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Ext. Abstract

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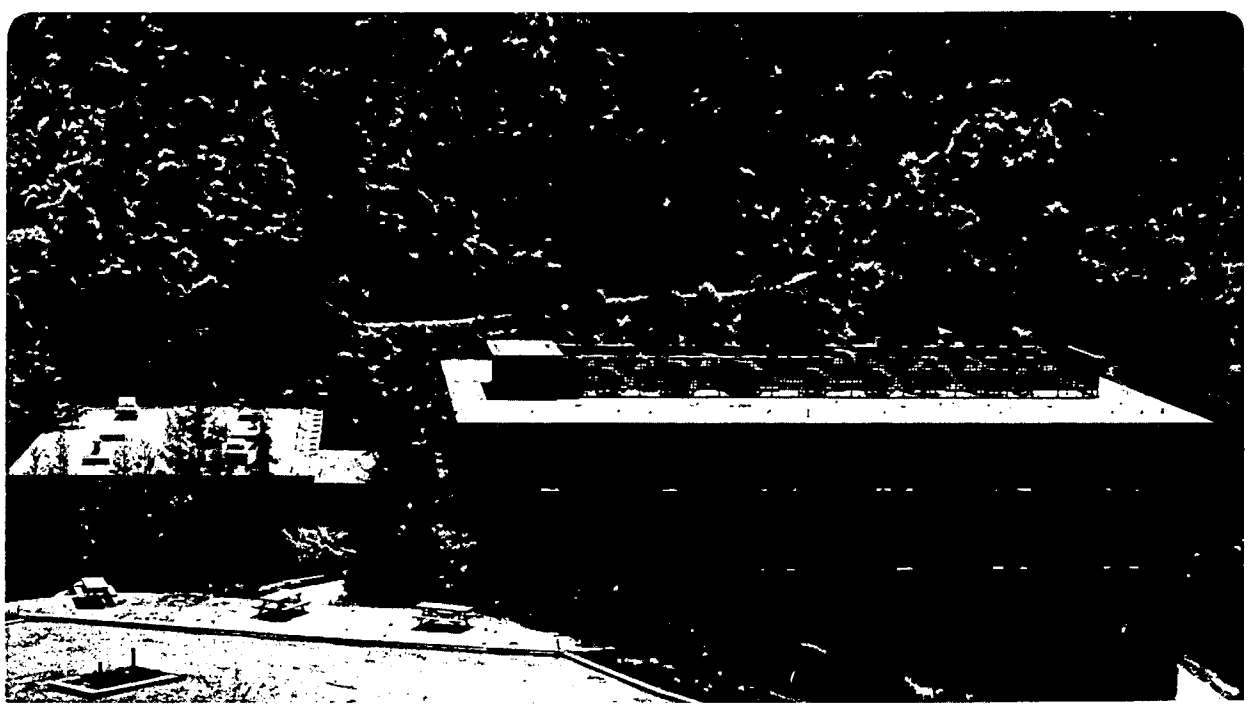

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IN-SITU SCANNING TUNNELING MICROSCOPY OF MULTILAYER Pb ELECTRODEPOSITS ON Ag

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SHORT ABSTRACT

The multilayer electrodeposition of Pb on polycrystalline Ag was studied using *in-situ* Scanning Tunneling Microscopy. Calculations of Amplitude Density and Autocorrelation functions are shown to be useful for quantitative analysis of STM images. Bulk Pb film growth is shown to occur via a series of roughening and smoothing stages. The sequence of events is interpreted in terms of repeated nucleation and growth at recessed regions of the surface.

Scanning Tunneling Microscopy allows the topographical investigation of metal surfaces with atomic resolution. The use of the instrument for *in-situ* studies on electrodes under potential control has been demonstrated before [1]. In this study, a commercially available STM (Digital Instruments, Inc. Nanoscope I) with a 0.6 μm scanner was interfaced with an AST personal computer. Both a digital to analog (x/y position control) and analog to digital (z height data) converter were employed. A 320x200 point array was used to store the data. Epoxy insulated etched platinum-iridium tunneling tips were used (Longreach Scientific Resources, Orr's Island, Maine 04066). Smooth silver surfaces (RMS roughness about 50 A^{O}) were prepared by vapor deposition of silver on a glass substrates. A platinum counter electrode and a Ag/AgCl reference electrode were connected to the working cell via TFE tubing. A solution of 5 mM lead acetate, 1M sodium acetate was used.

The cyclic voltammograms of the deposition and stripping of Pb on Ag taken in the STM cell were consistent with those reported in the literature. Formation of a Pb UPD was observed around 150 mV anodic of bulk lead deposition. Figure 1 shows some 3D line images (data acquisition time about 100 seconds/scan) taken during a 1 mV/sec cathodic potential sweep starting at -250 mV. The sweep was halted at the onset of bulk Pb deposition (around -650 mV), and the potential was maintained at this value while more scans were taken. The voltage between the working electrode and the tunneling tip was set to 300 mV. The set point for the tunneling current was 3.0 nA. The initial surface (not shown) is smooth, with roughnesses of long wavelength (1000 A^{O}) and low amplitude (100 A^{O}). Near the potential of underpotential Pb deposition, no obvious changes in the surface topography are evident in the line images. This lack of observed change is due to the relatively large roughness of the original surface and the relatively low resolutions (about 2.0 A^{O}) at which these images were taken. Once bulk deposition begins, a large number of small (50-100 A^{O}) growth center are seen to form near the rougher portions of the substrate (Figure 1A). These centers grow, reducing the short range roughness of the surface (Figure 1B). Later, longer range (about 500 A^{O}) waviness of the surface becomes evident (Figure 1C), and the amplitude and wavelength of the surface roughness continues to change. Preferential growth near the recesses of the surface is observed (cf. Figure 2C and 2D), and the surface undergoes a number of roughening and smoothing cycles.

Figure 2 compares the amplitude density functions (ADF) of the images shown in figure 1. The ADF of the initial substrate surface has a relatively sharp Gaussian peak, with some tailing off at positive heights indicating some 50-100 A^{O} protrusions (Figure 2A). The shape and the average relative height of the ADF changes as bulk Pb deposition occurs. A broadening and the development of peaks at negative relative heights of the ADF curve shows that the surface has roughened at the earliest stages of nucleation. 3-D

growth occurs preferentially on the rough portions (recesses) of the surface, leaving the smoother regions of the surface free of nuclei. This phenomenon causes the ADF curve to become bimodal (Figure 2B). The peak located on the negative side is associated with the original surface where litte growth has occurred. The second, broader peak is associated with the growth of Pb from the nucleation centers. If we assume that the nuclei grow approximately as hemispheres, recesses in the surface will form as the nuclei overlap. The recesses may then act as centers for renucleation, causing a reduction in surface roughness and removing the ADF curves fine structure (figure 2C). As one continues to deposit Pb, the ADF curves broadens, but preferential growth in regions between surface features continues on a larger scale (figures 2D and 2E).

Figure 3 compares the autocorrelation function (ACF) of the images show in figures 1. These ACF data are also consistent with the renucleation model indicated by the ADF data. The RMS roughness (ie., the square root of the zero lag distance ACF) and the correlation distance decrease during Pb renucleation (figureS 3A and 3B). If renucleation and growth occur preferentially in recesses on the surface as deposition continues, the distance over which the height is correlated should decrease, because the new nuclei cover the recessed portion of the previous nuclei, and the apparent size (as measured from the surface) of the older nuclei will decrease. A reduction of the RMS roughness is therefore expected from a deposition in the recesses. A similar process occurs on a larger scale during later stages of growth (Figure 3B).

ACKNOWLEDGMENTS

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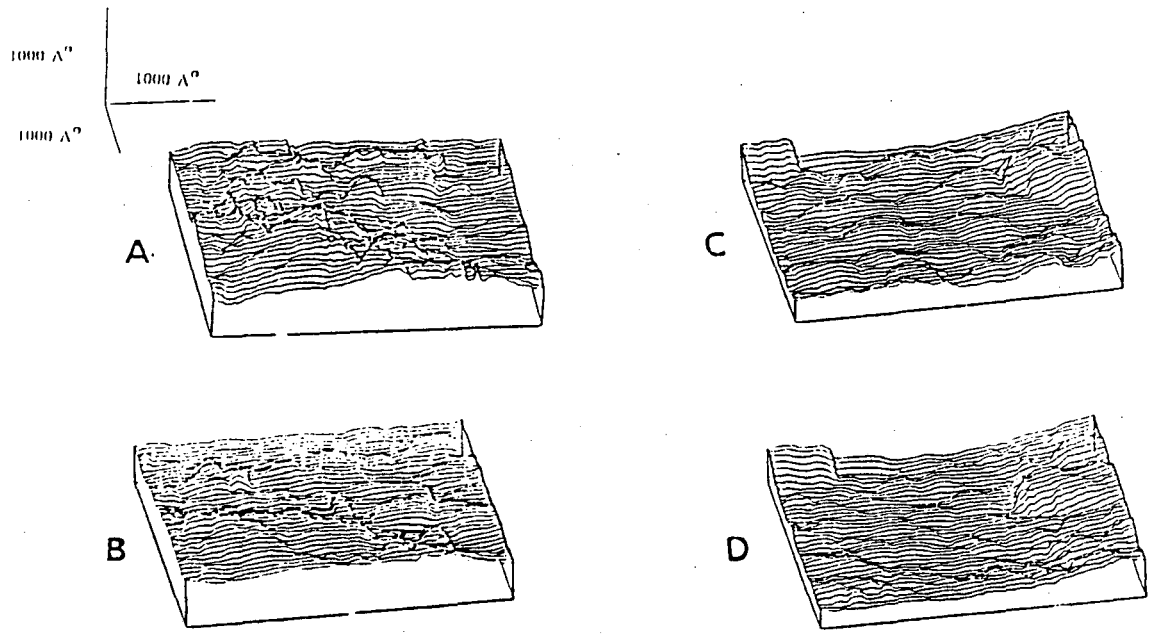

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FIGURE 1-- In-situ STM line image of the electrodeposition of Pb on Ag while the potential is held at -650 mV vs. Ag/AgCl for various deposition times. A) 100 seconds. B) 300 seconds. C) 1000 seconds. D) 1200 seconds.

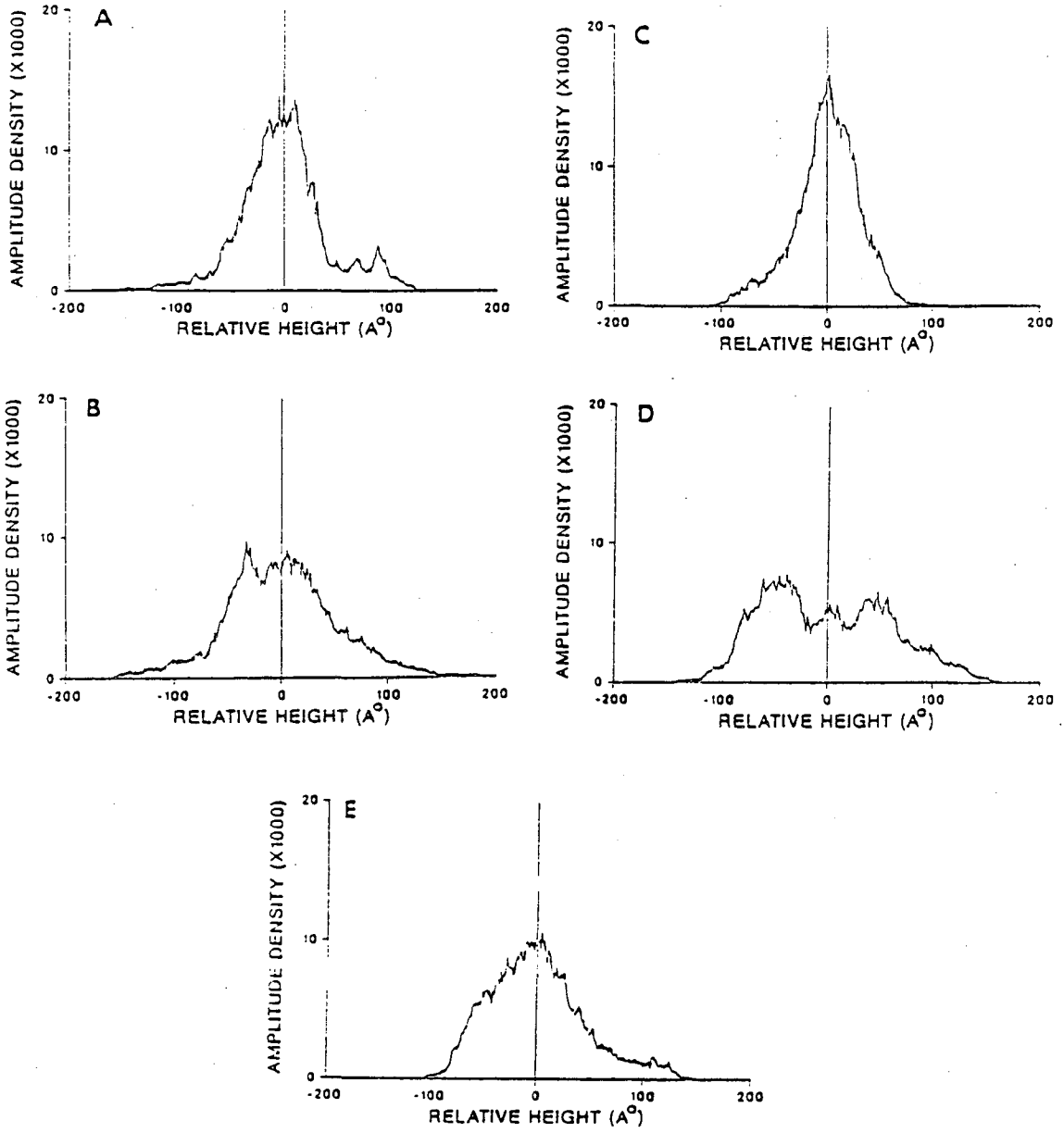

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FIGURE 2-- Amplitude density function for various times during the deposition of Pb on Ag at -650 mV vs. Ag/AgCl. A) Substrate B) 100 seconds C) 300 seconds D) 1000 seconds E) 1200 seconds.

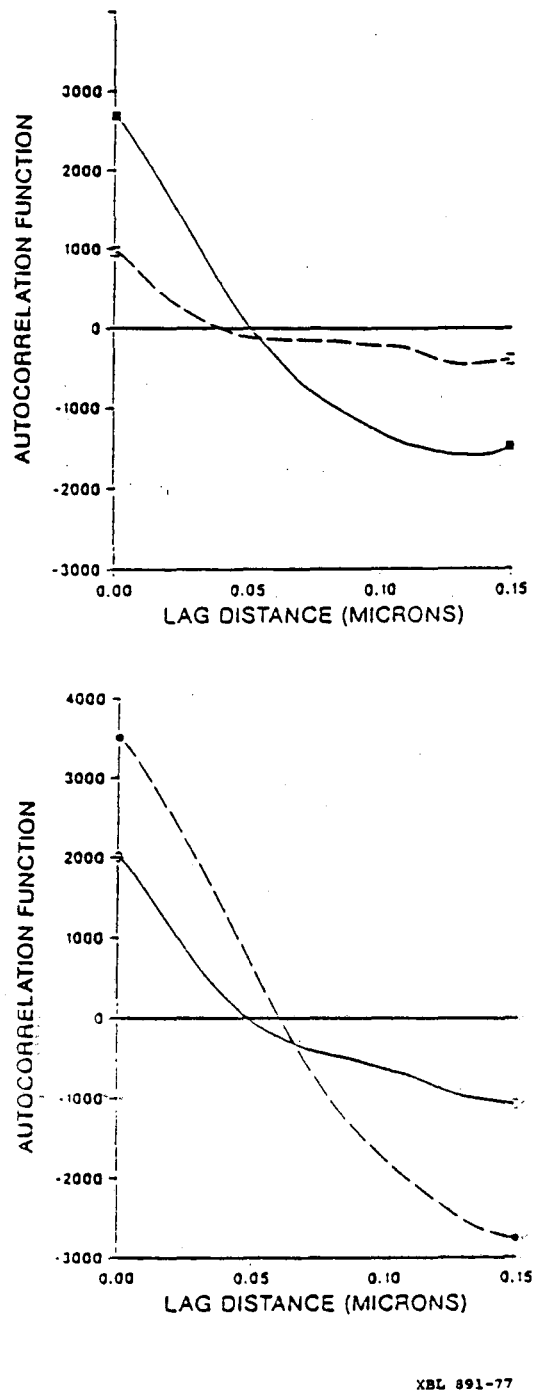

FIGURE 3– Autocorrelation function for various times during the deposition of Pb on Ag at -650 mV vs. Ag/AgCl. A) ■ 100 seconds; □ 300 seconds; B) • 1000 seconds; ○ 1200 seconds;

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