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Novel Coarsening of Pb Nanostructures on Si(111) 7 X 7

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Abstract

In order to study a possible means of controlling the growth of a self-assembled nanostructure grown epitaxially, Pb/Si(111) was analyzed. The experiments were performed with a Scanning Tunneling Microscope (STM) on a Si(111) 7 X 7 crystal prepared atomically clean under Ultra High Vacuum (UHV) conditions followed by Pb deposition. The islands were monitored in time to see how they coarsen and whether the classical theory of Ostwald ripening is applicable. STM Images of the resulting Pb islands were taken as they evolved in time. Height measurements indicated that initially, the majority (25 out of 33 islands) were 4 or 5 layer islands, but by the end of the experiment 68 minutes later, the majority (18 out of 24 islands) were 7 or 9 layer islands. Additional measurements of the area indicate that the total area of all the islands was reduced by 10%, but the total volume increased by ~40%, presumably coming from the wetting layer. Measurements of island area and height over time indicated that an increase in height was accompanied by a sudden (within 2-3 minutes) increase in volume and decrease in area. Some islands grew by adding a ring of higher height around the edge before filling in the center. These rings, on average, would fill in less than 5

minutes. Generally, the islands started in a random shape, and gradually became more like a regular hexagon over time. These observations are very unusual because they do not fit the classical expectations based on Ostwald ripening and they show the role of Quantum Size Effects upon the coarsening.

Introduction

One of the major goals of surface science has been the creation of self-assembled nanostructures of a controlled height, size, and shape. Many patterns have already been discovered in the formation of these nanostructures. The ability to control these nanostructures would be of great importance, both in practical applications such as computer miniaturization, and in basic understanding of how nature functions at the scale of 10^{-9} meters.

The particular goal of this experiment whether Pb on Si(111) 7 X 7 followed classical Ostwald Ripening. In Ostwald Ripening, atoms transfer from islands smaller than a certain radius to those larger than that radius so as to minimize the Gibbs free energy of formation [1:390]. This causes a coarsening process which results in fewer islands of a larger size, which continuously change volume while the total volume of all the islands remains constant [2:129]. Pb on Si(111) 7 X 7 has shown several unusual behaviors in the past which are not explainable by Ostwald Ripening, particularly its Quantum Size Effects (QSE)[3:406105] [4:10602] and ring growth[5:256101].

Some of the specific questions investigated during this experiment were: how did the height of the islands change over time? How did their size, volume and shape change over time? How did these change when the islands changed height? What were the sizes and durations of the rings that often accompanied a change in height? What was the growth mechanism causing the islands to grow?

Materials and Methods

A Si(111) 7 X 7 crystal was prepared atomically clean at a pressure of 2 x 10-11 torr followed by Pb deposition at a flux of (0.05 ML/minute) and a temperature of 242 K. Images of the resulting Pb islands were taken with a Scanning Tunneling Microscope (STM) using a constant voltage of 1.5V and a current of 1 nA over an area of 500 x 500 nm^2 as they evolved in time. Commercial imaging software (Scala 4.2 and Scion Image 4.03) was then used to take measurements of the islands on the resulting images.

Results and Discussion

Figure 1(a) shows the average volume for an individual island in each image. The large increase shows that some sort of coarsening process is going on. Figure 1(b) shows that the number of islands is decreasing, from 33 islands at time 0 to only 24 at after 68 minutes, which is further indication of a coarsening process. This coarsening can be easily seen in the differences between figures 1(c) and 1(d). Both have an area of taken with size 500 x 500 nm, a temperature of 242 K, and a voltage of 1.5 V. 1(c) was taken just after Pb deposition, but 1(d) was the last image taken, 68 minutes after the acquisition of 1(c). It is apparent in these images that the number of islands had dropped, while their height had grown. The islands with the smallest volumes had decayed completely. This is consistent with the coarsening process that occurs during Ostwald Ripening.

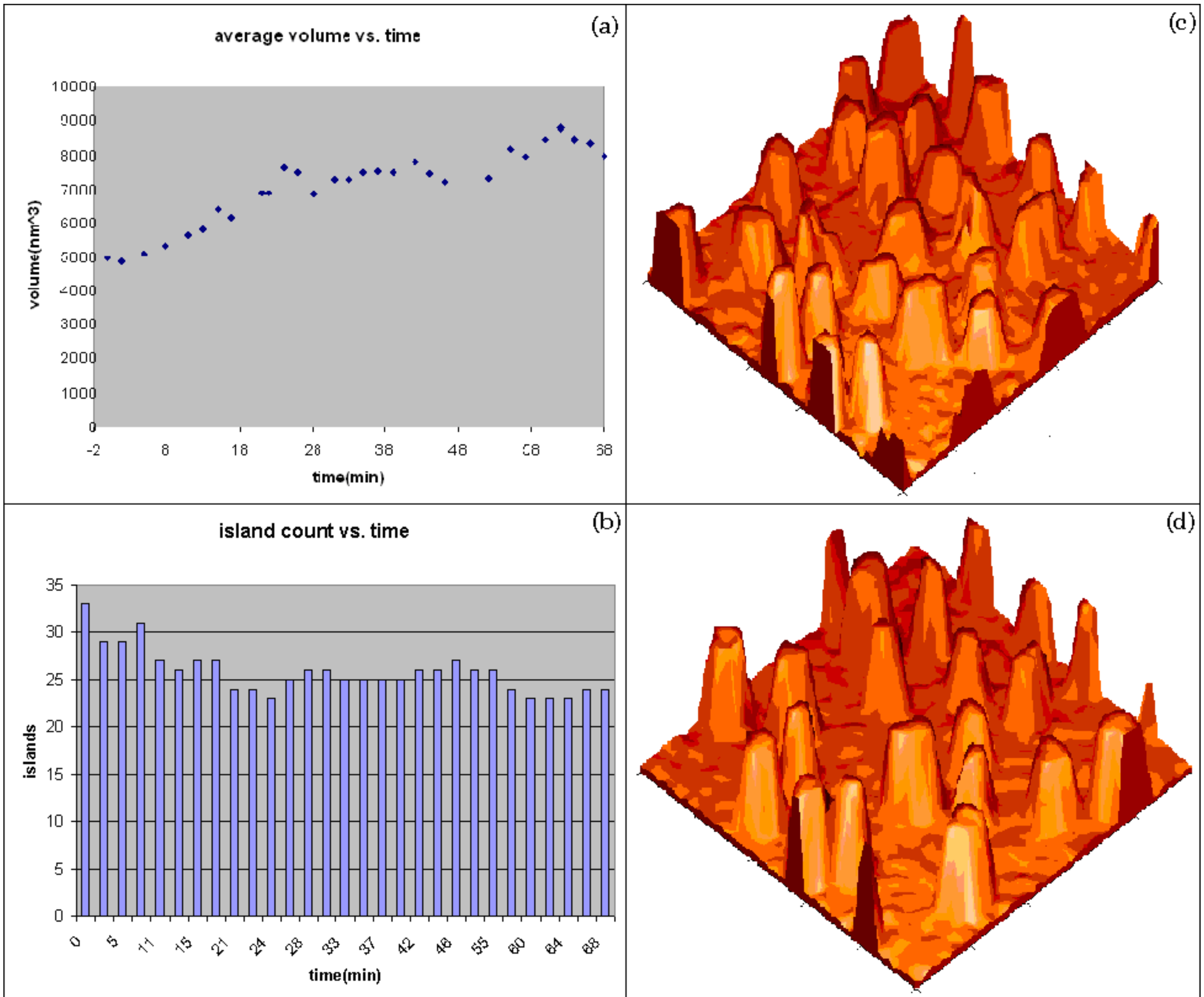

Figure 1: evidence of coarsening

Figure 2 shows the total volume to be increasing. In Ostwald Ripening, however, overall volume is conserved. This indicates that there is a transfer of atoms from the wetting layer to the islands throughout the experiment. Another important difference is that, in Ostwald Ripening, islands continuously shrink or grow depending on their size and the size of their neighboring islands [3:405], which is not the case here. Islands grow suddenly in volume when they grow in height, but before or after the sudden increase their volume changes very little. This increase in volume is also typically accompanied by a decrease in area.

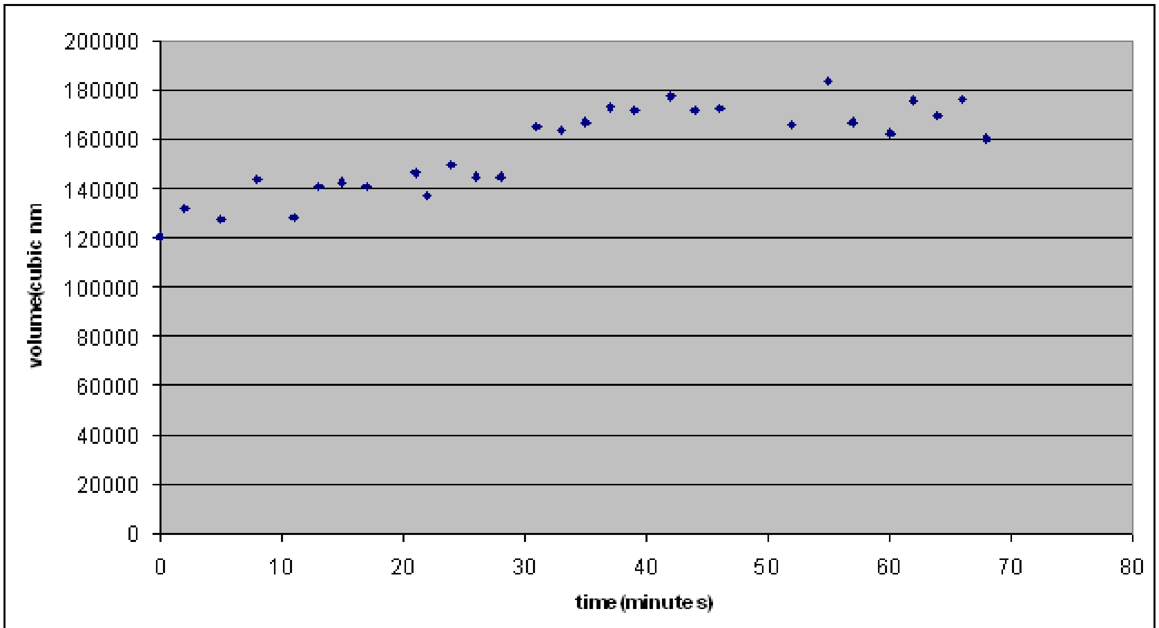

Figure 2: Total Island Volume vs. Time

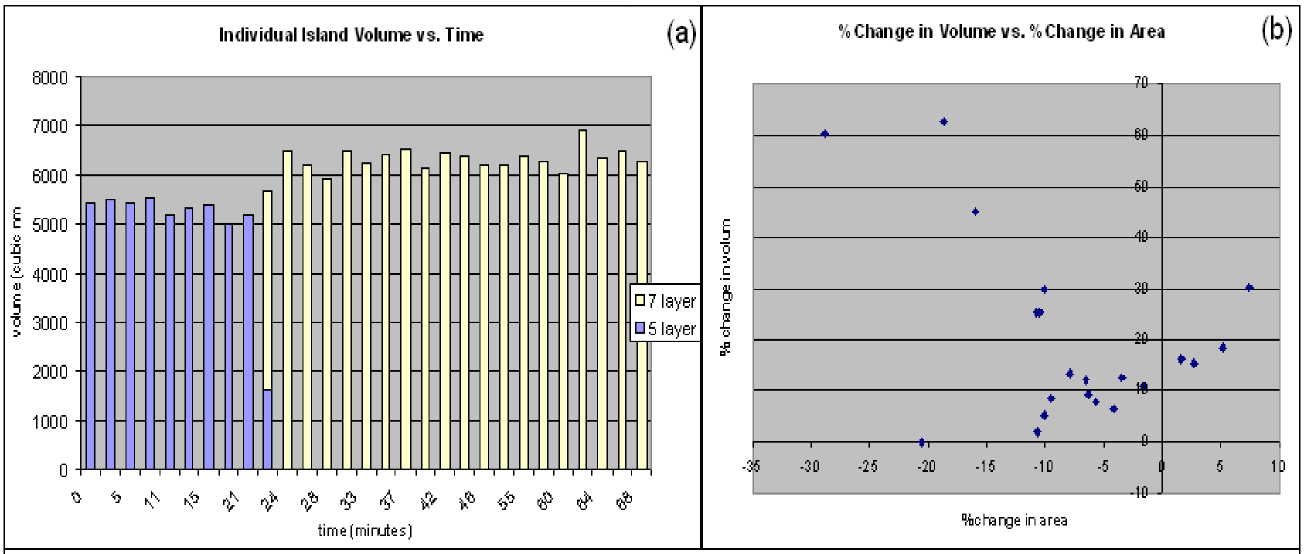

Figure 3: Growth Effects

Figures 3(a) and 3(b) show this behavior. 3(a) shows the volume of one typical island over time: the blue represents the volume of the island when it is 5 layers tall, and the yellow represents the volume of the island when it is 7 layers tall. At 23 minutes it grew a ring, so some of it was 5 layers tall and some of it was 7 layers tall. There is a ~20% increase in volume from time 21 to 24, but before and after the increase the volume remained constant. 3(b) shows the percentage change in volume and in area from every time that an island grew in height. 14 of the 17 changes in height were accompanied by a decrease in area. All increases in height led to an increase in volume.

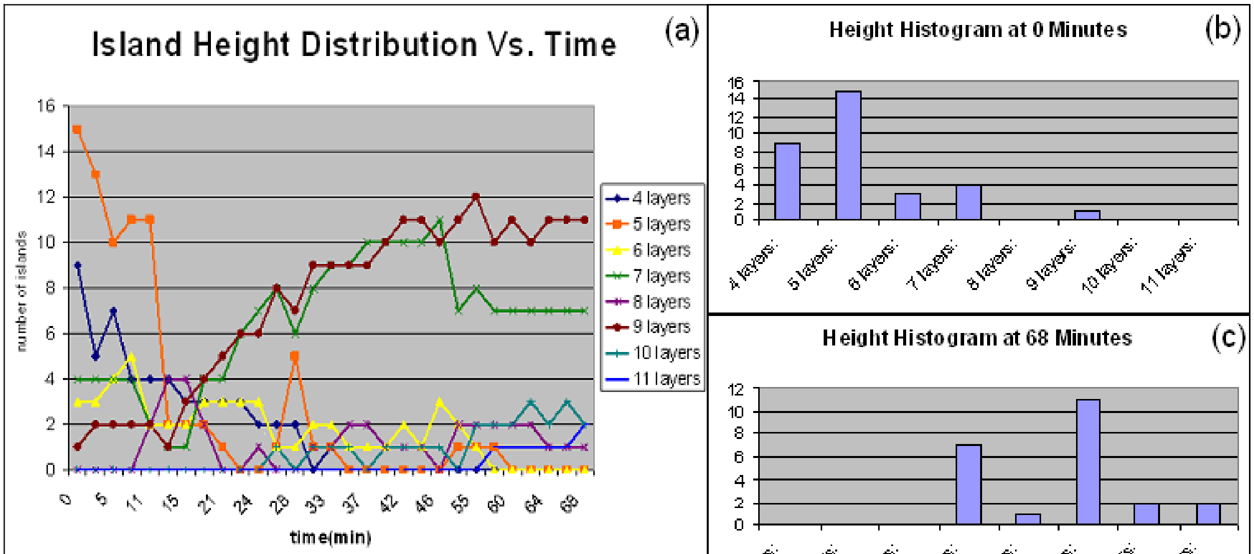

Figure 4: Quantum Size Effects

Figure 4(a) shows the height of the islands as they evolved in time. Initially, 24 of the 33 islands were either 4 or 5 layers tall. After 68 minutes, 18 of the 24 visible islands were 7 or 9 layers tall, and none of the islands were 4 or 5 layers tall. Figures 4(b) and 4(c) show this difference in the distribution of island heights between the first and last images taken. This is clear evidence of QSE, because it shows that 7- and 9-layer heights are the most stable [3:106105-3]. QSE are the result of the fact that the islands are metallic. Since the islands are metallic, some electrons move freely throughout the atoms in an island. These electrons are quantized in to certain energy levels, each of which corresponds to a different wavelength, and these wavelengths correspond to the preferred island heights. It should be noted that some of the small spikes in this graph are the result of islands which moved on or off the imaged area because of the drift of the instrument (an unavoidable problem with the STM especially for experiments that take long times).

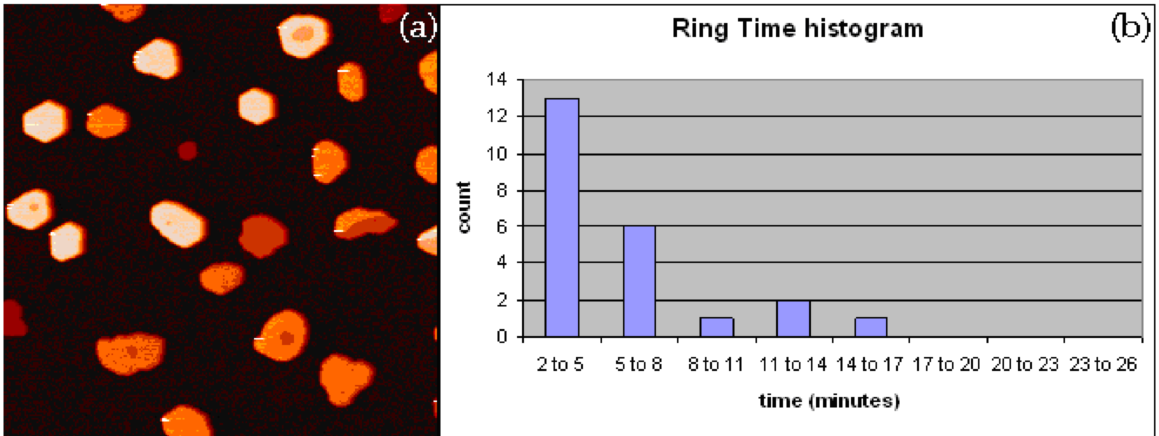

Figure 5: Rings

Figure 5(a) shows an STM image with numerous rings. The size is 500 x 500 nm, the temperature is 242 K, and the voltage is 1.5 V. These islands, instead of being atomically flat on top, have a section at least one level higher than the rest of the island. One of the rings in this image is still incomplete, because it simply divides the island in half instead of stretching around the edge the way complete rings do. Figure 5(b) shows a histogram of how long an island maintained a ring before becoming flat again. These rings appear to be unstable, and fill in to produce the next stable layer. 10 of the 20 rings lasted less than 5 minutes, and it is possible that many more lasted less than two minutes, but were not detected due to the 2 minute gap between images. The temperature of 242K is high for this sort of experiment, and lowering this temperature would lead to longer lasting rings.

Discussion and Conclusion

These results provide some insight in to the behavior of Pb on a Si(111) 7 X 7 crystal, but much is still unknown about its behavior. It is clear that QSE play a strong role in its coarsening process, due to the very strong preference for heights of 7- and 9-layers. It also seems clear that the coarsening process is not classical Ostwald Ripening. Although the growth in average island volume and the decay of the islands with the smallest volume shows that a similar coarsening process is going on, the increase in total volume and the stepwise growth in island volume are clearly a different process than classical Ostwald Ripening. The question of what causes these differences remains: it could be the result of QSE, or it could be a different process entirely.

One of the most unusual characteristics of Pb/Si(111) is its ring growth. The rings in this experiment were frequently associated with an increase in height, suggesting that whatever process is causing the coarsening of these islands is also causing their ring growth. The instability of these rings implies that they might be even more frequent than what was observed here. Any ring which lasted less than 2 minutes might not have been observed (due to the gap between images) - it is possible that any increase in height began with a ring.

The main question which remains to be answered is how the islands grow in height. The results of this experiment seem to indicate that there is a transfer of atoms from the wetting layer to the islands. This could be accomplished either by adding atoms from the wetting layer which push the atoms in the island higher, or by adding atoms from the wetting layer directly to the top of the island after diffusing on the facet planes. These two processes would be indistinguishable in this experiment, so further work must be done to establish the process by which the islands are growing in height. Understanding this process is crucial to understanding the overall coarsening process.

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