Epitaxial Growth of Rhenium with Sputtering [†]

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Abstract

We have grown epitaxial Rhenium (Re) (0001) films on α-Al_2O_3 (0001) substrates using sputter deposition in an ultra high vacuum system. We find that better epitaxy is achieved with DC rather than with RF sputtering. With DC sputtering, epitaxy is obtained with the substrate temperatures above 700 °C and deposition rates below 1 Å/s. The epitaxial Re films are typically composed of terraced hexagonal islands with screw dislocations, and island size gets larger with high temperature post-deposition annealing. The growth starts in a three dimensional mode but transforms into two dimensional mode as the film gets thicker. With a thin (~2 nm) seed layer deposited at room temperature

and annealed at a high temperature, the initial three dimensional growth can be suppressed. This results in larger islands when a thick film is grown at 850 °C on the seed layer. We also find that when a room temperature deposited Re film is annealed to higher temperatures, epitaxial features start to show up above ~600 °C, but the film tends to be disordered.

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1. Introduction

Epitaxial superconducting films of refractory metals are a promising new template for single crystal tunnel barriers in Josephson junction quantum bit (qubit) devices [1]. In existing Josephson junction qubits, it is believed that the widely-used amorphous AlO_x tunnel barriers have undesirable two-state fluctuators. It is speculated that single-crystal tunnel barriers such as sapphire (α-Al_2O_3) may be free of such decoherence sources [1]. The refractory metals are appealing because preparation of a single-crystal tunnel barrier requires an epitaxial base electrode of high melting temperature with a good lattice match

to the tunnel barrier. Along this line, Re is a good candidate because it has a very high melting temperature (3186 °C) and a hexagonal close packed (hcp) structure with a very good lattice match (a = 2.76 Å) to the oxygen sublattice (a = 2.77 Å) of α-Al_2O_3 (0001) [2]. Re also has a reasonably high superconducting critical temperature (T_c = 1.7 K) [3], which is compatible with the present qubit technology [1]. In addition, according to the free energy of oxide formation under the same oxidation condition, Re has much weaker tendency for oxidation than do most other elemental superconductors such as Nb [4], and thus a sharp interface between the base layer and the oxide tunnel barrier will be relatively easy to achieve with Re.

The most common epitaxial growth technique for refractory metals such as Re is the electron-beam (e-beam) based molecular beam epitaxy (MBE) technique [5], since the popular Knudsen cell based MBE [6] is not compatible with the high melting temperatures of refractory metals. On the other hand, the dominant thin film deposition method for device fabrication is sputtering [7]. While there are reports of epitaxial growth of Re by e-beam evaporation in the literature [3,8] and epitaxial growth of other metals by sputtering [7], in this work we give a detailed report on the epitaxial growth of Re using sputter deposition technique. We describe the relationship between epitaxy and

growth parameters using various *in situ* and *ex situ* analysis tools such as reflective high energy electron diffraction (RHEED), low energy electron diffraction (LEED), Auger electron spectroscopy (AES), atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

2. Experimental

All of the films in this report were grown in an ultra high vacuum (UHV) sputtering chamber and transferred into various analysis chambers for the RHEED, LEED, AES and STM studies without breaking vacuum. Base pressure of the system is about 1×10^{-10} Torr, and the system is composed of three isolated chambers and a load-lock. The sample is transferred between chambers using magnetically driven sample transfer rods. Among the three UHV chambers, the first one is dedicated to Re sputtering, equipped with a radiative sample heating stage (maximum 850 °C continuous), and pumped by a turbomolecular pump (TMP). The other two chambers are each pumped by an ion pump and a titanium sublimation pump in addition to a TMP, and are used for RHEED, LEED, AES and STM analysis. The epitaxy of the films was checked by RHEED and LEED, and the morphology studied by use of *in situ* STM and *ex situ* AFM (tapping mode).

RHEED and LEED are taken with 5.0 keV and up-to 1 keV e-beams, respectively. AES was used to check the cleanliness of the substrate and impurity levels of the film.

Sputtering was performed in an Ar environment (~5 mTorr) by used of a magnetron sputtering gun that is capable of both DC and RF operation and is fitted with a 1" diameter Re target (99.9 % purity). AES on the as-sputtered films showed no trace of Ar. This shows that Ar incorporation is negligible.

The substrate was an epi-ready α-Al_2O_3 (0001) cut from a commercial c-plane sapphire wafer. The substrate showed atomically flat terraces as measured by AFM. The substrate was scratch-free and the measured root mean square (RMS) roughness was about 2 Å. Prior to introducing the substrate into the chamber, it was ultrasonically degreased in acetone and isopropyl alcohol. The substrate was then cleaned *in situ* by annealing at 850 °C for one hour. There was no measurable trace of carbon or any other contaminants in the AES spectrum.

3. Results and discussion

As a first step for the epitaxial growth, we compared RF and DC operation using the same sputtering gun. Fig. 1(a) & (b) show the difference between RF and DC sputtered films grown both at 850 °C, respectively. The DC sputtered film shows better epitaxy even with a higher deposition rate than the RF sputtered film. AFM of these samples shows that the island sizes are much larger in DC sputtered films (> 100 nm in diameter) than for RF sputtered films (< 50 nm in diameter). In addition, DC sputtered films show atomic step terraces, while RF sputtered films show no terraces within the AFM resolution. Finally, the DC sputtered films show sharper hexagonal LEED patterns than the RF sputtered films. These differences are most likely due to the fact that RF sputtering has more of an etching effect on the sample surface during deposition than does DC sputtering. This observation indicates that DC operation is better for epitaxial growth. Accordingly, all the following growth studies were performed using only DC sputtering.

The quality of the epitaxy is sensitive to both the sputtering power and the substrate temperature. For example, when the deposition rate was higher than 1 Å/s (DC, 30 W), no diffraction pattern was seen in LEED. In contrast, with reduced deposition rate of ~0.3 Å/s (DC, 6 W), both a sharp diffraction pattern in LEED and terraced islands in AFM

were observed, as shown in Fig. 1(b). However, even with the lowest deposition rate of ~0.3 Å/s, for substrate temperatures below 500 °C, no measurable LEED pattern was observed. On the other hand, when the growth temperature was increased to 700 °C, a noticeable diffraction pattern showed up (Fig. 2). In fact, the epitaxial quality continues to improve as the growth temperature increases, as shown for an 850 °C grown film in Fig. 1(b). Comparison of both the AFM images and the LEED patterns shows that higher growth temperature is preferable for Re epitaxy.

With *in situ* STM studies, more accurate morphological information can be obtained with minimal surface contamination problems. The STM image in Fig. 3(a) shows that an 850 °C (DC, 7 W) grown film is composed of terraced, hexagonal islands that are typically ~100 nm in diameter. As shown in Fig. 3(b) the most commonly observed step is 3 Å high. This corresponds to two atomic Re layers, considering that the c-axis lattice constant of the tri-atomic layered hcp Re unit cell is ~4.5 Å. Frequently, two terraces merge into a 6 Å step and occasionally multiple steps converge to form steeper edges. Another interesting feature is that every hexagonal island has a screw dislocation at the center as shown in Fig. 3(c). This indicates that the growth proceeds in a spiral mode

with the screw dislocation as the growth flow axis. This spiral growth is a well-known phenomenon [9] and is commonly observed in other systems [10-12].

When the 850 °C grown film was annealed at 1200 °C for half an hour, the terraces got wider and the average island diameter increased to about 200 nm, as shown in Fig. 4. However, qualitative features of the epitaxial film such as the existence of screw dislocations and multiple step terraces remain unchanged.

The RHEED images in Fig. 5 show the epitaxial growth evolution at 850 °C. Initially, the film grows in a 3D fashion, which appears as a multiply oriented, spotty diffraction pattern shown in Fig. 5(a). As the film gets thicker, the 3D spots gradually diminish, and 2D streaks start to develop (Fig. 5(b)). Eventually when the film gets much thicker (> 50 nm), only 2D streaks remain (Fig. 5(c)). This indicates that the initial heteroepitaxy (Re on sapphire) starts as Volmer-Weber (VW) type (3D growth) but that later the Re homoepitaxy (Re on Re) proceeds with Frank-Van der Merwe (FV) mode (2D growth) [13].

The initial VW 3D mode can be avoided by use of a seed layer technique [14]. When a thin (2 nm) Re is deposited at room temperature, no discernible RHEED pattern is observed (Fig. 6(a)), indicating that the film is not ordered. However, high temperature (850 °C) annealing of this seed layer transforms it into a single crystalline 2D structure, which appears as a streaky RHEED pattern in Fig. 6(b). When more Re is deposited on top of the seed layer at 850 °C, the RHEED remains 2D throughout the whole growth (Fig. 6(c)). The effect of this seed layer scheme is shown also in the STM images of Fig. 7(a)&(b). When the seed layer is annealed at 850 °C, the film remains flat with randomly shaped small islands (Fig. 7(a)). At this stage, the surface morphology reflects the combined roughness of the substrate and the film. After another 130 nm of Re is deposited onto the seed layer at 850 °C, large hexagonal islands are observed (Fig. 7(b)). Compared with the film in Fig. 3(a), which was grown without any seed layer, the most significant difference is that the islands are a factor of two larger (~200 nm vs. ~100 nm in diameters). Other than that, other features are similar. This shows that the epitaxial features such as hexagonal islands, screw dislocations and multiple steps are not due to the initial VW growth mode but are an intrinsic thermodynamic property of Re (0001) growth.

Finally, in order to see the effect of temperature on the surface morphology of Re, we performed annealing tests on room temperature (RT) sputtered Re films. According to RHEED (very diffuse and not shown here), a RT sputtered Re film grows polycrystalline. The STM image in Fig. 8(a) shows that the RT sputtered film (130 nm thick) is composed of small islands with c-axis normal to the surface and tubular structures with c-axis along the tube direction. When the film was heated, a major morphology transformation occurred at around 600 °C, above which temperature c-axis oriented hexagonal islands emerged together with other complicated structures (Fig. 8(b)) (RHEED also showed streaky but diffuse diffraction (not shown here)). This implies that although the annealed RT grown films show some epitaxial features, they are not completely single-crystalline. Additional annealing to higher temperatures (up to 1200 °C) induced no further qualitative change in the morphology.

4. Summary

We described growth of epitaxial Re film on sapphire substrate with sputtering. Under similar growth conditions, DC sputtering gives noticeably better epitaxy than RF. The best epitaxy is obtained at the lowest deposition rate and at the highest growth temperature. With DC sputtering, considerable epitaxy is obtained only below 1 Å/s in

deposition rate and above 700 °C in growth temperature. Epitaxial Re (0001) films are composed of hexagonal islands with screw dislocations and multiply stepped terraces. High temperature epitaxial growth directly onto the base sapphire surface starts with initial 3D growth mode and gradually transforms into 2D growth. A thin seed layer grown at room temperature and annealed at a high temperature helps suppress the initial 3D growth and results in island sizes larger by a factor of two. However, all of these epitaxial films showed evidence of multiple steps that appear to be converging into larger, a-plane faces that are perpendicular to the film plane. The question of whether or not these are atomically flat planes could not be resolved in this study due to the finite radius of the STM tip. We are currently investigating the efficacy of these films as the bottom electrode for tunnel junctions in superconducting quantum bit devices.

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Figure Captions

Figure 1: AFM and LEED images of RF vs DC sputtered films grown at 850 °C; both are 130 nm thick. Scan area is 1 μm × 1 μm. (a) RF 30 W, 0.17 Å/s. (b) DC 6 W, 0.26 Å/s. DC sputtering results in sharper LEED patterns and much larger islands even with a higher deposition rate.

Figure 2: Epitaxy obtained at 700 °C with DC 6 W; film thickness is 130 nm. Scan area is 1 μm × 1 μm. No measurable LEED pattern is observed up to the growth temperature of 500 °C. When the growth temperature is increased to 700 °C, a clear diffraction pattern emerges as shown here. However, compared with the 850 °C grown film presented in Fig. 1(b), the 700 °C grown film has inferior epitaxial quality; the surface is rougher, island sizes are smaller, and the LEED pattern is not as sharp.

Figure 3: STM images of an epitaxial film (DC 7 W, 0.35 Å/s, grown at 850 °C, 130 nm thick). (a) Scan area is 500 nm × 500 nm and the full gray scale corresponds to ~15 nm in height. Hexagonal islands (~100 nm in diameter) are commonly observed,

which is related to the c-axis oriented hcp structure. (b) Zoomed-in view of (a) (220 nm × 220 nm scan area). The line scan covers two single steps and two double steps, and results in height variation of ~1.8 nm. This implies that the single step (~3.0 Å) corresponds to two Re atomic layers since the c-axis lattice constant of hcp Re, which is composed of three Re atomic layers, is ~4.5 Å. Occasionally multiple steps merge together to form steep edges. (c) Zoomed-in view of a typical hexagonal island, which has a screw dislocation at the center: 200 nm × 200 nm scan area.

Figure 4: STM image taken after 1200 °C annealing of an 850 °C grown epitaxial film (500 nm × 500 nm of scan area). Compared with Fig. 3(a), the island sizes are about twice as large in diameter (~200 nm) and the terraces have also become noticeably wider.

Figure 5: RHEED images at different stages of epitaxial growth (850 °C, DC 7 W). (a) After 2 nm of Re, multiply oriented 3D spots are observed. (b) After 10 nm of Re, 3D spots are weaker and 2D streaks are more pronounced. (c) After 100 nm of Re, 3D spots are completely gone and only bright 2D streaks are observable.

Figure 6: RHEED images for the seed layer growth scheme. (a) After 2 nm of Re is sputtered at room temperature, no diffraction pattern is observed. (b) When the seed layer is annealed at 850 °C, a streaky diffraction pattern shows up, which implies that the seed layer has become 2D and single-crystalline. (c) 130 nm of Re is sputtered on top of the seed layer at 850 °C and a sharp 2D diffraction pattern is observed; 2D growth mode is maintained throughout the whole growth.

Figure 7: STM images for the seed layer growth scheme (500 nm × 500 nm of scan area). (a) After 2 nm of RT sputtered Re is annealed at 850 °C, the surface is composed of tiny islands (~10 nm in diameter). The full gray scale corresponds to ~3 nm in height. (b) After 130 nm of Re is deposited on top of the seed layer at 850 °C, large islands (~200 nm in diameter) with many terrace steps are formed. The full gray scale corresponds to ~15 nm in height. Note that the islands are significantly bigger than those of the regular 850 °C grown films (Fig. 3(a)).

Figure 8: Annealing test of RT grown films (500 nm × 500 nm of scan area). The full gray scale corresponds to ~10 nm in height for both images. (a) 130 nm of Re sputtered at RT. Circular islands with c-axis normal to the surface and tubular

islands with c-axis along the tubular axis are observed. (b) After the RT sputtered Re film is annealed above 600 °C, the surface morphology is completely changed. This particular image is obtained after 750 °C annealing. Not only hexagonal islands, but also other complicated oriented features can be seen. Although not clearly shown in this image, screw dislocations are also observed on the hexagonal islands.

Figure 1

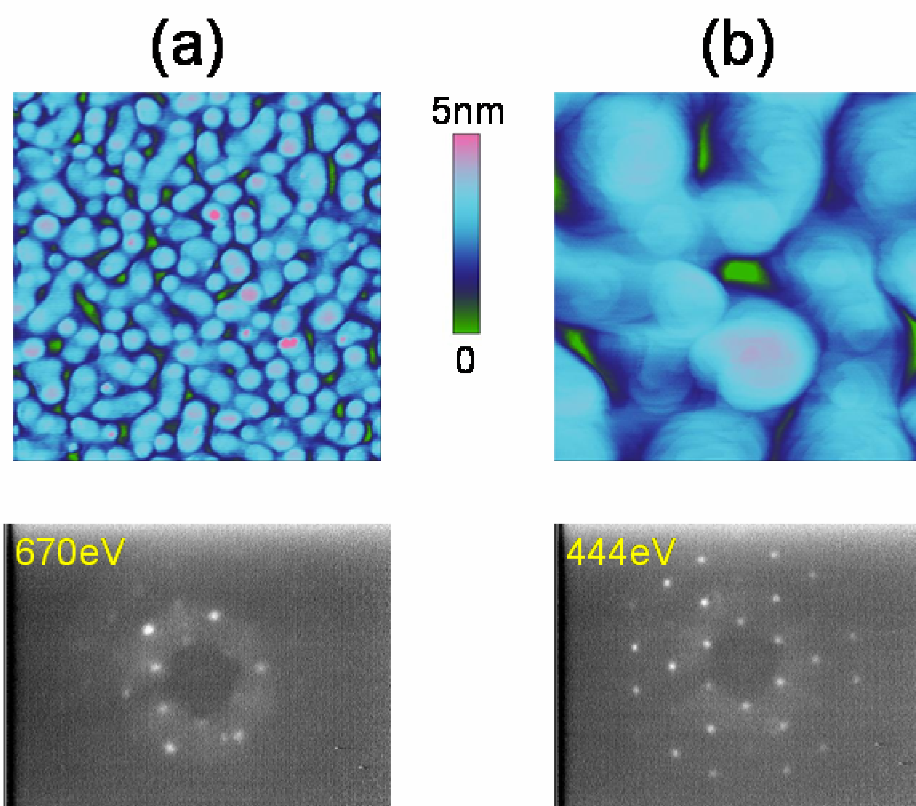


Figure 2

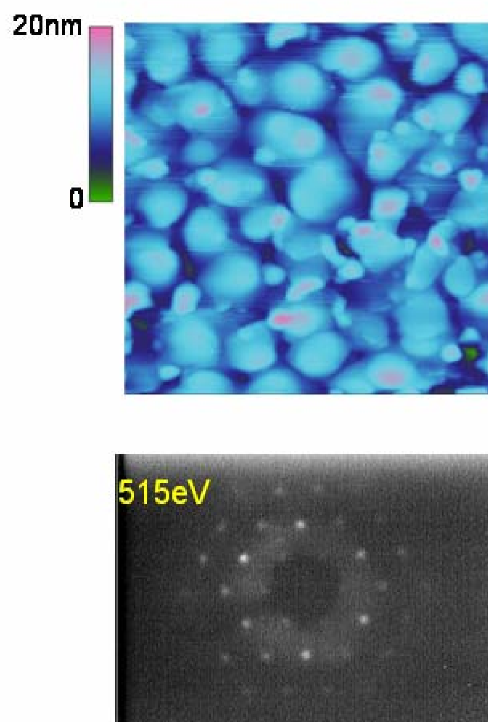


Figure 3

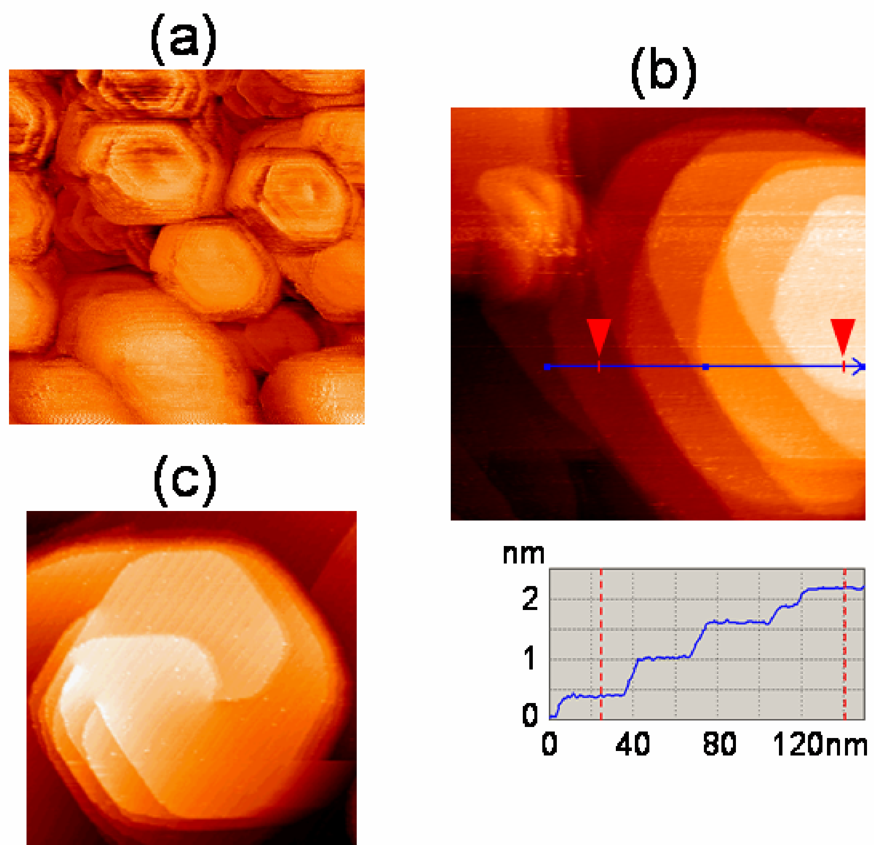


Figure 4

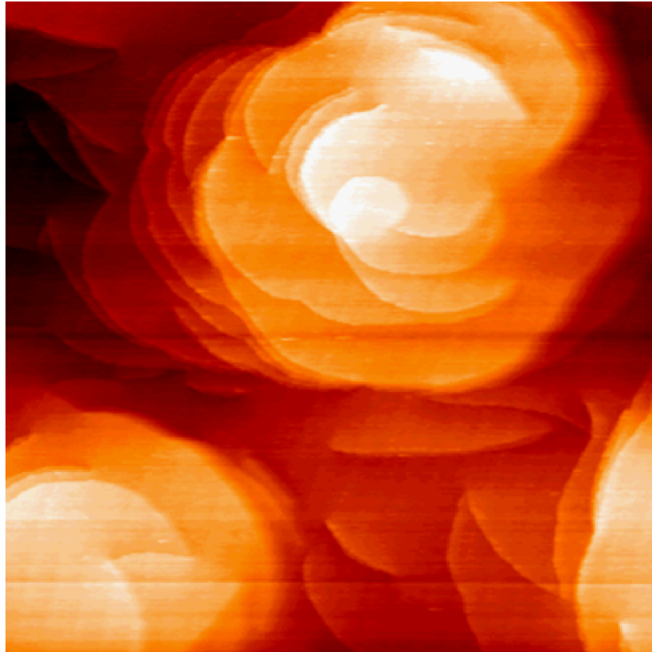


Figure 5

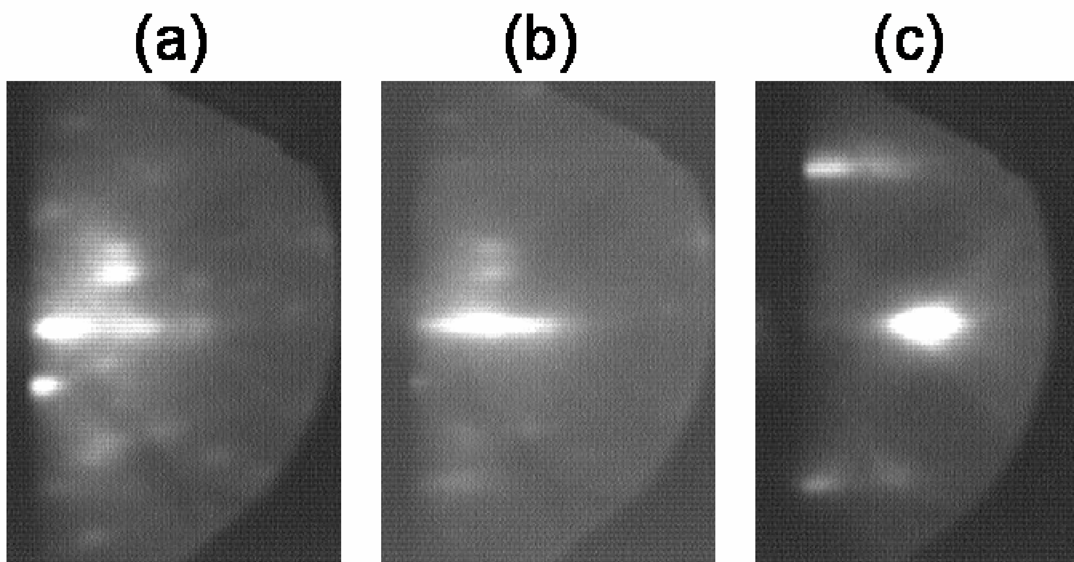


Figure 6

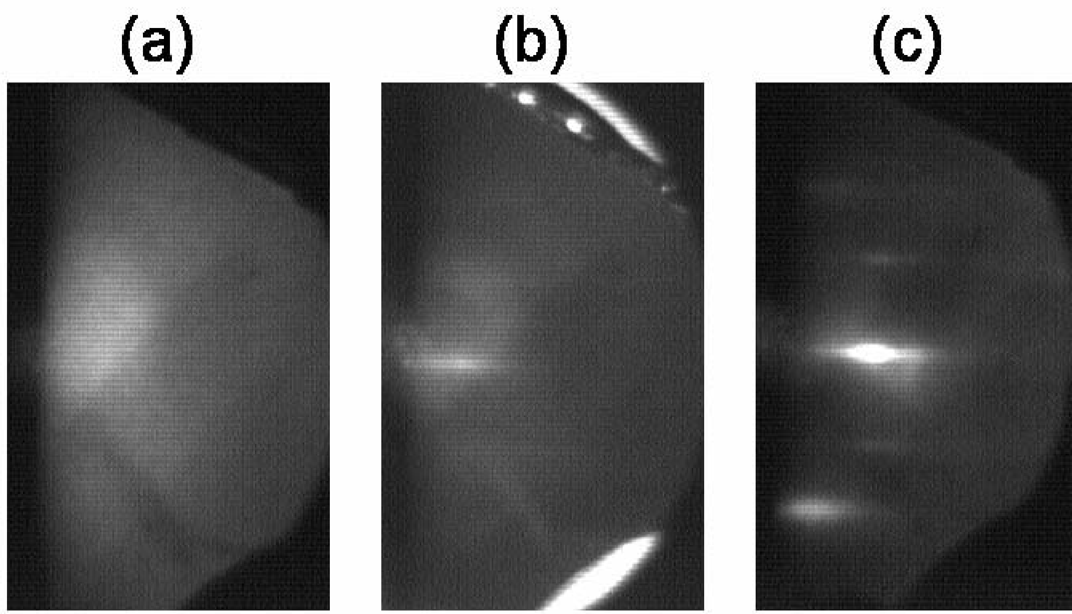
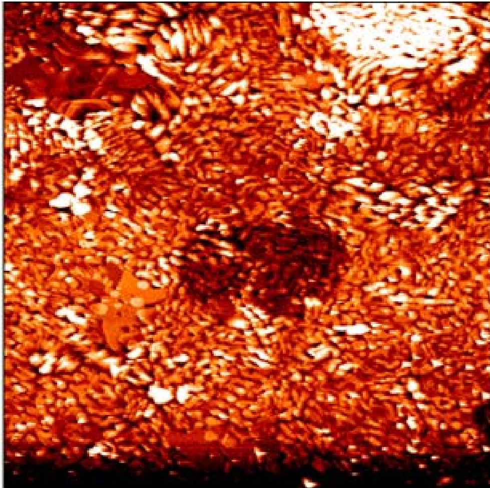


Figure 7



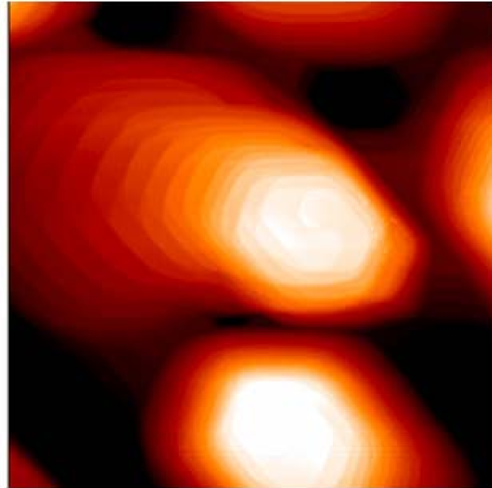


Figure 8