Microstructure of Au Film Prepared by Magnetron Sputtering Deposition *

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We study the formation of microstructure of gold films that generally undergo three processes: nucleation and nuclear growth, normal grain growth, and abnormal grain growth. Here the grains grow as a column in the normal grain growth process. When the grain size becomes larger than and comparable to the film thickness, the grains with favourable orientation will grow at the expense of the grains with unfavourable orientation, leading to abnormal grain growth. The abnormal grains grow along the favoured orientation (111), which has been certified by x-ray diffraction spectroscopy. Finally, the processes of the normal and abnormal grain growth are fitted using the Lifshitz–Slyozov–Wanger theory.

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Au films have exhibited extensive applications in many fields, such near-field optical strengthen effect, and surface plasmon resonance (SPR).[1] In most previous studies, Au films were semicontinuous and in highly disordered states. Until now, there have been no reports on the characteristics of the sequential ordered microcrystalline films. That is because the grain growth of the Au films cannot be technically controlled yet. Therefore, it is significant to develop simulations and experiments on the processes of grain growth and orientation evolution.

In this Letter, grain characteristics of Au films in different processes are discussed according to experimental results. Using an atomic force microscope (AFM) we observed the surface phenomena of the thin films and the grain size distribution. The orientation of the grains was certified by x-ray diffraction (XRD) spectroscopy, and its correlation to the grain size is also discussed.

A series of Au films were deposited onto clean glass substrates at temperature 200°C by dc magnetron sputtering. The Au target purity was 5 N and the sputtering power was 0.26 kV × 25 mA. The thicknesses of the films were 3 nm, 6 nm, 12 nm, and 24 nm, respectively. The base pressure was 10^{-3} Pa, and the Ar gas pressure during the deposition was 3.0 Pa.

The surface morphology of the Au films was observed using the AFM and the texture was detected by XRD. The favoured orientation of the films was discussed according to the relative density of (111), (200), (220), (311) peaks in the XRD patterns. The grain size has also been calculated using Scherer's formula.

Figure 1 shows the AFM micrographs of the as-deposited films with different thicknesses. The Au films have become continuous as reaching the thickness of 6 nm [see Fig. 1(a)] and the morphology of Au films at this stage is similar to that of diamond-like carbon (DLC) films also deposited by the magnetron sputtering method.[2] Grains have already impinged upon each other and grown as a column. Some large grains grew much higher than the small ones. The columnar holes can be observed in some areas, where some grains have much lower growth velocity. It can be predicted that the average grain size in the plane of the film is smaller than that perpendicular to the plane of the films, indicating that the area of the free top surface is smaller than that of the boundary interface.[3]

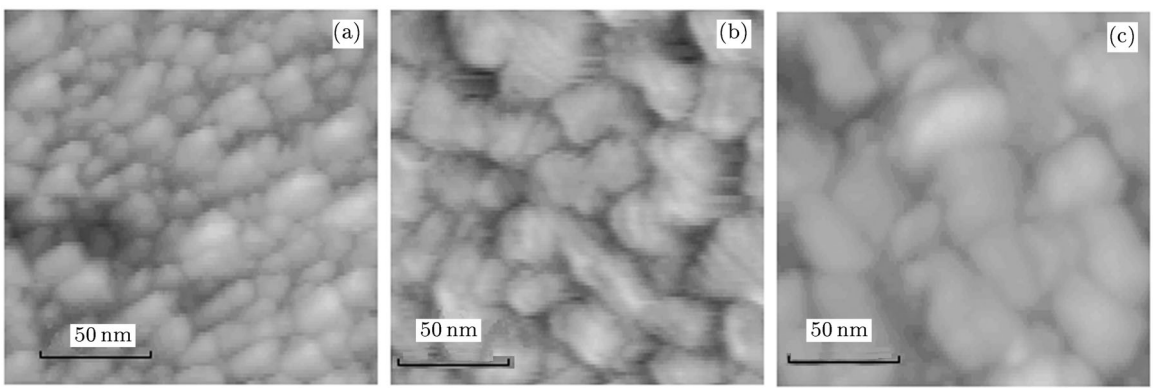


Fig. 1. AFM images of Au films deposited on 200°C substrates at different thicknesses: (a) 6 nm, (b) 12 nm, (c) 24 nm.

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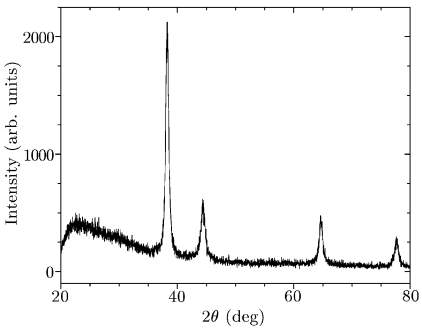


Fig. 2. XRD pattern of the Au film.

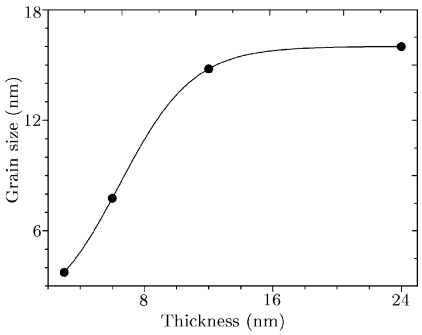


Fig. 3. Grain size as a function of thickness of the Au films deposited on a 200°C substrate.

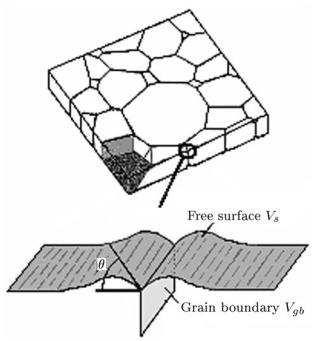


Fig. 4. Geometry of a stagnation in the normal grain growth.

As the film thickness reaches 12 nm, the grain matrix becomes more compact. The surface of the films becomes more planar, and the average grain size is much greater, as shown in Fig. 1(b). The grooves have developed along the lines where the grain boundaries meet the free surface, though a few boundaries are not very clear. It can be predicted that the two grains with this unclear boundary will subsequently combine into a bigger one.[3] The average grain size increases with the thickness. Although a few grains are bigger than the others, an obvious disparity in size cannot be found. The shape of free surface of the grains is a polygon, also shown in Fig. 1(b).

Figure 1(c) shows the microstructure of the sample films with the thickness of 24 nm, the surface of which becomes coarser. It is observed in the AFM that the higher grains are much larger in size. The size distribution becomes more disparity. Blurry groove lines could be found on some big grains, this could be ascribed to the combination of several small grains. Such a phenomenon has also been observed on Cu films,[4] which is known as abnormal grain growth.

The grain texture was detected by an XRD spectroscope. Figure 2 shows the (111) advantage orientation growth, while some disadvantages of the (200), (220), (311) peaks can also be observed. The average grain size has been calculated using Scherer's formula.

The relation between the grain size and the film thickness was fitted by the Boltzmann function. The increase rate of grain size versus thickness slows down (see Fig. 3) as the size approaches to a steady value of 16 nm. This is similar to the behaviour of Cr films.[5]

The grain growth can be treated by the particle growth theory, which was developed by Lifshitz and Slyozov[6] and by Wanger[7] (often referred to as the LSW theory). Hillert[8] developed the normal and abnormal grain growth theory. Some extensive studies and computer simulation, such as Thompson,[9] considering the energy associated with the two free surface of the film, established a detail theory deducting the grain growth process by using the treatment of Hillert.

Film evolution can be separated into three processes: nucleation and nuclear growth, normal grain growth and abnormal grain growth.

The formation of the film microstructure is determined by the nucleation conditions and growth conditions (see Ref. [10]). As grains impinge upon each other, the boundaries formed and column-growing mode initially starts at the film thickness of 5 nm according to our experiment. Most columnar grains grow to be much longer than their diameter. When the film thickens and the columns grow, there may be an increase of the average column diameter, although a few columns grow wider.

The normal grain growth will stagnate when the average grain size is comparable with the film thickness, which is known as the specimen thickness effect.[11] At this point, the grains of the Au film are columnar and their boundaries will completely traverse the thickness of the film. Mullins[12] suggested that the stagnation of the normal grain growth was caused by the grooves where film boundaries meet the free surface. The tension equilibrium should be achieved in the groove:

$$\theta = \arcsin\left(\frac{\gamma_{gb}}{2\gamma_s}\right) \approx \frac{\gamma_{gb}}{\gamma_s}, \tag{1}$$

where θ is the angle between the grain boundary and the normal line of the substrate, γ_{gb} and the γ_s are grain boundary surface energy and the free surface energy, respectively. The AFM micrograph of stagnation in the Au films is shown in Fig. 1(b), in which the grooves on the film surface are clear, and the grain boundaries deviate from the perpendicular in the triple lines. The stagnation mode made by Mullins is shown in Fig. 4.

Figure 1(c) shows the subsequent process of the abnormal grain growth. In metal films, the driving force for the boundaries migration is provided by the differences between the surface energies for grains with different crystallographic orientations. The grains that have lower surface energy can grow to be very large by consuming the grains with higher surface energy.

Hillert[8] has given the growth velocity function of

a grain:

$$\frac{dr}{dt} \cong \frac{M\gamma_{gb}}{2}\Big(\frac{1}{r^*} - \frac{1}{r}\Big), \qquad (2)$$

where r^* is the critical radius, i.e. the radius of a grain that neither grows nor shrinks, and M is a mobility. Considering of the effect of free surface energy further, the ratio of the large grain to the average grain size as a function of time t was given by Thompson:[9]

$$\frac{d}{dt}\Big(\frac{r}{r^*}\Big) = \frac{\gamma_{gb}M}{r^{*2}}\Big(\beta - \frac{2r^*}{r} - \frac{R}{2r^*} + \frac{2\Delta\gamma r^*}{\gamma_{gb}h}\Big). \qquad (3)$$

Since in thin film $r^* \approx h$, the last term in Eq. (3) can lead to faster relative growth of the abnormal grain if $\Delta\gamma$ is large, indicating that grains with lower surface energy grow at a higher velocity than the average one, leading to the abnormal grain growth.

From Eq. (2), the grains whose radius is smaller than the critical radius have the negative growth rate, while abnormal grains reach the comparative higher positive growth rate. A bimodal distribution of grain sizes can then be observed in the abnormal growth process. Although the average grain size increases continuously, the abnormal grains have the higher growth rate primarily by annihilating normal grains around. This kind of growth will be kept until all the abnormal grain boundaries contact each other, where all the normal grains have been annihilated and the grain size distribution returns to monomodal.

It is found from Boltzmann fit graph (Fig. 4) that when the films reach a comparatively thickness, the average grain size will ultimately approach a steady value (about 16 nm), indicating that the growth of the bottom grains has ceased upon this thickness. Then new crystals nucleate on the former bottom grains, and the same grain evolution starts again.

As is well known, the grains with the (111) orientation parallel to the films plane should be favoured in *fcc* (face-centered cubic) metal films (such as Al),[13] and the surface energy can reach its minimization on (111) planes.[9] Therefore, the grains in our Au films with the (111) orientation parallel to the films plane should be favoured. According to our XRD result, the ratio of each diffraction peak in the 24-nm-thick gold film sample is $I_{(111)}$: $I_{(200)}$: $I_{(220)}$: $I_{(311)} = 92 : 25 : 13 : 10$. As a comparison, the ratio in gold films with random orientation is $I_{(111)}$: $I_{(200)}$: $I_{(220)}$: $I_{(311)} = 25 : 13 : 8 : 9$. Therefore we can reach the conclusion that the gold film samples have obvious (111) favoured orientation. Previous research of Au films deposited on mica substrates has also shown the (111) favoured orientation.[14]

From the above discussion, the diversity between the surface energy and the interface energy provides a driving force for favoured texture evolvement in the grain growth process, and the surface energy minimization in the favoured orientation can lead to texture evolution. A specific favoured orientation is then formed. Although the driving force has no influence on the evolution of film texture in the normal grain growth process,[15] grains on the favoured orientation in the abnormal grain growth process have more boundary mobility and grow at a rate much higher than the other grains, and grains will become bigger by annihilating the surrounding grains. Consequently, in the abnormal grain growth process, the Au films become obvious in (111) favoured orientation, leading to texture evolution of the film microstructure.

In summary, Au grains will impinge upon each other and grow as a column when the thickness increases to 5 nm. The average grain size then increases continually. The thickness effect will appear when the grain size increases to that of the film thickness. The equilibrium of surface tensions should be achieved at the triple lines where the boundary interfaces meet the free surface, leading to the stagnation of the normal grain growth. The differences between the surface energies of the normal and abnormal grains drive the abnormal grain growth, in which grains with the favoured orientation grow at a higher rate by annihilating the surrounding normal grains. The abnormal grain growth will be kept until all the abnormal grain boundaries meet each other, and then the new grains nucleate on the grown grains. The growth process of new grains is similar to the grown grains. As a result, the average grain size ultimately approaches to a steady value. The XRD graphs show that grains with the (111) orientation is favoured, and the (200), (220), (311) diffraction peaks can also be observed.

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