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Evolution of a preferred orientation of polycrystalline grains in obliquely deposited gold films on an amorphous substrate

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By measuring the azimuthal dependence of the optical second-harmonic response from gold films that are obliquely deposited on fused silica, we study the evolution of the film texture as a function of the film thickness. As the latter increases from 10 to 30 nm, we observe that the symmetry of the optical second-harmonic generation (SHG) changes from having only a mirror plane that coincides with the incidence plane of the deposition to having a three-fold rotation axis in addition to the mirror plane. When combined with the x-ray diffraction measurements, the nonlinear optical measurement shows that (1) the polycrystalline grains in the obliquely deposited gold films are terminated mainly with (111) facet planes; (2) at the film thickness of 30 nm, the terminating facet planes are tilted away from the substrate normal by a few degrees towards the deposition flux and have a preferred in-plane orientation such that one of the [110] axes in the terminating facet plane is perpendicular to the incidence plane of the deposition.

Thin solid films are one of the main material forms in condensed-matter research and in industrial application. Although much attention has been given to atomic-scale mechanisms of the growth and properties of single-crystalline films on well-defined crystalline substrates, most thin films of industrial application are polycrystalline made at high rates of deposition and on substrates that may or may not be single crystalline. Polycrystalline films are inevitable as high throughputs (that call for high rates of deposition) and low costs (that necessitate the use of noncrystalline substrates) are key factors of consideration in addition to the properties of the films. Metal thin films used in magnetic storage and read-head media are examples. Thin solid films used to anchor or control functional molecular overlayers in applications such as flat panel display are other examples.[1]

Though polycrystalline, crystalline grains in thin films may possess certain out-of-plane or even in-plane textures. Vapor-phase depositions often lead to crystalline grains terminated with Miller-index planes that have the minimum surface energy and that are more or less parallel to the substrate surface. Such films are termed to have out-of-plane textures (fiber texture).[2] Out-of-plane textures are desirable as they may provide an easy axis of magnetization along the surface normal for ferromagnetic films.[3,4] For many metals, the terminating Miller-index plane is the close-packed atomic plane. For example, a (111) plane is usually the terminating plane for face-centered-cubic (fcc) metals and a (110) plane is usually for body-centered-cubic (bcc) metals. When the deposition is at an oblique angle or when a thin film is bombarded with ions at an oblique angle during growth, the resultant crystalline grains may also develop a preferred in-plane orientation with respect to the incidence plane of the deposition or bombardment.[4–6] Such films are termed to have both out-of-plane and in-plane textures (sheet texture). In-plane textures can be very desirable as well since they may provide an easy axis of magnetization in the surface plane for magnetic films. They may also cause molecular overlayers to have a preferred orientation with respect to the in-plane texture.[1,7] Recently Gupta and Abbott observed that on an obliquely deposited gold film (on fused silica) covered with an *n*-alkanethiol self-assembled monolayer (SAM), a liquid crystal overlayer consisting of 5′-pentylcyanobiphenyl (5CB) was aligned either along the in-plane direction of the deposition or perpendicular to it, depending on whether the alkane chain of the *n*-alkanethiol has an even or odd number of CH_2 groups.[8] Such an odd-even effect may conceivably be related to an in-plane texture if the latter is present in the gold film.

In this work, by measuring the optical second-harmonic response and the x-ray pole figures, we find that an obliquely deposited gold film on fused silica indeed develops an in-plane texture as well as an out-of-plane texture when the thickness increases from 10 nm to 30 nm. The development of a preferred in-plane orientation can be attributed to a self-shadowing effect and thus is expected to occur in other metal thin films.

The gold films are prepared on fused silica substrates at room temperature in an electron beam evaporator. The evaporator chamber has a base pressure of 4×10^{-6} torr. The substrates are cleaned with the same method as reported by Skaife and Abbott.[9] The gold deposition rate is roughly 0.02 nm/sec. To help the gold films to adhere to the fused silica surface, we first deposit a 2-nm titanium (Ti) layer as the buffer. For obliquely deposited gold films, the gold flux is incident at 50° from the substrate normal and along a fixed azimuth. For comparison, we have also made ''uniformly deposited'' gold films by varying the incidence polar angle from 0° to 70° and the incidence azimuth from 0° to 360° during deposition. Conventional powder x-ray diffraction measurements show that the polycrystalline grains in both obliquely deposited and ''uniformly deposited'' gold films are terminated with (111) facet planes. We have also measured the x-ray pole figures of these gold films with a Huber pole figure goniometer. The pole figures give the angular distribution of the polycrystalline grain orientation.[2] The results show that (1) the terminating (111) facet planes for the

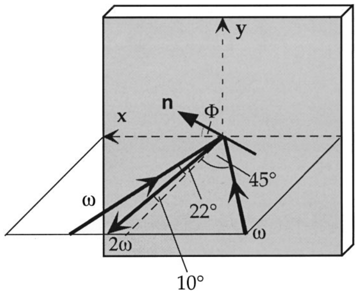

FIG. 1. The excitation and detection geometry of the optical second-harmonic generation (SHG) from a gold film obliquely deposited on a fused silica substrate. The substrate surface coincides with the *x*-*y* plane. Two *p-polarized* excitation beams at ω are incident in the *x*-*z* plane: one at 22° from one side of the substrate normal and the other at 45° from the opposite side. The reflected SHG at 2ω is emitted at 10° from the substrate normal. The gold flux is deposited onto the substrate at 50° from the normal. The unit vector **n** denotes the projected direction of the deposition in the *x*-*y* plane. Φ is the azimuthal angle between **n** and the *x*-axis.

30-nm obliquely deposited films are tilted by $\theta \sim 5°$ towards the deposition flux, while the terminating facets for the 30-nm ''uniformly deposited'' films are parallel to the substrate surface; (2) the polycrystalline grains in the 30-nm obliquely deposited films seem also to have developed a preferred in-plane orientation such that one of the three [110] axes in the terminating facet plane is perpendicular to the incidence plane of the deposition. Unfortunately the signal-to-noise ratio in the pole figure measurements was not high enough to exhibit the in-plane texture distinctly. The in-plane texture and how it evolves as the film thickness increases are much better exhibited in the optical second-harmonic response of the films.

The measurements of the optical second-harmonic generation (SHG) from the gold films are performed in air. We use 20-picosecond optical pulses at $\lambda_\omega = 532$ nm as the fundamental beams. The optical pulses are obtained by frequency-doubling the output of a Nd:YAG laser with a repetition rate of 10 Hz. In Fig. 1, we show the sketch of the optical set-up. We choose the substrate surface (also the gold film surface) as the *x*-*y* plane and the incidence plane of the optical beams as the *x*-*z* plane with the *z*-axis pointing into the substrate. We employ a co-planar, sum-frequency generation geometry such that one fundamental beam (*p-polarized* with a single pulse energy of 0.1 mJ over an area of 0.3-cm^2) is incident at 22° from one side of the substrate normal while the other fundamental beam (also *p-polarized* with a single pulse energy of 0.3 mJ over an area of 0.4-cm^2) is incident at 45° from the opposite side. We detect the *p-polarized* optical second harmonics (at $\lambda_{2\omega} = 266$ nm) in reflection direction at 10° from the substrate normal. In this geometry, the measured optical second harmonics is predominantly generated by the *x*-component of the nonlinear polarization $P_x(2\omega)$ in the gold film. $P_x(2\omega)$ is sensitive to the in-plane structure of the film.[10] The overall detection quantum efficiency is 7% and the absolute SHG signal is in the range of 0.2 counts per pulse. We measure the azimuthal dependence by rotating the gold film about the substrate normal over 360° at a step size of 10°. Let **n** be a unit vector in the *x*-*y* plane along the projected direction of the deposition. The azimuthal angle Φ is defined as the angle between **n** and the *x*-axis.

In Fig. 2, we display the optical second-harmonic genera-

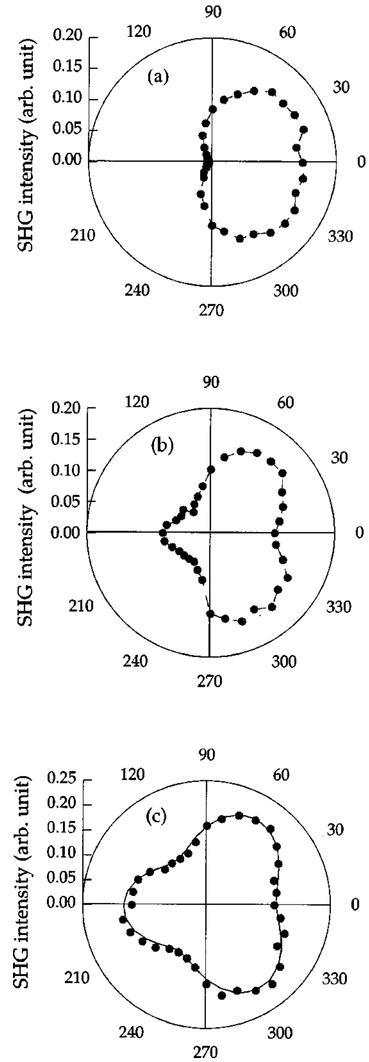

FIG. 2. Azimuthal dependence of the *p-polarized* SHG intensity (in unit of photon counts per pulse) from obliquely deposited gold films vs the film thickness: (a) 10 nm; (b) 20 nm; (c) 30 nm. The solid line shown in (c) is the best fit of a function $\beta(1-\gamma\cos 3\Phi + \eta\cos\Phi)^2$ to the data with $\beta = 0.15$, $\gamma = 0.23$, and $\eta = 0.14$.

tion (SHG) signal versus Φ from obliquely deposited gold films of three different thicknesses: 10 nm [Fig. 2(a)], 20 nm [Fig. 2(b)], and 30 nm [Fig. 2(c)]. The SHG signal originates from the electric quadrupole and magnetic dipole responses of the gold film.[10] As a result of the attenuation at the fundamental and the second-harmonic frequencies, the SHG signal and its azimuthal dependence comes from the topmost 10 nm of the film and the contribution from the 2-nm Ti buffer layer can be neglected. This is consistent with our observation that the averaged SHG signal is roughly the same at all three film thicknesses. For the 10-nm gold film, the SHG has only a mirror plane coinciding with the incidence plane of the deposition as one would expect from the geometry of deposition. It has a minimum at $\Phi = 0°$ and a broad maximum at $\Phi = 180°$. At the film thickness of 20 nm, a small peak emerges at $\Phi = 0°$ while the maximum at $\Phi = 180°$ shrinks. At the film thickness of 30 nm the azimuthal dependence has evolved to having a three-fold rotation axis just like the SHG from a single crystalline Au(111).[11] The peak at $\Phi = 180°$ is noticeably smaller than the peaks at $\Phi = 60°$ and 300°. It seems that at 20 nm the evolution of the azimuthal dependence is incomplete. For comparison, the SHG from the ''uniformly deposited'' films is azimuthally isotropic, indicating that the in-plane orientations of the polycrystalline grains in these films are random.

The presence of a three-fold rotational axis in SHG from 30-nm obliquely deposited gold films, after an average over an area of 0.3 cm^2, is indicative of a preferred azimuthal orientation of the polycrystalline grains in these films. Our SHG measurement should be compared to the measurement of a nonresonant optical sum-frequency generation from a single crystal Au(111) by Yeganeh and co-workers.[11] Similar to Fig. 2(c), these authors observed a three-fold rotation axis with the SHG maxima appearing at 60°, 180°, and 300°. As we will show shortly, the asymmetry of the three SHG peaks in Fig. 2(c) can be attributed to a small tilt of the terminating facet planes of the gold grains towards the deposition flux.

In our case, the optical second harmonics is predominantly generated by the *x*-component of the nonlinear polarization $P_x(2\omega)$ in the topmost 10-nm layer of the gold films. It is an average of the nonlinear polarization over many polycrystalline grains. From a single crystalline grain (e.g., the j-th grain), the nonlinear polarization $P_{x,j}(2\omega)$ has an isotropic part $P_{x,j}^{\text{isotropic}}(2\omega)$ and an anisotropic part $P_{x,j}^{\text{anisotropic}}(2\omega)$.[10] Let θ be the tilt angle of the normal of its terminating facet plane from the substrate normal. Let ϕ_j be the angle between **n** (see Fig. 1) and one of the [211] axes in the terminating facet plane. For a small tilt angle θ, it can be shown that $P_{x,j}^{\text{anisotropic}}(2\omega)\sim[-\cos 3(\Phi-\phi_j)+(3/\sqrt{2})\,\theta\cos(\Phi-\phi_j)]$ and consequently

$$P_x(2\omega)=\sum_j P_{x,j}(2\omega)\sim\sum_j\,[1-\alpha\cos 3(\Phi-\phi_j)+\alpha(3/\sqrt{2})\,\theta\cos(\Phi-\phi_j)]. \quad (1)$$

The total SHG signal as a function of Φ is given by $S(\Phi)\sim|P_x(2\omega)|^2$. α is a constant determined by the geometry of the experimental set-up. Equation (1) is equivalent to an ensemble average over a distribution of the azimuthal orientations around $\phi=0°$ for those polycrystalline grains within a macroscopic area of 0.3-cm^2. As a result, we have

$$S(\Phi)\sim|P_x(2\omega)|^2\sim|1-\alpha\langle\cos 3\phi\rangle\cos 3\Phi+\alpha(3/\sqrt{2})\,\theta\langle\cos\phi\rangle\cos\Phi|^2. \quad (2)$$

If the azimuthal orientations of the grains are random (as one would expect of films deposited on amorphous substrates like fused silica) such that ϕ varies from $-60°$ to $+60°$, $\langle\cos 3\phi\rangle$ vanishes and the resultant $S(\Phi)$ only have a weak mirror plane given by the $\alpha(3/\sqrt{2})\,\theta\langle\cos\phi\rangle\cos\Phi$ term. If the tilt angles of the terminating facets are also randomly distributed about $\theta=0°$, the resultant $S(\Phi)$ becomes isotropic as we found for ''uniformly deposited'' gold films. If instead there is a preferred orientation along $\phi=0°$ so that ϕ varies over a significantly narrower range than 120°, $\langle\cos 3\phi\rangle$ survives the ensemble average and $S(\Phi)$ has a three-fold rotation axis in addition to a weak asymmetry coming from the tilt angle. This is what we observed for obliquely deposited gold films with thicknesses over 10 nm. The data in Fig. 2(c) is best fit to Eq. (2) (solid line) by assuming that *one of the [110] axes in the terminating facet plane is perpendicular to the incident plane of the deposition* [as shown in Fig. 3(a)] and with $(3/\sqrt{2})\,\theta\langle\cos\phi\rangle/\langle\cos 3\phi\rangle=+0.6$.

We now explore the atomic-scale mechanism and the geometric effect that may have led to the preferred in-plane orientation of the polycrystalline grains. Since the gold grains are terminated with (111) facets with the lowest surface energy, we infer that gold atoms have a sufficiently high surface mobility (transient as well as thermal) at room temperature to maintain the shapes of the grains close to that at equilibrium. As recently shown by Hansen and co-workers in a scanning tunneling microscopy study, room-temperature deposited Pd clusters on an Al_2O_3 surface have a hexagonal shape (or a shape of a truncated equilateral triangle) and are terminated with (111) facet planes.[12] Of the six side facets of a hexagonal cluster, three are (111) facets and the others are (100) facets as illustrated in Fig. 3(a). The lengths of these two types of facets are determined by the respective surface free energies. The shapes of Pd clusters serve as a general representation of fcc metal grains or clusters on an incommensurate substrate. More relevant to the present study, Mahoney and co-workers recently studied the morphology of uniformly deposited gold films on (0001) MoS_2 (an incommensurate substrate) at 400 °C.[13] They found that the gold grains have the shapes of equilateral triangles or equilateral triangles with truncated apices as illustrated in Fig. 3. The STM images reported by these authors revealed that the triangularly shaped gold grains have the form of a truncated tetrahedron by having its apices cut off and thus exposing four (111) facet planes. The apex oriented along the substrate normal was truncated more than the other three. We shall assume that the polycrystalline grains in the obliquely deposited gold films have the shape of a truncated tetrahedron with the (111) side facets being much longer than (100) facets so that the shape is close to be triangular. On an amorphous substrate like fused silica, we expect gold grains of all azimuthal orientations to be present at the early stage of growth. During the subsequent deposition, the grains with certain orientations outgrow others and a preferred in-plane orientation develops as a result of the oblique deposition. From the SHG measurement, we have established that one of the side (100) facets preferably orient towards the incidence flux ($\phi=0°$) as illustrated in Fig. 3(a). We show that a simple geometric effect is likely to have caused such a preferred orientation.

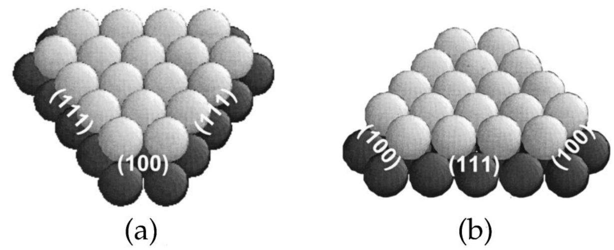

FIG. 3. A hexagonally-shaped gold grain terminated with a (111) facet plane and with (a) a (100) side facet facing towards the incidence flux (or $\phi=0°$); or (b) with a (111) side facet facing towards the incidence flux (or $\phi=\pm 60°$). The grain is viewed along the incidence angle of 50°. The SHG measurement shows that the azimuthal orientation $\phi=0°$ is preferred by the crystalline grains in 50°-obliquely deposited gold films.

As shown by Karpenko and co-workers[14] in a numerical study of in-plane texture development in polycrystalline thin films, if the number of captured gold atoms differs for different azimuthal orientations, particularly at the early stage, the grains with higher capture rates will outgrow and eventually dominate those with lower capture rates. Initially we expect the ''triangularly-shaped'' gold grains to have roughly the same size and shape, and to have random azimuthal orientations. The incidence gold atoms captured by the long (111) side facets of a gold grain determines *the difference* in growth rate. Let A be the average area of a (111) side facet. When a (111) side facet faces towards the incidence flux (i.e., $\phi = \pm 60°$) as illustrated in Fig. 3(b), only this facet and the terminating (111) facet capture the incident gold atoms. Recall that the gold flux is incidence at 50° from the substrate normal. Since the angle between the normal of the (111) side facet and that of the terminating (111) facet is 70°, the incidence angle of the gold flux with respect to the side (111) facet is 20°. As a result the capture rate is proportional to $A \cos 20° = 0.93A$. In contrast, when a short (100) side facet faces towards the gold flux ($\phi = 0°$) as illustrated in Fig. 3(a), two (111) side facets and the terminating (111) facet capture the incident gold atoms. The incidence angle of the gold flux with respect to the two (111) side facets is 55° and therefore the capture rate is proportional to $2A \cos 55° = 1.15A$. As shown numerically by Karpenko *et al.* (Fig. 5 of Ref. 14), this difference in capture rate is sufficiently large for gold grains with initial azimuths ϕ around 0° to outgrow those with initial azimuths ϕ around $\pm 60°$.

The observed in-plane texture and tilt angle θ towards the deposition direction for the polycrystalline grains in an obliquely deposited gold film may have a significant effect on the macroscopic alignment of the terminal methyl groups of an *n*-alkanethiol self-assembled monolayer (SAM) on such a film.[8] It is known that the methyl groups of a $(2m)$-alkanethiol SAM on Au(111) are more or less oriented along the substrate normal.[15] On an obliquely deposited gold film with the terminating (111) facets tilted towards the deposition direction, the methyl groups of a $(2m)$-alkanethiol SAM on these facets would be also tilted towards the deposition direction. On the other hand, the methyl groups of a $(2m+1)$-alkanethiol SAM on Au(111) are tilted along an in-plane [110] axis.[15] On an obliquely deposited gold film, one of the [110] axes in the terminating facet plane is perpendicular to the incidence plane of the deposition and the other two [110] axes are at an angle of 60° from the plane of the deposition. On these facets, the orientations of the methyl groups will be determined both by the orientation of the [110] axes and the tilt of the terminating (111) facets. We speculate that short-ranged interactions between the oriented methyl groups and liquid crystal overlayers may provide part of the explanation, at least, for the previously reported effects on liquid crystals of *n*-alkanethiols with odd and even numbers of CH_2 groups on obliquely deposited gold films.[8] We caution, however, that the orientations of the methyl groups on these substrates need to be determined directly using techniques such as the infrared-visible sum-frequency generation.[16]

In conclusion, we have shown that a thin gold film obliquely deposited on fused silica (with 2-nm Ti buffer layer) develops an in-plane texture as well as an out-of-plane texture. The out-of-plane texture is characterized by that (1) the polycrystalline grains are terminated with (111) facet planes; and (2) the terminating facet planes are tilted by a few degrees towards the deposition direction. The in-plane texture is characterized by a preferred azimuthal orientation of the polycrystalline grains with one of the [110] axes in the terminating facet plane oriented perpendicular to the incidence plane of the deposition. The development of the observed in-plane texture can be attributed to a geometric or self-shadowing effect on the capture rates of gold grains with different initial azimuthal orientations. If this model holds, we expect similar in-plane and out-of-plane textures to develop for thin films of other metals under oblique deposition conditions. Such in-plane and out-of-plane textures can find desirable applications in magnetic thin films and in anchoring molecular overlayers as soft-hard material interfaces. We should note here that unlike gold, most metals are reactive with residual gases in a conventional evaporation chamber with a base pressure of 4×10^{-6} torr. The reaction of a freshly deposited metal film with an ambient gas can significantly change the balance of the surface kinetics that govern the morphology of the film and thus may be detrimental to the self-shadowing effect that we described here. In these cases, it is preferable to perform oblique deposition either under ultrahigh vacuum condition or in a controlled ambient gas so that the effect of the ambient gas on the film morphology and the subsequent texture development can be ascertained. Such a work is under way.

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