Understanding the thermal annealing process on metallic thin films

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Abstract. Thermal annealing is an unusual process used for intrinsic stress liberation, structural improving, and surface roughness control in materials. In a qualitative way, annealing modifies the surface morphology of materials with temperature and time. In this work, a methodology to explain the surface modification of thin films when they are submitted to an annealing process is discussed. Two thermally evaporated Au films with 200 nm-thicknesses were post-annealed in a vacuum chamber at 100 °C with an argon atmosphere, and annealing times from 0 to 1000 minutes. Each Au film grown at different rate deposition was cyclical annealed and imaged under different annealing times. Data obtained from high quality AFM images after different annealing times of Au samples were used to calculate surface parameters such as roughness, grain size, and slope at the border, also the respective exponents as a function of the annealing time. The experimental results allow understanding the temporal evolution of the annealing process, as a rearrangement of the surface protrusions.

1. Introduction

Different analytical models based on intrinsic stresses and relaxation processes have been proposed to explain the surface evolution during the growth of metallic thin films [1]. Nevertheless, the occurring phenomena during thermal annealing have not been completely understood. Early studies explain that, during thermal annealing of Au thin films, plastic and elastic effects produce the partial collapse of the boundary network of surface protrusions (SPs), promotes relaxation processes driven by surface diffusion, diffusion into grain boundaries, and bulk diffusion [2].

In a previous work on Au(111) films [3] studied by atomic force microscopy and x-ray diffraction, authors explain the surface evolution by means of a continuum model that combines different mechanisms of stress (grain zipping and shear stress) and their correspondent mechanisms of relaxation (gap filling and grain rotation) with the interactions occurring between surface grains or surface protrusions. In those studies, different Au films samples were used for each annealing process.

In this work we proposed a quantification of the annealing phenomena by means of a statistical analysis of the temporal evolution of the surface parameters such as the lateral size, the slope at the border, and the surface roughness of the surface protrusions estimated from high-resolution AFM images. The same Au film sample was thermally annealed and imaged after each annealing process.
2. Experimental process and image analysis

In this section, the process to obtain the annealed Au thin films and the image analysis are detailed. This section is divided in four sub-sections. First, the films preparation is explained. Secondly, the methodology to calculate the slope distributions from AFM images is described. Thirdly, the methodology to obtain the grain size is discussed; and finally, the relations to estimate the rms-roughness values from surfaces are highlighted.

2.1. Thin film preparation

Two Au thin films (A and B) were deposited by thermal evaporation on Si substrates heated at \( \approx 85 \) °C. During evaporation the substrate heats by radiation reaching an oscillating temperature between 80 and 95 °C. For this reason, the initial condition (as-grown) of samples A and B slightly differs between them. Otherwise, A and B samples were deposited separately under similar conditions. The pressure chamber during growth was \( 10^{-7} \) mbar. Au (99.999% purity) on Si Ox/Si (111) substrates was deposited. The p-type Si substrates have an electrical resistivity of 0.025 \( \Omega \)-cm. The films were deposited at a growth rate of \( \approx 1 \) nm/s, and a thickness of 200 nm. Au films were annealed in a vacuum oven with Argon atmosphere. The annealing temperature for all samples was 100 °C but annealing time ranged from 0 (as-deposited) to 1000 minutes. In this work, the annealing process was applied on the same sample for different annealing times. After each annealing time, a high resolution and a high quality atomic force microscopy image was taken. All AFM images were obtained into the same zone of the film. This process is repeated after each annealing time (accumulated annealing time), which produces a cyclic thermal annealing on the Au thin film. For obtaining the surface images, an atomic force microscope (AFM) was used in tapping mode. The AFM images were obtained with 512 x 512 pixels of resolution by using high aspect ratio tips with radius of 2 nm. Each AFM image was 2 x 2 \( \mu \text{m}^2 \) size.

2.2. Slope distributions

To obtain the slope distributions from the AFM images, a mathematical procedure consisting in a Lagrangian interpolation on the AFM image data matrix of the local heights and their conversion in a continuous function \( (r, \rho) \) (with \( \rho \) as vector position) was done. The local slopes \( m(\rho) \) can be obtained by means of the equation:

\[
m(\rho) = \tan \left( \cos^{-1} \left( \frac{\rho \cdot \hat{k}}{||\rho||} \right) \right)
\]

Where \( \hat{n} \) is the normal vector to surface \( \vec{n} = (n_x, n_y, n_z) \propto \left[ -\nabla_x h(\vec{r}), -\nabla_y h(\vec{r}), 1 \right] \) and \( \hat{k} = (0, 0, 1) \) the upward unit vector [4]. With these calculations the matrix of slopes and their slope distributions \( N(m) \) were obtained, being the maximum peak, the slope mean value.

2.3. Grain size of surface protrusions (SP).

In order to calculate the mean grain size \( \lambda \) (or lateral size) of the film surface, contour maps were obtained from the AFM images. Contour maps were obtained by means of the identification of the local minimum and saddle points of the \( h(\vec{r}) \) values. These last points are located into the periphery that delimits and surrounds the grains (grain boundaries). The grain size distributions were obtained by measuring the distances between intersections of the contour points in the x-y plane and assigning the maximum distance value to the SP lateral size. The maximum value in these distributions represents the mean grain size.

2.4. Rms-roughness values
The rms-roughness value $w$ is the standard deviation or the fluctuations of the local heights of the AFM image. The expression to calculate $w$ form AFM image data is given by:

$$w = \frac{1}{L} \sqrt{\sum_{LxL} \left( h(\vec{r}) - \langle h(\vec{r}) \rangle \right)^2}$$  \hspace{1cm} (2)

Where $\langle h(\vec{r}) \rangle$ is the mean height, and $L$ is the window size of AFM image.

3. Results and Discussions

Figure 1 shows AFM images of the surface of the sample B annealed at different times. The images correspond to as-grown, 2, 20, 50, 200 and 1000 minutes of thermal annealing. Insets in figure 1 are the corresponding contour maps as obtained by the described process. In a similar way than the scaling laws proposed for the growing processes; as far as we know, we proposed for the first time, similar scaling laws of some involved parameters with time $t$, but for the annealing process. Figure 2 shows the behavior expressed as a power law, $w \propto t^\gamma$, of the surface roughness as a function of the annealing time for two Au annealed samples. Each point in Figure 2 represents data obtained from the corresponding AFM image. Initial rms-roughness value of the samples depends on the experimental growth conditions (such as the substrate temperature during deposition). The two analyzed samples show a similar behavior with roughness-exponent values $\gamma$ of samples A and B fitted as $\gamma_A = 0.014 \pm 0.013$, and $\gamma_B = 0.015 \pm 0.007$, respectively. The roughness values increase with the annealing time, meaning a vertical growth of the surfaces protrusions during the annealing process.

From figure 3, the grain size of the surfaces protrusions is plotted as a function of the annealing time. Contrarily to figure 2, a decrease of the grain size with the annealing time can be observed. By fitting this behavior as a power law, $\lambda \propto t^\delta$, the grain size-exponent $\delta$ values for samples A and B are estimated as $\delta_A = -0.019 \pm 0.012$, and $\delta_B = -0.020 \pm 0.007$, respectively. In this case, we can affirm that while the surface roughness (vertical size) increases, meanwhile the grain size (lateral size) decreases; that is, the surfaces protrusions grow vertically while their base (grain size) diminishes. Note the similar value of the exponents for both samples. The high dispersion reported for the exponents is understood if we take into account that each AFM image was not obtained on the same site of the sample after each annealing process. Similar dispersion values were reported for the slope in ref. [5] during Au growth.

Figure 1. High-resolution AFM images of Au films (sample B) after different annealing process: a) as-grown, b) 2 min, c) 20 min, d) 50 min, e) 200 min, and f) 1000 min. Each inset is the corresponding contour map.
Figure 4 shows the evolution of the mean slope with the annealing time on the borders of surfaces protrusions. By fitting this behavior with annealing time as a power law, $m \propto t^\varepsilon$, the slope-exponents $\varepsilon$ for samples A and B are estimated as $\varepsilon_A = 0.033 \pm 0.030$, and $\varepsilon_B = 0.027 \pm 0.010$, respectively. In good agreement with the roughness plot, the mean slope value increases with the annealing time as a result of the vertical growth of surface protrusions. In a complimentary way, Figures 5 and 6 show comparative plots between roughness and mean slope, as well as grain size and mean slope, respectively, as a function of the annealing time for sample A. From figure 5, it can be observed that roughness and mean slope parameters follow a similar behavior, affirming that these parameters have a similar behavior with annealing time. However, in figure 6, a contrarily behavior between the grain size and the mean slope with annealing time are observed. Similar behavior, but with different values were obtained for sample B (figures 7 and 8).

**Figure 2.** Log-log plot of roughness vs. accumulated annealing time. The annealing time ranged from 0 to 1000 min.

**Figure 3.** Behavior of grain size of surfaces protrusions with accumulative annealing time.

**Figure 4.** Mean slope at the borders of surfaces protrusions vs. annealing time.

Figures 7 and 8 show the plot of roughness and slope, and grain size and slope with the accumulated annealing time as obtained for sample B. A similar qualitative behavior of these parameters between sample A and sample B is observed. However, different absolute values of roughness, grain size and
slope are reported for samples A and B, given the different growth conditions between the two gold samples.

Figure 5. Rms-roughness and mean slope vs. annealing time as obtained for sample A. Parameters follow similar behavior.

Figure 6. Grain size and mean slope vs. annealing time for sample A. Parameters show contrarily behavior.

Figure 7. Rms-roughness and mean slope vs. annealing time as obtained for sample B. A similar behavior than sample A can be observed.

Figure 8. Grain size and mean slope vs. annealing time for sample B. A similar behavior than sample A can be observed.

In conclusion, our reported results are in good agreement with the objective of the annealing process: relaxation and intrinsic-stress liberation through surface protrusions reorganization with temperature. Furthermore, surface roughness $\nu$, grain size $\lambda$, and the slope $m$ at the border grain parameters were quantified as a function of the annealing time from the analysis of the high quality AFM images taken on surface film after each annealing process. Scaling law exponents for each parameter were reported. Our results are in good agreement with reported works but for different materials. For example, from AFM images of FePt epitaxial thin films [6], authors report that the grain size reduces, meanwhile the magnetic properties improves when the films are annealed at 550 °C. In other work [7], the grain size decreases when L1$_0$ phase of FePt thin films deposited on oxidized Si (100) substrates are thermally annealed at 700 °C, at different heating rates (between 20 and 100 °C/s). In a recent work [8], a model to explain the surface morphology evolution by means of surface parameters as studied in this work, but using different films for each annealing process, was proposed.
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