnetic materials with characteristic and uniform scale. This is also the major driving force of the present thesis research.

In this chapter, a brief introduction to the nanoscience is presented. Further discussions are focused on the topic of nanomagnetism, especially the physics of nanomagnetic dots. The motivation of the thesis project is demonstrated. In the end of the chapter, the outline of this thesis is presented.

1.1 The nanoscale world

The macroscopic world appears continuous, for example, macroscopic matter and energy are continuous. While in the microscopic world, these are found to be discrete.

One extreme case is the energy of electron confined in an atom or a molecule. The bridge between these two distinctive realms is the mesoscopic world where the size of the matter is between 1 to about 10 nm [3]. A typical mesoscopic system is the quantum dots system in which quantum size effect plays an important role. As the dot size becomes comparable with the electron wavelength, the geometrical boundaries of the dots form constraints for the electrons. As a result of such quantum confinement, electrons adjust their energy according to the dot size.

Fig. 1.1 Bulk energy band vs. quantum dot energy band. Quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels. [4]

One of the best examples is the size dependence of the quantum optical property of nanodots. In bulk semiconductors, the energy gap is a fixed parameter depending on the material. Decreasing the size to nanometer range, the electron can be treated as confining in a 3-d infinite potential well due to the quantum size effect. The energy gap is simply proportional to $1/R^2$, implying that the gap increases as the quantum dot size decreases. In addition, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels shown as Fig. 1.1 [4].

Besides their optical property, the quantum dots show a lot of other intriguing properties strikingly different from those of the bulk materials. For example, different size of the quantum dots may prefer icosahedral to decahedral structure while their bulk structure is close-packed, thus changing electronic properties [5]. The resistance of metallic nanoclusters shows Coulomb blockade feature instead of obeying the Ohm's law of its bulk [6]. Further more, spin-orbital and spin-spin interaction in nanoscale materials will differ from these in the corresponding bulk, such that the magnetic ordering and magnetic properties will emerge with nano-size effects. For example, magnetic metal such as Co becomes superparamagnetic in nanometer range as a contrast to the ferromagnetism in the bulk of Co crystal [7, 8].

At the same time, the particular cluster size creates a high surface to volume ratio making the surface effect very crucial to the quantum dots. A major fraction of the atoms in a nanometer-size particle is located at the surface whereas this fraction is extremely small for macroscopic crystals [9]. As a result, many noble metals become much more active in its nanodots form. The simple example is that Au and Ag nanoparticles are widely used as catalysis in chemical reactions [10, 11]. The enhanced surface effects in nanoclusters also play a dramatic role in the nanomagnetism which is the central goal of this research project.

1.2 Nanomagnetism

Nanomagnetism is the discipline dealing with magnetic phenomena specific to structures having dimensions in the nanometer range [1]. A typical magnetic domain lies in sub-micrometer range. Exchange length for most materials is usually between 1 and 10

nm. As the size of magnetic structures approaches this range, new magnetic properties are expected from these structures [12].

Besides the fundamental physics in nanomagnetism, its wide applications also made the subject at the forefront of the emerging nanotechnology era. Nanomagnetic structures are considered candidate for the next generation of ultra high density magnetic recording devices. The limit of current information storage media is almost 100 Gbit/in², and with new approaches in nanomagnetism, it is likely to advance the storage density to the order of Tbits/in² [1].

In order to obtain the identical magnetic properties in a system, such as saturation field, coercivity and remanence, uniform magnetic dots with identical size and density are expected. Evidently, this posts a grand challenge to nanomagnetism community about how to synthesize/fabricate such uniform magnetic nanostructures for both fundamental understanding and technological applications. This is also the motivation for the present thesis project. To take such a challenge, three important issues need to be considered: 1) how to identify a prototype system potential for magnetic nanodot growth; and 2) how to tune the corresponding growth parameters for optimizing uniform dot growth thermodynamically; and finally, 3) how to microscopically visualize/characterize in-situ these grown magnetic dots. In this thesis, we intend to explore these issues with a new novel approach: growing magnetic dots on an oxide surface.

1.3 Magnetic nanodots

Extensive research has been conducted on the growth of different nanodot systems, e.g. metal dots on metal surfaces [13-16], metal dots on insulating substrates

[17], Co dots on Al_2O_3 [18], Ag, Ni or Cu dots on TiO_2 [19-22]. Among them, metal dots grown on metal surfaces systems have been most widely studied. The results show that although the metal islands can be formed on metal surfaces, metals, in general, tend to wet the substrate instead of forming clusters due to the high substrate surface energy. Only in very few systems or under very delicate growth conditions can metal grow in dot/island form on a metal surface. Besides, magnetic coupling between magnetic dots on a metal substrate is normally governed by the well-known RKKY interaction which is relatively strong compared with other magnetic interaction. Such a strong interaction sometimes is not beneficial in technological applications such as magnetic memory devices. Searching for and understanding alternative system with non-RKKY type coupling is an attractive option. This leads to the attempt of growing magnetic nanodots on semiconductor surfaces. The advantage of a semiconductor surface is that the tunability of magnetic coupling by substrate doping controls both the transport properties and the itinerancy of carriers. Co and Fe can form nice arrays on Si (111) surface [23]. However, alloys are normally formed at the interface between the dots and the substrate, drastically affecting the properties of the nanodots. To obtain an ideal system, we need a semiconducting surface with sufficiently low surface energy, which is chemically stable for the dot growth.

The rutile TiO_2 (110) surface is an ideal candidate. It enjoys a high popularity in surface science, and especially the rutile (110) surface has evolved as the model system in the surface science of metal oxides [24]. TiO_2 (110) is one of the most studied oxide surfaces and is considered one of the most easily prepared and stable oxide surfaces [9]. Recent studies have shown that a few metallic materials like Ag, Fe, Cu, can form

uniform nanoscale clusters on rutile TiO_2 (110) surface by using molecular beam epitaxy (MBE) [19, 25]. The results of this thesis research demonstrate that fabrication of Co nanodots on the TiO_2 (110) surface is achievable.

In this thesis I present investigations of the growth of Cobalt nanoparticles on the rutile TiO_2 (110) 1×1 surface. As is stated above, the choice for TiO_2 as substrate is because it is semiconducting with a well characterized surface. The major surface investigation was carried out by a Variable Temperature Scanning Tunneling Microscope (VT-STM) and Low Electron Energy Diffraction (LEED), which are described in Chapter 2 followed by explanations of experimental set-up in Chapter 3. Detailed structural and properties of the rutile TiO_2 (110) 1×1 surface will be discussed in Chapter 4 and the specific growth of cobalt nanoparticles will be discussed in Chapter 5. Finally, Chapter 6 will be devoted to the conclusions of this thesis.

In this chapter, two important surface investigation techniques are introduced: Scanning Tunneling Microscopy and Low Energy Electron Diffraction. The brief principles of both techniques are presented followed by the detailed explanation of the ways they work. Finally, the rolls they play in this thesis project are demonstrated. A brief introduction to the growth technique: Molecular Beam Epitaxy is also included at the end of the chapter.

2.1 Scanning Tunneling Microscopy

The Scanning Tunneling Microscopy (STM) is a powerful technique to explore the surface science at the atomic scale. Invented by Binnig and Rohrer at the IBM research facilities in Zürich in the early eighties, STM has been greatly assisting scientists “seeing” atoms on many kinds of surfaces revealing the structural and electronic states of those surfaces. As a tool to manipulate nanometer scale objects on a surface, STM can even create a “man-made” chemical reaction between molecules.

The Scanning Tunneling Microscopy is based on the concept of quantum tunneling. When a conducting tip is brought very close to a metallic or semiconducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them. For low voltages, this tunneling current is a function of the local density of states (LDOS) at the Fermi level, E_F , of the sample [26]. The tunneling current is roughly given by $I = cV \exp(-d\sqrt{\Phi})$ where V is the bias, d is the thickness of the barrier in angstroms and Φ is the work function measured in electron volts [27]. The formula

suggests that the tunneling current is very sensitive to the thickness of the barrier which is the vacuum gap between the tip and the sample, thus a small change in this distance will lead to a big variation in tunneling current and vice versa.

Fig. 2.1 Schematic demonstration of Scanning Tunneling Microscope. A tip is scanning the sample. Electrical potential is applied between the tip and sample. Electrons tunnel through the vacuum gap and create a tiny current which is captured by the sensors. A piezoelectric tube is used to precisely control the position of the tip. The tunneling current gives feedback signals to decide the z position of the tip. Therefore, its up-and-down motion reflects the surface morphology and electronic states, and is recorded by a computer.

The basic operation of the STM is illustrated in Fig 2.1. The microscope probes the surface using the tip of a very sharp needle normally with one single atom at the top. The tip is mounted on the end of a piezoelectric tube, which can extend, shrink and bend corresponding to different electronic potentials applied on the tube. Therefore, by controlling the electronic potentials on the piezoelectric tube, we are able to move the tip in x, y and z directions. Further more, with the precise control of the movement of the piezoelectric actuator, the tip can be moved over distances up to a few micrometers with accuracy down to one percent of an Angstrom [9]. When a bias is applied between the

sample and the tip, the tunneling current happens if the tip is brought very close to the surface of the sample. As explained above, this current is an extremely sensitive measure of the distance between tip and surface. Usually the STM is operated in constant current mode, in which the tip adjusts its z direction in order to keep the tunneling current as a constant. When the tip is scanning in x and y directions, the z coordinate is recorded as a function of x and y so that a topographic map of the surface is obtained.

Strictly speaking, a STM image is not a purely topographic display of the surface; instead it mixes the electronic and topographic information. This is because an area of high electron local density induces bigger tunneling current and consequently appears to STM as a local protrusion even though it is at the same topographic level as surrounding areas. Therefore, one needs to be very careful in interpreting the “peaks” and “valleys” of a STM image, particularly those of oxide surfaces where electron local density vary strongly along the surface.

Fig. 2.2 The STM image of a circular corral of Fe atoms on Cu (111) surface. This STM image shows the direct observation of standing-wave patterns in the local density of states of the Cu (111) surface. These spatial oscillations are quantum-mechanical interference patterns caused by scattering of the two-dimensional electron gas off the Fe adatoms and point defects. This picture is the best evidence that the STM image is a combination of surface morphology and electronic state information [28].

When STM is used for imaging a surface of a semiconductor, the surface corrugation obtained will reflect the corrugation of surface atom arrangement, since the electron “cloud” follows the arrangement of atom cores at the surface. In this sense, an image of STM reflects the surface structure. However, while imaging a surface of metal, the surface corrugation does not necessarily reflect the lattice structure but the itinerant electron density of states. For a metal surface, the electrons are itinerant and normally form standing waves covering the lattice cores. A typical image of surface standing wave of electrons is shown in the Fig. 2.2.

The resolution of the STM originates from the strong dependence of the tunneling current on the distance between tip and sample. The effective tunneling area is only few atoms at the very top of the tip which are closest to the sample and produce the major tunneling current. Although the actual tip size does not affect the resolution when STM is scanning a flat surface, it does have an influence on the image when the surface is corrugated. For the nanodots grown on a substrate, this so called “tip convolution” effect creates a deviation from the actual size of the dots [9].

An STM image is built up line by line, and it normally takes several minutes to obtain an image. During this time, the atoms are moving constantly especially at room temperature. As a result, the image records the averaged behaviors of the localized atoms; while for those fast moving unbounded single atoms, STM cannot detect them. Normally, the typical time resolution of a STM is in ms range.

In this project, the STM is mainly employed to characterize the surface morphology and local density of states. First of all, the STM is used to investigate the surface morphology of the substrate which in our case is TiO_2 (110) surface. Secondly,

STM images are taken to examine the surface atomic structure of TiO_2 . Thirdly, defects concentration is evaluated by the STM. The above three steps serve as references for preparing the substrate. Finally, after cobalt deposition, the size, shape and distribution of the cobalt clusters are explored by the STM. The Scanning Tunneling Microscope is the major characterization technique in this thesis research.

2.2 Low Energy Electron Diffraction

The Low Energy Electron Diffraction (LEED) is another sensitive while effective technique to investigate the crystalline structure of the few outermost layers of the sample. As a contrast to STM which can probe the local arrangement of the atoms, the LEED provides an overall view of the long range ordering of the surface reflected in the reciprocal space. Thus provides complementary information on surface structure.

Fig. 2.3 The schematic view of LEED. The electrons are emitted from the cathode, and are focused by a set of electron lens before perpendicularly incidence onto the sample. The diffracted electron intensity is shown on the phosphor screen and form different patterns correspond to the sample surface structures.

The schematic view of LEED is demonstrated in Fig. 2.3. A beam of electrons is generated by an electron gun. The electron beam is focused when it passes through a set

of electron lens and incident perpendicularly onto the surface of the sample. A fluorescence screen is used to display the pattern of electrons scattered by the sample.

Since LEED is a surface sensitive technique, the diffraction wave vectors satisfy two-dimensional Bragg conditions $2d\sin\theta = n\lambda$. The observed LEED pattern is a two-dimensional reciprocal lattice of the ordered surface projected onto a two-dimensional real plane. From the kinematics point of view, the surface unit cell size and symmetry can be determined. Although multiple scattering of the electrons is prevalent in LEED, preventing determination of the exact positions of the atoms, the kinematics approximation can still be very useful in obtaining important information about a surface structure [29].

The LEED was used to examine the TiO_2 (110) surface structure in this project. First of all, the LEED pattern reveals the symmetry of surface structure. Secondly, LEED pattern serves as the criteria in determining the surface structure and cleanness. For a well ordered surface, the LEED pattern is sharp without obvious background. However, when the surface is not well ordered or contaminated, the LEED pattern shows a bright background and weak reciprocal lattice points.

Fig. 2.4 Illustration of Bragg diffraction. The separately reflected waves will remain in phase if the difference in the path length of each wave is equal to an integer multiple of the wavelength. The constructive interference creates bright spots and the destructive interference creates dark spots.

2.3 E-beam Molecular Beam Epitaxy (MBE)

Supported nanocluster has been an important subject for decades. The scientific quest in nanocluster is to create, explore and understand such systems and their novel properties. One of the biggest challenges is to fabricate nanometer-scale clusters with uniform size and distribution. Among various growth techniques, molecular beam epitaxy (MBE) is the most widely used technique in depositing thin films and supported nanoclusters [30].

The basic component of MBE is the e-beam evaporator in which the source is heated by electron bombardment (see Fig.2.5). Atoms are evaporated from the source and deposited on the substrate. The MBE growth requires high quality vacuum and ultra clean source to avoid contaminations since in this growth technique, materials are grown in a very slow rate. One of the advantages of MBE growth is that the growth rate and time can be precisely controlled. For thin film deposition, the precision can reach to sub-atomic layer.

The experiments described in this thesis were conducted mainly in our Ultra High Vacuum (UHV) chamber which is equipped with a Variable-Temperature Scanning Tunneling Microscope (VT- STM), a Low Energy Electron Diffraction (LEED), an ion gun, a Residual Gas Analyzer (RGA), and an e-beam evaporator for thermal Molecular Beam Epitaxy (MBE). The description of the whole system is given in the beginning part of this chapter followed by the specific illustration on the details of the experimental set-up. The procedures of the substrate preparation and cobalt deposition are described in the remaining part of the chapter.

3.1 The Ultra High Vacuum (UHV) Experiment System

Vacuum environment is crucial to surface investigations. It is even more critical to the study of magnetic quantum dots due to the large surface area of dots as compared to thin films. In the first place, the surface probes are normally sensitive only to one or a few atomic layers in the surface area of the sample. In atmosphere, a surface normally adsorbs free atoms and molecules such as O₂, H₂, and H₂O, which contaminate the surface and drastically affect the surface measurements. Furthermore, many of the surfaces get oxidized by the O₂ in the air thus change the stoichiometry of the original surface. Especially, the oxidization of the surface of a magnetic dot will affect the magnetic properties of the dot.

The UHV is a vacuum regime characterized by pressure lower than 10⁻⁹ torr which is about 10⁻⁷ Pascal. To generate such a high vacuum, a combination of three

vacuum pumps is needed: a mechanical pump, a turbomolecular pump and an ion pump. The mechanical pump serves as the base pump; it starts at the atmosphere pressure and can ultimately bring the system pressure down to about 10^{-3} torr. To reach the high vacuum, a turbo molecular pump is employed, which can create a vacuum at the 10^{-8} torr range. In order to bring the system to UHV, a delicate baking of the system is necessary. Finally an ion pump is used to maintain the ultra high vacuum as low as 10^{-10} torr or even 10^{-11} torr.

For our UHV system, we use a Pfeiffer turbomolecular drag pumping station TSH071 E with a pumping speed of 60 l/s; a Varian Turbo molecular pump V250 with a pumping speed of 250 l/s; and a Physical Electronics ion pump with the pumping speed of 400 l/s. The whole chamber is baked to 150 °C in order to remove water and hydrocarbons adsorbed on the walls. Filaments are outgassed to achieve a vacuum blow 2×10^{-10} torr. Even with such an ultra high vacuum, it takes less than a day to cover a full surface with contaminant due to residual gas molecules in the chamber. As a result, we have to constantly “refresh” the surface before characterize it with STM.

As a sacrifice for the advantages the UHV brings, the complexity of performing the experiments is greatly increased; even seemly simple operation as putting in a sample takes considerable effort. The sample is placed into a preparation chamber which is connected to the main characterization chamber by a valve. Thereafter, the preparation chamber is baked at 150 °C for 5 hours and pumped down to high vacuum. The valve between the two chambers is opened and the sample transferred into the main chamber using a magnet transfer arm.

The main experimental system is demonstrated in Fig. 3.1. The VT-STM is a commercial STM from Omicron. The design of this microscope allows measurements within the temperature range between 25 K and 1500 K with a special cooling and heating mechanism. The measurements in this thesis were conducted at room temperature. The STM adopts an Eddy current stage as a damping system, such that vibrational noise is effectively reduced to ensure the precision of measurements.

Fig. 3.1 A photo of the UHV system. The system is maintained at a pressure about 10^{-10} torr. STM, LEED, RGA, ion gun, and e-beam evaporator are integrated on the chamber at the position shown by the arrows.

The manipulator is responsible for receiving a sample from preparation chamber, transferring a sample within the main chamber and to the STM stage. The sample is placed in the sample slot at the manipulator head. The manipulator has 5 degrees of freedom: translational motion in x, y and z directions; rotational motion about the z axis and tilt rotation about the x axis, though it lacks the azimuthal rotation mechanism (a rotation about the y-axis). The manipulator and the sample can literally reach every place along the central axis within the main cylindrical chamber. Except during STM

characterization and Co growth, the sample is parked on the manipulator head. Moreover, the manipulator head is equipped with both direct resistance heating and e-beam bombardment heating mechanisms for sample annealing. There are two pairs of calibrated thermocouples for measurement of sample temperature.

In order to reduce the noise of mechanical vibrations, the system is mounted on a heavy steel frame with 4 air spring legs. The mechanic pump is connected to the chambers via soft bellow tubes to lower the vibration noise. During the STM measurements, the mechanic pump and turbo pump were turned off to eliminate the vibrational noise.

3.2 Setup and Procedures

A standard molybdenum holder is purchased from Omicron as a sample supporting plate to mount sample. The holder has a rectangle hole in the center in order to facilitate sample heating by electron beam bombardment. As shown in Fig. 3.2, a thin tantalum foil of the same size as the sample holder is spot welded on the sample holder to evenly distribute heat in the annealing process. A $5 \times 5 \text{ mm}^2$ TiO_2 sample is mounted by two stripes of tantalum foil spot welded on the sample holder.

Fig. 3.2 Sample mounting procedure. (a) The molybdenum sample holder. (b) A tantalum foil is welded on top of the sample holder. (c) A $5 \times 5 \text{ mm}^2$ TiO_2 crystal is placed in the center of the sample holder. (d) The TiO_2 crystal is fixed by two stripes of tantalum foil.

Rutile TiO_2 (110) crystals were purchased from Kristalltechnology with 1 side polished. For each experiment, one $5 \times 5 \text{ mm}^2$ sample was used. Before mounting, the sample was cleaned with methanol in an ultrasonic cleaner for 15 min to remove contaminants from the surface.

The substrates were prepared by a combination of ion sputtering and annealing. An ion gun provides high energy electron beam which ionize the argon atoms. The pressure of the argon gas inside the chamber can be precisely controlled by a UHV leak valve. Normally the argon pressure for sputtering ranges from 3×10^{-6} to 5×10^{-5} torr, depending on the sputtering power required. The power of sputtering is monitored by the reading of the current created by the Ar^+ ions hitting the surface, which depends on the energy of the electron beam and the ambient pressure of the argon gas.

Fig. 3.3 Schematic view of surface preparation and Co dot deposition. The surface is prepared by Ar^+ sputtering (a), and annealing (b), and cobalt dots are deposited onto the TiO_2 surface via an e-beam evaporator and the morphology is characterized by a STM (c). The design of the system allows real time STM scanning while cobalt deposition.

Sample sputtering is followed by annealing which will heat the sample to about 900 K. The set up for heating the sample employ the “hot” electron beam to bombard the

sample. A tungsten cathode filament was installed in the manipulator head, below the sample slot. A current up to 10 A is allow to flow through this filament. However, the radiant heat alone from the filament is not sufficient for heating the sample to such high temperature as 900 K. Therefore, the sample was held at a much higher positive electron potential than the filament to attract the electrons emitted by the incandescent filament. The accelerated electrons thus bombard the back of the sample holder and heat it up. The rectangular window in the center of the sample holder shown in Fig 3.2 (a) allows the electrons to directly bombard the tantalum foil and distribute the heat through the sample.

Fig. 3.4 A schematic illustration of experimental procedure.

The LEED is employed to confirm the ordering of the surface structure and STM is used to further characterize the local morphology and lattice structure of the substrate. An e-beam evaporator is used to deposit cobalt clusters. The evaporator is assembled on the STM chamber, allowing real time deposition while imaging. In the evaporator, a

filament ring is used to emit electrons and a cobalt rod is placed concentricly to the filament ring. A positive potential is applied on the cobalt rod with the filament grounded. Therefore, the rod attracts electrons and can be heated up to more than 1000 °C, creating cobalt vapor which passes through a nozzle hole and condenses at the TiO_2 surface to form nanodots. To control the deposition, there are two parameters to tune: deposition strength and time which is discussed in the next chapter. At the nozzle hole of the evaporator, there is an ion flux sensor to monitor the deposition rate, though the sensor needs to be calibrated frequently. The most precise calibration of deposition coverage is based upon STM measurements.

The entire experiment procedure is shown in Fig.3.4. The first step is the TiO_2 surface preparation followed by the surface characterization. Cobalt dot deposition is carried out if the surface is qualified. Otherwise, we have to continue to treat the surface until it is of good quality. After deposition, the sample is characterized again by STM to check the surface morphology. The sample is annealed afterwards if needed and again characterized by STM.

The rutile TiO_2 structure is introduced in this chapter. The investigation of the treatment effects on the TiO_2 (1 $\times$ 1) surface is discussed and a feasible set of preparation parameters for obtaining an optimal surface is provided.

4.1 The TiO_2 (110) surface

The surface study of oxides is a relative young area compare to the extensive study conducted on the surfaces of simple metals and simple semiconductors such as Ge and Si. Partially because of the discovery of oxide superconductors like cuprates, much more attention has been drawn recently to both fundamental and applied research of oxide surfaces and interfaces [31-35]. However, the study of oxide surfaces is limited by several practical problems. The major problems include the stoichiometry control and possible complex reconstruction at the surface, mainly due to the polar character of many oxide surface and oxygen vacancies created by broken symmetry. Surface reconstructions often occur with oxide compounds making the surface investigation much more complicated compared with that for simple metals of semiconductors. Another problem is that most oxides are insulators or very poor semiconductors. Many of the surface characterization techniques require the sample to be conducting [9]. Therefore, the actual number of systems of oxide surfaces being well studied is very modest, and titanium dioxide is one of the most investigated single-crystalline systems in the surface of metal oxides [24].

The extensive applications of TiO_2 have made it attract a great deal of research interests. Titanium dioxide is widely used as heterogeneous catalysis, photocatalyst in solar cells, gas sensor, white pigment, optical coating and biocompatible bone implants, magnetic spin-valve systems as a spacer material, etc. Furthermore TiO_2 serves as a supporting material of many kinds of nano metal particles, which have been widely used as catalysis [24].

Fig. 4.1 The rutile TiO_2 unit cell. The titanium dioxide has a tetragonal unit cell with the lattice parameters $a = b = 4.584 \text{ \AA}$ $c = 2.953 \text{ \AA}$ [49].

TiO_2 is considered a model system in the surface science of metal oxides and has been well tested. This is because it fits for many experimental techniques. TiO_2 crystals with high surface quality can be purchased from various vendors. The TiO_2 (110) surface is considered stable and easy to prepare [36]. While for most of the oxide surfaces surface, it is difficult to obtain atomic resolution in STM investigation, TiO_2 (110) surface seems very friendly to STM study. Treated properly, the surface shows well ordered atomic structures with few contaminates. Although TiO_2 is not a good conductor, it can be reduced easily to achieve a relatively high conductivity [36].

The bulk titanium dioxide has three crystal structures: rutile, anatase and brookite. Rutile is the most common and most stable structure among them. We will focus on the

rutile structure since the rutile TiO_2 is used as the substrate in this thesis. The unit cell of rutile TiO_2 is shown in Fig. 4.1.

In fully oxidized phase of TiO_2 , the bulk band gap is about 3 eV, which is relatively large for a semiconductor. However, TiO_2 has a rich phase diagram with many stable phases of different crystal structures. As a result, the TiO_2 can be reduced easily by creating oxygen vacancies [37]. When annealed at a high temperature or sputtered with electrons, TiO_2 crystal will show oxygen vacancies, resulting in n-type doping and high conductivity [24]. With the presence of the oxygen vacancies, the color of TiO_2 crystal change dramatically from transparent to light blue, dark blue and finally black, depending on the density of oxygen vacancies [38, 39]. Although the change in color is prominent, the actual change in composition is actually quite small: the change in Ti:O ratio is far less than 1% [39, 40].

Among many surfaces of rutile TiO_2 , the (110) has the lowest surface energy and is considered the most stable crystal surface [24]. According to the Tasker and LeFemina's auto-compensation criterion, the crystal is truncated as showed in Fig.4.2, which provides the most stable (1×1) surface as shown in the 3D ball model in Fig. 4.3.

Fig. 4.2 Ball and stick model of rutile TiO_2 truncation creating (110) (1×1) surface.

Fig. 4.3 Schematic ball model of TiO_2 (110) surface. White balls stand for oxygen atoms, and black ball stand for Titanium atoms. The unit cell is shown by the rectangle with 6.5 Å along the $[1\bar{1}0]$ direction and 2.96 Å along the $[001]$ direction. The oxygen bridging rows is along the $[001]$ direction.

Fig. 4.4 STM image and LEED pattern of the TiO_2 (110) 1×1 surface. (a) A STM image of TiO_2 surface with atomic resolution. (b) Well ordered $p(1 \times 1)$ structure of the TiO_2 (110) surface.

Figure 4.4 presents both typical STM image and LEED pattern of the TiO_2 (110) 1×1 surface obtained at room temperature. LEED pattern of the (110) surface shows a rectangle Brillouin Zone, perfectly matching the lattice constants in reciprocal space. In STM images, atomic chains are found along the $[001]$ direction, further confirmed the (110) surface structure. However, one must be very careful in interpreting the protrusion rows in the STM image from the surface. If only considering the topographic structure of the (110) surface, one would conclude that the bring-protrusion rows are the bridging oxygen atoms. However, as stated in chapter 2, the STM investigation is a combination

of topographic and electronic features. Here the image of the surface characteristically reflects that STM image probes the integrated density of electron states. In fact, the bright-protrusion rows are confirmed to be Ti atoms in most of the cases. By observing the adatoms which have preference of the adsorption sites- either Ti or O, Onishi and Iwasawa [41] and many other groups found that the bright rows are actually Ti atoms. The appearance of surface oxygen vacancies also causes additional bright protrusions instead of “dark” ones confirming the assignment.

The theoretical calculation provides a clearer view. Based upon the results from local density approximation calculations, Figure 4.5 shows the charge density contours for the [001] surface of TiO_2 or the cross section view of the (110) surface by looking along [001] direction [42, 43]. The plot is the charge density of conduction-band states integrated from 0 to 2 eV above the conduction-band minimum, thus it resembles surface corrugation in the STM image obtained with a bias voltage of 2 V. In the first approximation, the STM tip would follow the charge density contours few angstroms above the surface. As shown in Fig.4.5, only the closest two or three contour lines follow the oxygen atoms on bridging rows, while the remaining contour lines bump up at the Ti sites. Therefore, unless the tip is extremely close to the surface, in most cases when it keeps few angstroms away from the surfaces, the Ti sites accounts for the bright protrusions in the STM images.

Fig. 4.5 Charge density contours for the (001) surface of TiO_2

4.2 Treatment effect on the TiO₂ surface morphology

The fresh TiO₂ surface is prepared and characterized in the UHV chamber. The details in mounting the sample are described in chapter 3. Combinations of sputtering and annealing are used to clean the surface inside the chamber.

By sputtering the surface with high energy ions, the few top most atomic layers are damaged but contaminants are removed from the surface. The sputtering strength is controlled by the ion gun power and argon pressure. In most of the cases, the ion gun power is kept at 0.5 k eV and the pressure is adjusted in the range of 3×10^{-6} to 5×10^{-5} torr to achieve different Ar⁺ flux sputtering the surface which is monitored by an ampere meter. Too weak sputtering will not be able to remove contaminants on the surface while too strong sputtering could severely damage the surface making it difficult to recover the ordered surface by the annealing process. It is essential to choose the appropriate sputtering energy and time to obtain the result needed. After sputtering, the surface crystalline structure order is complete broken- LEED patterns show only the background without any lattice points, and STM images show no local ordering structure of the surface [9].

To recover the surface to an ordered state, annealing is introduced. By heating the sample, the atoms move around to form a smooth orderly surface. The annealing process also requires the proper combination of time and power to achieve a well ordered surface.

The surface is prepared this way for the purpose of deposition. For better deposition results, the surface has to be i) well ordered 1×1 structure; ii) contamination free; iii) very smooth with large flat terraces, and with few defects. Well ordered structure provides a uniform surface as the substrate. Surface free of contaminants can achieve

better atomic resolution which is necessary for accurate identification and characterization of the nanodots. Usually defects and vacancies become the nucleation sites for adatoms thus the existence of defects/vacancies may affect the initial growth and distribution of the nanodots. A flat terrace is defined as the exposed area within the same atomic layer. Small terrace size makes it very difficult to characterize the nanodots, since the height of dots is comparable to terrace height which equals the height of one atomic layer in TiO_2 .

Fig. 4.6 STM image of the TiO_2 (110) surface (a) Sputtering at $0.7 \mu\text{A}$ for 20 minutes; Annealing at 853 K for 20 minutes (b) Sputtering at $0.8 \mu\text{A}$ for 20 minutes; Annealing at 863 K for 35 minutes (c) Sputtering at $0.6 \mu\text{A}$ for 10 minutes; Annealing at 873 K for 35 minutes.

Fig. 4.7 STM image and LEED pattern of the reconstructed 1×2 structure.

The annealing process directly affects the surface morphology. To illustrate such effects, Fig. 4.6 presents a series of images from a $600 \times 600 \text{ nm}^2$ surface after annealing at different temperature (853, 863 and 873 K). In Fig. 4.6 (a), which has the lowest

annealing temperature of the three, terraces are formed, but with many small islands and vacancies on the terraces. In Fig. 4.6 (b), the annealing temperature is increased by 10 K and the annealing time by 15 minutes, apparently, the terraces has restored better than that in (a)- small islands merged to form bigger islands and tiny vacancies combine to become bigger holes. The tendency become even more obvious when we look at Fig. 4.6 (c), where most of the islands merge into the adjacent terraces with holes expelled from them. For deposition, a flat area of surface with the same atomic layer is favored in characterizing the surface defect and geometric properties of the nanodots. Therefore, high annealing temperatures are preferred for the treatment. Figure 4.8 shows the image of the surface after optimal preparation procedure.

Fig. 4.8 Large terraces with atomic resolution. (a) Surface with large flat terraces on which an atomic flat layer of $50 \text{ nm} \times 50 \text{ nm}$ is easily found. (b) Zoomed in image of the terraces with atomic resolution.

Ideally, flat and large terraces could be obtained just by increasing the annealing temperature. However, this is not the case. As discussed in chapter 3, the titanium-oxygen phase diagram is very rich with many stable phases, and the TiO_2 (110) surface structure reconstructs when annealed at a high temperature, limiting the maximum temperature. The most commonly observed reconstruction has a 1×2 structure, simply missing the bridge-site oxygen rows and relaxing the surface. As found in the experiment,

when the annealing temperature is above 1000 K, the surface will become 1×2 structure, which is confirmed by LEED and STM. The 1×2 structure is characterized by a LEED pattern of half the reciprocal lattice length along the $[1\bar{1}0]$ direction and the STM image of doubling the row spacing along the $[1\bar{1}0]$ direction. The detailed structure of the 1×2 is discussed elsewhere [24, 44, 45]. The occurrence of reconstruction not only depends on annealing temperature, but also depends on sample treatment history and original sample status. Once the surface reconstructs, it is very hard to restore the 1×1 structure. Therefore, a moderate annealing temperature is preferred for the first several cycles of treatments. Due to the uniqueness of individual single crystal which is actually quite common in oxide compounds, samples from different single crystals have different tendency of reconstruction sensitive to temperatures of 950 to 1000 K. For most of the samples in our experiments, 890 to 923 K is considered an ideal temperature range for annealing, which will ensure 1×1 structure and relatively large terraces.

Achieving the large terraces is only part of the requirement for a qualified surface for deposition. In an image of $50 \times 50 \text{ nm}^2$ scale, a lot of bright dots of about 1 nm in diameter are still distributed over the surface. These bright dots are of the same size as the nanodots at the initial stage of deposition; therefore, they make observation difficult and statistics less reliable. Such point defects are thought to be oxygen vacancies [24, 46, 47]. Normally, oxygen vacancies are created by annealing or electron bombardment. Results are compared for different treatments in Fig. 4.8. The four images were acquired after similar sputtering power and time. Figure 4.9 (a) has the lowest annealing temperature than the rest with annealing time of 30 min. The density of the defects is at the middle of the four images. Figure 4.9 (b) and (d) have the same treatments except for

that Fig. 4.9 (b) was exposed to the LEED measurement before STM measurement. It shows that Fig. 4.9 (b) has more defects than Fig. 4.9 (d), which could be due to the bombardment of the electron beam from LEED. Being exposed to LEED the same time, image Fig. 4.9 (c) shows more defects than Fig. 4.9 (b). The obvious difference is the sputtering temperature, which records the sample temperature before sputtering. Figure 4.9 (c) has higher sputtering temperature than Fig. 4.9 (b). The other difference is the annealing time, which is likely to contribute for more defects.

Fig. 4.9 Surface defect concentrations corresponding to different treatments. Defects-bright dots are of 1-2 nm in diameter. The treatment parameters for (a)-(d) are shown in table 4.1.

Fig 4.9	Sputtering Power/Time	Annealing Temperature	Annealing Time	Exposed to LEED	Sputtering temperature
(a)	0.4 μ A /10 min	870 K	30'	No	<373 K
(b)	0.4 μ A /10 min	895 K	20'	Yes	<373 K
(c)	0.35 μ A /10 min	895 K	30'	Yes	~423 K
(d)	0.4 μ A /15 min	896 K	20'	No	<373 K

Table 4.1 List of treatment parameters for Fig. 4.9 (a) – (b).

The above discussion is based on experience and comparison with results from other groups. Although no quantitative statistics were conducted on the density of defects as a function of treatment parameters, images above provide sufficient evidence which qualitatively demonstrate how these surface treatments affect the surface quality. Therefore, one can conclude that in order to reduce the density of defects, it is necessary to control the annealing time, keep the sputtering temperature below 373 K, and avoid exposure to LEED before STM imaging.

The entire surface characterization procedure is illustrated in Fig. 4.10.

Fig. 4.10 Flow chart of the substrate characterization procedure. Every step in characterization is also an evaluation of the surface quality. The substrate surface has to “pass” all the examinations before the cobalt deposition.

4.3 Discussions

A set of surface treatment parameters was found to obtain a well-ordered TiO_2 (110) (1×1) surface with reasonable low density of defects and large terraces. A combination of relative strong sputtering at 0.6 μA and moderate annealing at 900 - 920 K is required to remove the contaminates. The sputtering power should be lower than 0.5 μA and annealing at the same temperature of 900 - 920 K. During the sputtering, the sample temperature should keep below 373 K to avoid inducing high density of point defects. Any unnecessary exposure of the surface to electron beam (such as for LEED imaging) should be avoided.

The morphology of cobalt clusters on TiO_2 (110) (1×1) surface is characterized and analyzed. Statistical results are demonstrated. Both the morphology study and statistical analysis indicate that a stable Co cluster size at about 4.0 ± 0.5 nm is achievable. A conceptual understanding is provided based upon jellium model for metallic clusters.

5.1 Quantum Dot Growth Mechanism

As shown in Fig. 5.1, there are generally three modes of growth: Frank-van der Merwe (layer-by-layer) growth, Volmer-Weber (island or 3D) growth and Stranski-Krastanov (layer + island) growth [48]. Some materials prefer Frank-Van der Merwe growth, in which the deposited atoms form a thin film on the substrate and when the substrate surface is covered by one atomic layer, the new atoms start to build another layer. In this growth mode, a thin film is formed with ordered crystalline structure. However, in some systems, the growth happens in a different way: the deposited atoms nucleate to form clusters leaving rest of the substrate uncovered, and the new atoms either start new clusters or pile up on old cluster to make them bigger. This growth mode leads to development of islands or 3D clusters on the substrate and is called Volmer-Weber growth. Stranski-Krastanov growth is the combination of the above two growth modes. In this so called layer plus island growth, the deposited material first form a wetting layer, and after the wetting layer reaches a certain thickness, the continuous deposition results in “coarsen” the wetting layer, and quantum dots “bump up” from the

layer. The difference between this growth mode and the Volmer-Wber growth is that the substrate is covered by a wetting layer.

Fig. 5.1 Schematic view of three growth modes: (a) Frank-van der Merwe(layer-by-layer) growth, (b) Volmer-Weber (island) growth and (c) Stranski-Krastanov (layer + island) growth.

5.2 Control of cobalt nanodot morphology

Various growth parameters contribute to different growth morphologies. The basic growth parameters include deposition temperature, growth rate, growth time and post-annealing temperature. The deposition temperature controls the kinetic energy of the deposited atoms. The growth rate and time are the two major controlling parameters in deposition, the multiplication of the two gives the total amount of atoms deposited which is coverage. However, even if the coverage is the same, different combinations of the rate and time lead to different growth morphologies. At a higher deposition rate, the atoms prefer to form bigger clusters, while at a lower deposition rate, the atoms are likely to form smaller clusters. The post-annealing process provides kinetic energy for the clusters to self-organize.

In this thesis project, efforts have been focused on searching for the optimized growth pathway to fabricate uniform sized nanodots, identify the deposition sites and morphology of grown Co superlattice and understand the mechanism and thermodynamic process of Co nanodots' deposition on TiO_2 surface.

Uniformity in dot size and density makes it possible for later characterization, especially for the understanding of quantum size effects on nano-magnetism. Viability of dot size and density enables the investigation of magnetic interaction between dots.

Co atoms are deposited by an e-beam evaporator onto the TiO₂ (110) surface previous described, and images are taken by STM to record the information of deposition sites, dot size, shape, and density. Statistical analysis is performed based on the data.

Growth analysis is based on STM images. Detailed deposition sites and density can be obtained from the images and systematic analysis of the images. Dot shape and size can also be determined from the images; diameters and heights can be measured by the data process functions in the STM software. To study the growth mechanism, some terminologies are introduced as follows:

Growth Control	Characterization	Uniformity
Deposition rate (flux)	Coverage	1. Size uniformity
Deposition time	Density	2. Distribution uniformity
Substrate temperature	Size	

Table 5.1 List of controlling and characteristic parameters of the deposition.

5.3 Statistical Analysis

VT-STM is employed to probe the surface and investigate the nanodots deposition. An STM image provides abundant information of the nanodots regarding deposition sites, dots size and height, number of dots and dots shape.

The direct information obtained from the STM images are the growth mode, nanodots shape and size, distribution, and uniformity. Take an example, from Fig. 5.2, one can clearly conclude that the growth mode is Volmer-Weber mode and that the nanodots projection in 2-d are in regular round shape. The size is about 3 to 4 nm in

diameter and although the size does vary for individual dots, the distribution of the size is quite narrow. The nanodots distribute evenly all over the surface.

Fig. 5.2 An example of STM image for observing the cobalt nanodot morphology.

However, to analysis the growth morphology, it is not sufficient by only observing the images. In order to understand the growth process, quantitative statistics are required. Therefore, the key issue becomes how to process the images and extract the useful information from them. Furthermore, some corrections are also needed. One particular issue is the correction due to the thermal drifting during STM imaging. This is a very common problem in STM community for finite temperature imaging.

In addition to the initial process from the software from Omicron STM, the images are all further processed by the software WSxM [49], which is designed for data analysis for the SPM measurements.

5.3.1 Flooding

Flooding is one of the functions in WSxM which allows one to distinguish the dots from the substrate. From Fig. 5.3 (a) we observe the Co dots and the (1×1) TiO_2 substrate. In the line profile in Fig. 5.3 (b), the substrate is indicated by the bottom coarse

sections of the line profile while in Fig. 5.3 (d) those corrugated sections became straight lines. Another noticeable change is the height. In Fig. 5.3 (b) the highest point is about 0.8 nm, but the highest point in Fig. 5.3 (c) is about 0.6 nm. This is because the flooding process filters the features below 0.2 nm and presents the landscape above 0.2 nm. Although it seems that some information is lost in this process, the flooding separates the nanodots from the substrate and makes it possible to conduct statistics on the nanodots.

Fig. 5.3 Compares of the image before and after apply the flood function. (a) shows the original STM image. (c) shows the same image after flood, the “lower” part of the landscape merges under the “sea level”. Clearer view is illustrated by (b) and (d).

Number of dots	First neighbor distance	Flooded area	Flooded volume
50	4.31 nm	9.37%	49.99nm ³

Table 5.2 The statistical data from flood function

By choosing an optimal cutoff height and cutoff size, the most important features of the nanodots are preserved and the statistical data have very small errors. Table 5.2 shows one example of statistics acquired by flooding function.

5.3.2 Coverage

The coverage describes the total amount of atoms deposited on the substrate, which is calculated in terms of monolayer (ML). 1 ML is equivalent to the nominal surface atom density of hcp Co(0001) or fcc Co(111), i.e., $1 \text{ ML} = 1.83 \times 10^{15} \text{ atoms/cm}^2$ [50].

Coverage is obtained from the STM image using flooding function. For example, from the above table, flooded volume is 49.99 nm^3 and the image size is $50 \times 50 \text{ nm}^2$. For Co hcp structure, volume per Co atom is 0.0111 nm^3 . Therefore, the volume of Co dots converted to number of Co atoms equals 4503.6. Thus the number of Co atoms on 1 cm^2 is 1.8×10^{14} atoms. Finally the coverage is calculated as 0.098 ML.

5.3.3 Size distribution

Size distribution is the most important feature we want to investigate. The flooding function provides the perimeter histogram as shown in Fig. 5.4. Therefore, the size distribution of the cobalt nanodots is obtained. However, this process works only for the low coverage.

Fig. 5.4 Perimeter histogram of the nanodots. This gives us the size distribution of the nanodots.

Fig. 5.5 Connected nanodots cannot be distinguished in the flood function. (a) shows the original STM image. Although the neighboring dots are very close, they are still easily distinguished as individual dot by direct eye observation. (b) shows the situation after flooding, the program recognized the “connecting” dots as one big dot and enclosed them into the same perimeter, which is presented in white curve.

For higher coverage, the first neighbor distance becomes shorter and some of the nanodots connect with the neighboring dots. Although from the STM morphology, the connecting nanodots are still appear as two dots, they are identified as one big dot in the flooding function as presented in Fig. 5.5.

As coverage approaching 1 ML, all the nanodots get “squeezed” and appear to the computer as one or two huge clusters. Obviously, to get a more reliable way of statistics, new methods are required and we decided to approach the problem from an entirely different way.

As shown in Fig. 5.6 (a) the density of the dots on the surface is quite high with a large number of nanodots close to their neighbors. The line profile of two adjacent nanodots connects at the border. If Fig. 5.6 (b) is taken a first derivative, we can easily know that the peaks and valleys in the landscape which correspond to the dots top and borders, become inflexions. Taken the second derivative, the profile will show maximum or minimum at the inflexions. As a result of the Laplacian operator on Fig. 5.6 (a), Fig. 5.6 (c) shows rings along the borders of the nanodots. The line profile in Fig. 5.6 (d)

shows peaks at the borders and valleys at the dots top as expected. In this way, the borders of each nanodots can be easily identified even though they connect with their neighbors.

Fig. 5.6 The nanodots morphology before and after Laplacian operator. Compare (b) with (d), the borders of the nanodots became sharp peaks in (d).

The next step concerns how to obtain the cluster size. To do this, Fourier transforms is introduced which catches the “ring” feature and shows their intensity in the reciprocal space as presented in Fig. 5.7 (d).

For an ideal ring of radius a , the function is $\sigma(r-a)$, whose 2D Fourier transform is given by $aJ_0(ka)\sum \exp(i\vec{k} \cdot \vec{r}_i)$. The actual FFT image shows the intensity which is $|aJ_0(ka)\sum \exp(i\vec{k} \cdot \vec{r}_i)|^2$. With the dots randomly distributed, the phase shift term $\sum \exp(i\vec{k} \cdot \vec{r}_i)$ only contributes to the background noise. Consequently, the intensity mainly depends on the radius as the function $a^2 J_0^2(ka)$. However, if the ring is not ideal and has a certain width, the inner edge induces a negative function of the intensity. The

positive and negative parts add up to present the intensity of the ring which is indicated by Fig. 5.7 (f).

Fig. 5.7 The data analysis procedure. The original STM image (a) is taken Laplacian operator to obtain (b), which emphasizes the borders of the nanodots. The FFT transform of (b) is shown in (d), which illustrates the intensity corresponding to the diameter in reciprocal space. A line profile (e) accurately shows the intensity. Finally, it is converted to the real space and gives the size by comparing to the standard Bessel function (f).

As demonstrated in Fig. 5.7 (f), the intensity oscillates in the reciprocal space with one major peak at $k = 0$, and the rest of peaks symmetrically located about zero. We name this major peak the zeroth order peak and its nearest two peaks the first order peaks. A line profile is taken from the Fourier transform image, and as shown in Fig. 5.7 (e), Δk_1 is the distance between the two first order peaks. According to standard Bessel function $J_0^2(x)$, this value is 7.66, which indicates $\Delta k_1 \cdot a = 7.66$. As a result, the radius is given by $7.66 / \Delta k_1$. However, if take a closer look at Fig. 5.7 (f), one will notice the peaks are shifted in total intensity shown by the blue line. This shift causes deviation in calculated value from the actual dot diameter. On the other hand, different sizes of the dots generate

different Δk_1 , which shift or even split the peaks. In order to obtain the most probable size, more information is required. Therefore, the distance between the second order of peaks Δk_2 and third order of peaks Δk_3 are measured and compared to the Bessel function. The most probable size is obtained from the mean value and the error from the standard deviation.

To reduce the effect of drifting in the STM image which is discussed in Chapter 2, the distance was calibrated by two lattice points shown in Fig. 5.7 (d). From the TiO_2 lattice constants, the distance between the two lattice points in the reciprocal space is 3.71 nm^{-1} . Therefore the calibration coefficient for real space is obtained by dividing the measured lattice points distance by 3.71 which is the actual distance.

Fig. 5.8 Height vs. diameter. The fitting is $y = 0.249x - 0.2202$

5.3.4 Height Vs Diameter

The other important parameter is the nanodots height. To study the relationship between the height and diameter, the height and diameter are measured and plotted in the Fig. 5.8. The ratio of height and diameter suggests that the shape of dots is disk-like.

5.4 Results of the nanodot growth

5.4.1 Morphology

The initial growth was at a very low rate and this allowed us to observe the early stages of the cluster formation. With a clean TiO_2 (110) surface of atomic resolution, clusters can be observed even when small amount of cobalt are deposited. Figure 5.9 (a) is the clean surface with a few visible defects. At around the same surface area, 0.02 ML of cobalt was deposited on the substrate. The small clusters of cobalt are randomly distributed over the surface and the 1×1 substrate structure can be clearly observed, which indicates the growth mode is Volmer-Weber mode. The average diameter of the cluster is about 1.5 nm, which indicates that the deposited cobalt atoms have enough energy to overcome the energy barrier at the surface to form clusters. The cobalt clusters did not show a preference of the nucleation sites, however, the surface defects, especially oxygen vacancies, is generally believed to be preferred nucleation sites for adatoms.

Fig. 5.9 STM investigation of the initial stages of the cobalt nanodots growth.

Fig. 5.10 Nanodots morphology at a higher coverage and after post-annealing.(d) shows the general trend of the dependence of dot size and density

In the continuing growth, the small clusters begin to increase their size. In Fig. 5.9 (c), a few big clusters of 3 nm are coexisting with the small ones. Meanwhile, the density of the cobalt dots increases. This tendency becomes even more obvious in further growth which is demonstrated in Fig. 5.9 (d). At coverage of 0.17ML, more small dots grow into big ones with 3- 4 nm of diameter, and the overall dots density increase drastically. At this coverage, the 1×1 substrate structure is still observed. As a matter of fact, with the tip in good condition, the substrate is always detected expect when the surface is all covered by the cobalt clusters shown as Fig. 5.10 (b). Image Fig. 5.10 (a) shows a higher density of the big dots with size similar as those in Fig. 5.9 (d). This indicates that there could be a stable or at least meta-stable size of the cluster; and this give the hope for achieving the uniform size dots. Image Fig. 5.10 (b) confirmed this scenario. At the coverage as high as 1.5 ML, instead of growing into bigger dots, the dots size is kept around 3- 4 nm, indicating that there's a "stop" size in growth. Even though the dots stopped growing,

the size and shape of dots in Fig. 5.10 (b) is not very uniform. In the hope of getting a better result and to check the stability of the dots, we annealed the sample to about 670 K. The result was quite amazing: the cobalt atoms re-organized themselves and formed much more uniform dots as is shown in Fig. 5.10 (c).

By observing the morphologies of the growth process, we are convinced of the scenario that there exists a stable cluster size and the uniform size distribution is achievable. When the clusters on the surface reach the stable size, any further increase of Co coverage only contributes the density. Figure 5.10 (d) shows a schematic and qualitative view of both the size and density of the Co clusters deposited on $\text{TiO}_2(110)$ (1×1) surface.

5.4.2 Statistics

To quantitatively study the growth process, we have conducted statistic on the dots size, shape as functions of the coverage.

Fig. 5.11 Size of cobalt nanodots as a function of coverage. A stable size at around 4.0 ± 0.5 nm is observed.

Detailed data process is described in the previous section and the result is shown in Fig. 5.11. At the lowest coverage of 0.02 ML, the dominant cluster size is around 1.7 ± 0.5 nm. As the coverage increases, the cluster size becomes bigger. At 0.24 ML, the dominant size is 3.2 ± 0.5 nm with some other smaller size of the clusters. When the coverage kept growing, the curve for 0.33 ML coverage shows the major peak at 3.9 ± 0.5 nm. The size of the dots becomes stable after 0.4 ML. Up to 1.52 ML, the cluster size is still within the range of 4.5 ± 0.5 nm, indicating there is a stopping size of the cluster growth. The most probable dot size concentrates at 4.0 ± 0.5 nm range.

Fig. 5.12 Post annealing effects on the dot size. The change in diameter as a function of post annealing temperature indicates the self-organization of the Co atoms.

From the previous section, the morphology of Co clusters is discussed. By comparing images before and after post annealing shown by Fig 5.10 (b) and (c), one can easily conclude that the dots are more uniform in size and shape after post annealing. In Fig 5.12, the diameter is observed to change at various annealing temperatures implying the self-organization of cobalt atoms. At the first point at 300k, the coverage is 1.5 ML. The diameter decreased as the post annealing temperature went up. However, in Fig 5.10

(c), the density of the dots was observed to decrease. It seems that the sample “lost” cobalt atoms after post annealing. The question is where did the “lost” cobalt go? It is almost impossible for large amount of cobalt to evaporate into the vacuum at such a low temperature. One reasonable explanation is that during post annealing, cobalt clusters acquire more ordered structures and eliminate previous defects from growth.

5.5 Discussions

From the experimental results and data analysis, we have confirmed that the cobalt deposition mode is Volmer-Weber growth. A stable size of the cluster is 4.0 ± 0.5 nm, independent of the coverage. The post annealing process promotes the uniformity of the dot.

The most amazing feature about this system is the existence of a most stable size of the cluster. To understand this phenomenon, we employ the jellium model.

The jellium model is defined by a Hamiltonian that treats the electrons as usual but the ionic cores as a uniform positively charged background. This naturally leads to a description of the electron density in terms of single-particle wave functions that extend over the entire cluster [51]. In jellium model, each metal atom carries an certain electron density and as an atom is add on the cluster, its electron interact with the background positive charges, thus affect the total energy. The typical cluster in our system is 4.0 nm in diameter which contains over hundreds of the cobalt atoms. For jellium model, a cluster contain more than 100 atoms is treated mesoscopically and its total energy only depend on the r_s and the diameter of the cluster. The r_s represents the electron density of the jellium which affects the total energy of the jellium cluster.

For free cluster of cobalt hcp structure, the energy per electron of a jellium cluster was calculated and three curves represent the energy of the cluster as a function of the radius corresponding to different r_s .

Fig. 5.13 Theoretical calculation of energy per electron of a jellium cluster.

Energy per electron of a jellium cluster is also given by $\frac{E}{N} = \varepsilon(bulk) + \frac{\sigma(surf)}{R}$,

where surface energy is $\sigma = \sigma(free\ surface)(1 - \delta) + \sigma(interface)\delta$. The energy per electron of jellium cluster is also calculated, and the results are shown in Fig. 5.13. If the energy increases with the radius, $\sigma(surf)$ must be negative. If the energy decreases with the radius $\sigma(surf)$ must be positive. If the energy is a constant, the $\sigma(surf)$ must be somewhere close to zero.

For $r_s=3.0$, $\sigma(surf)>0$, the energy decreases with increase in radius. Therefore the dots in this range will keep grow to approach minimum energy. For $r_s=2.0$, $\sigma(surf)<0$, the energy increases with radius. In this case, the atoms do not like to form clusters since this is not energetically favorable. There is a range where $r_s\sim 2.4$, and $\sigma(surf)\sim 0$, in which the cluster can stay in any size.

When the surface energy is very close to zero, a small change in r_s can make it switch sign, and give a minimum energy. Therefore, the stable size is achieved.

There are two requirements:

1) $\sigma(\text{surf})$ close to zero. For the cobalt hcp structure, $r_s = 3$ corresponds to 0.7 conducting electron; $r_s = 2.4$ corresponds to 1.3 conducting electrons; $r_s = 2$ corresponds to 2 conducting electrons.

2) r_s varies with radius. Cobalt has 7 3d electrons, which serve as an electron reservoir. As the radius grows, the d electrons get delocalized thus change r_s .

The cobalt cluster system meets the above two requirements, thus a stable size is achievable.

The growth process of cobalt clusters was observed. The cobalt clusters are deposited on the clean TiO_2 surface, and the growth mode is Volmer-Weber. Small dots of about 1.5 nm size are observed at the low coverage. For coverage about 0.1 ML, bigger cluster of about 4 nm are formed, and density of the clusters increase. Most of the dots stop growing when they reach the size about 4 nm. In higher coverage about 0.3 ML, the big dot density becomes dominant, although smaller dots are still observed. At a very high coverage at 1.5 ML, the clusters overlap but are still clearly distinguished, and the most preferred size is about 4.5 ± 0.5 nm. However, after post-annealing, the atoms reassemble and a uniform size at 3.5 ± 0.5 nm is achieved.

The above scenario is quantitatively supported by statistics. Figure 5.11 clearly shows that the most stable size is about 4.0 ± 0.5 nm which did not vary with the coverage. Dots uniformity is greatly promoted by post-annealing.

Both morphology observation and statistic data indicated that there exists a stable size at about 4.0 ± 0.5 nm. To understand this, jellium model is introduced. Although the model cannot predict which size is the most stable, it does show that there is great possibility of a most energetic favorable size, which is consistent with the experiment.

In this chapter, the results from the thesis project are summarized and conclusions of the thesis are drawn. Prospective work is proposed on the basis of the current conclusions.

With appropriate preparation, the TiO_2 (110) surface was proven to be a well ordered, contamination free surface which promotes Volmer-Weber growth. The detailed treatment recipe was demonstrated.

Both morphology and statistical data showed that there was a most stable dot size with a diameter of 4.0 ± 0.5 nm for different coverage which was supported theoretically based on jellium model. An optimal set of fabrication parameters was established for the uniform magnetic nanodot growth.

6.1 TiO_2 as a substrate for quantum dot growth

The rutile TiO_2 (110) is one of the most studied and prominent oxide surfaces for the growth of metallic quantum dots. It is well ordered and easily prepared to achieve atomic resolution. The surface is with little corrugation and has large flat terraces formed by single atomic layer. Although the fully oxidized TiO_2 has a relatively large gap about 3 eV, it is easily reduced by introducing oxygen vacancy and drastically increasing its electric conductance. Therefore, the surface is promptly characterized by LEED and STM. As a result, the well-ordered TiO_2 (110) surface serves a perfect substrate surface for material deposition. In particularly, the low surface energy of TiO_2 (110) promotes the Volmer-Weber growth for metal nanoclusters.

The growth of cobalt clusters requires the substrate surface to be well ordered $p(1\times 1)$ structure with large flat terraces and few defects. In order to achieve this, we have carefully prepared the TiO_2 (110). The sputtering strength and annealing temperature must be in a delicate balance: low sputtering power is not sufficient to remove the contamination on the surface, while high sputtering power damages the surface making it hard to be restored by the annealing process. On the other hand, low annealing temperature lacks the energy to recover the surface to create large terraces, while high annealing temperature generates oxygen vacancies and produces defects. At sufficient high temperature the surface reconstructs into a (1×2) structure. Compared the surface morphologies after different combinations of the treatments, we have found that it is most likely to get a good surface by sputtering with $0.7\text{ }\mu\text{A}$ ion current for 30 minutes and then annealing at 900 K for 20 minutes for the first several cycles of treatment, and followed by a couple of moderate sputtering with $0.4\text{ }\mu\text{A}$ ion current for 10 minutes combined with the annealing at 900 K for 20 minutes. Particularly, to reduce oxygen vacancies, the sample has to be sputtered with the sample temperature below 373 K, and avoid LEED measurements before STM imaging to reduce the concentration of defects.

6.2 Co dots with a uniform size

The cobalt clusters are deposited on the substrate via an e-beam evaporator. The deposition time and rate can be precisely controlled.

We discovered, at the initial stage of growth, cobalt atoms nucleated at random sites forming very small dots about 1.5 nm and the rest of the surface showed clear TiO_2 (1×1) substrate. However, some initial grown clusters are likely to register at the surface

defect or vacancy sites. In the continuous growth, small dots grew bigger and the density increased. At coverage about 0.3 ML, the big dots with a size of 4 nm became dominant though small dots can still be observed. When the coverage reached 1.5 ML, the surface was all covered with cobalt dots, however, the average dot size was still around 4 nm though the density of clusters increased with coverage. This suggests that there is a “cutoff” value of cluster size during the growth of Co dots. Furthermore, post annealing promotes the uniformity of cluster size indicating there exists a characteristic value to govern the growth of Co nano dots on TiO₂(110) surface. A most favored cluster size with a value of 4.0 ± 0.5 nm was conformed by statistic data analysis.

A Co clusters with the character size of 4 nm contains hundreds of atoms. For such a large cluster of atoms, the electronic states near the Fermi level are nearly continuous. The ‘magic number’ of small metallic spheres is no longer adequate to explain the size distribution. Therefore, a conceptual understanding, as we proposed, is given by jellium model controlled by the electron density or r_s . The unique feature in Co dots is that the d-orbital electrons in cobalt atom serve as a reservoir to provide the conduction electrons thus allow the r_s varying with change of dot size. For positive surface energy, the energy per electron of a jellium cluster decreases with the increase of size, result in no “stop size” of the cluster. On the other hand, at negative surface energy, the energy increases with the increase of cluster size; and the atoms will not coalesce. The energy minimum only appears at the range where surface energy is close to zero. The cobalt hcp structure is likely to exist in this range, and as the dots grow, the variation of r_s makes the surface energy to switch sign, by which the minimum energy is achieved.

Therefore, this scenario predicts that the stable size of the cobalt cluster is achievable, in consistent with experimental observation.

6.3 Future work

This thesis research mainly provided a pathway for the growth of Co nanodots in uniform size and uniform density and a basic understanding of the growth mechanism. Yet, several important issues are still to be resolved in the future studies.

6.3.1 The role of surface defects

One main unresolved issue for the growth of uniform Co nanodots on $\text{TiO}_2(110)$ surface is: what is the role of oxygen vacancy at the very initial stage of growth? The atoms were observed to nucleate at random sites, but are these sites really randomly chosen, or there are actually more possibilities for the oxygen vacancy sites to attract the atoms? To answer this question, real time imaging is required. And very high resolution images are necessary for the observation.

6.3.2 The internal structure of Co dots

The internal structure of nanodot has prominent effects on its properties. Although the bulk structure for cobalt is known to be hcp, it is not granted the internal structure of cobalt nanodot is the same. To investigate the nanodot structure, the lattice structure determination of nanodots is necessary. One way to do is using high-resolution TEM to image the cross section of nanodots.

6.3.3 The scaling behavior of Magnetic properties

The final goal of this project is to investigate the magnetic property of the nanodots as function of dot size and density on non-metallic surface. In addition to understand the superparamagnetic properties of nanodots as a function of size, a density controlled NON-RKKY dot-dot magnetic correlation is extremely interesting. Studying these magnetic properties with technique like SQUID and surface magneto-optic Kerr effect is highly desirable.

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