Quantum Oscillations and Beats in X-Ray Diffraction during Film Growth

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X-ray diffraction from a growing film at an anti-Bragg point should exhibit bilayer oscillations caused by interference. In an experiment of TiN film growth by laser ablation onto sapphire, an unexpected beating envelope function is found to modulate the oscillations. The successive nodes and antinodes are identified with the development of new growth domains separated by one atomic layer in thickness. This effect allows atomic layer counting of the film thickness distribution. The results imply that the growth is not characterized by a continuum stochastic process, as usually assumed.

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Thin film deposition in vacuum involves the landing and subsequent bonding of atoms or molecules on surfaces; the randomness of the process causes roughness buildup [1–3]. While the film structure may consist of discrete atomic layers, the roughness, as measured by the average variation of film thickness over the substrate surface, is generally a continuous quantity, increasing steadily as film deposition proceeds. Our experiments reported herein, however, show unexpected signatures of atomic-layer-resolved increments of roughness during TiN film growth performed by pulsed laser ablation. The evidence is a beating pattern as a function of time, observed in x-ray reflectivity at an anti-Bragg point of the film [4–8], where waves diffracted (by specular reflection) from two adjacent atomic layers are out of phase and cancel each other. Films consisting of even numbers of atomic layers yield a null diffracted amplitude, whereas films consisting of odd numbers of atomic layers yield a diffracted amplitude equivalent to one atomic layer. As the film grows, the diffracted intensity should oscillate between these two limits with a bilayer period. However, an increasing surface roughness as a result of formation of multiple thickness domains tends to smear out the oscillations gradually, and the damping provides a measure of the roughness evolution [4–9]. Our experiment on TiN film growth shows damped oscillations in the diffracted x-ray intensities, as expected, but also a superimposed beating pattern with successive nodes and antinodes corresponding to the development of growth domains separated by one atomic layer in thickness. These unusual results are attributed to a very smooth growth that does not allow full statistical averaging at the stochastic limit. The phenomenon reported here should be quite general, and the method of analysis should be broadly applicable to crystal growth that is nearly layer-by-layer.

Roughness development is an important issue for device and coating applications of thin films. As device and thin film architectures are increasingly built with nanoscale dimensions, film thickness fluctuation or uncertainty at the atomic level can have large consequences [10–14]. The characteristics of roughness development are thus of technological concern, in addition to the fundamental scientific interest in the nature of stochastic processes. TiN is chosen for the present study partly because of its widespread industrial applications as antifriction, -wear, and -corrosion coatings and as diffusion barriers in electronic applications [15].

The experiment was performed in hutch D at the undulator beam line of Sector 33, Advanced Photon Source, Argonne National Laboratory, using a vacuum system specifically designed for in situ x-ray studies of pulsed laser deposition. The vacuum chamber was directly coupled to a large diffractometer, resulting in excellent system stability. Monochromatic 10-keV x rays were used for the measurements. The coherence length of the beam is nominally ~10 microns in the horizontal direction and ~100 microns in the vertical direction. This length scale limits the size of the domain structure that can be analyzed by our method. Commercial (0001) sapphire substrates, with dimensions 10 × 10 × 0.5 mm, were annealed to 1600 °C to remove surface contaminants prior to loading into the chamber. TiN films with the (111) orientation were grown by ablating a TiN target using a KrF excimer laser with an output of 600 mJ per pulse at a repetition rate of 0.1 Hz. The target-to-substrate distance was 50 mm. During growth, the sapphire substrate was maintained at an elevated temperature, which was deduced from the measured Bragg angle of the sapphire and a known thermal expansion coefficient of 1.2 × 10⁻⁵ K⁻¹.

Figure 1(a) shows an atomic force microscopy (AFM) image of a sapphire substrate after a high temperature anneal for cleaning. Large terraces separated by mostly single and double steps and some triple steps are observed (the height of a single step is 2.17 Å). Figure 1(b) is an AFM image for a substrate after a high temperature anneal.
and subsequent deposition of \( \sim 75 \) monolayers (ML) of TiN at \( 500 \) °C. The step structure looks very similar to that in Fig. 1(a). These results indicate that deposition of the TiN film does not cause much increase in surface roughness under our experimental conditions. The growth domains are too large and too few for us to perform a reliable statistical analysis of the domain structure using AFM.

Figure 2(a) presents the x-ray reflectivity at the (0,0, 1/2) anti-Bragg point of the TiN lattice as a function of film thickness, measured in real time during deposition at a substrate temperature of \( 500 \) °C. The rapid intensity oscillations, somewhat similar to the familiar RHEED oscillations [1,16], have a bilayer period and correspond to even-odd switchings of film thicknesses. Perfectly layer-by-layer growth should preserve the surface morphology and perpetuate the bilayer oscillations. The observed damping of the oscillation amplitude indicates that the growth is close to, but not exactly layer by layer, and the roughness increases with increasing film thickness. The inset in Fig. 2(a) shows details of a segment of the data. The gaps in the data are dead times for data transfer, and the laser plume arrives at the beginning of each data acquisition cycle. The prompt intensity change after each laser pulse suggests a very rapid diffusion and ripening rate for the growth process at the chosen growth temperature, a condition conducive to smooth growth [6–8].

The damping and beating effects can be qualitatively understood as follows. At the initial stage of deposition, the film has just one domain of growth with its thickness changing alternately between odd and even numbers of atomic layers. Roughness develops with the formation of a minor domain with its thickness differing by one monolayer from the dominant domain. As the film grows, each of the two domains gives rise to bilayer oscillations, but the oscillation amplitudes are out of phase and partially cancel each other. The net amplitude is proportional to the difference in area between the two domains, \( A_1 - A_2 \). As the minor domain area grows, corresponding to an increasing roughness, the net oscillation amplitude decreases and eventually reduces to zero when the two domain areas become equal. The result is a node in the envelope function of the x-ray intensity. As seen in Fig. 2(a), a node occurs at an average film thickness of \( \sim 34 \) atomic layers.

As the film deposition continues, more domains form. The next node occurs when four domains are simultaneously present, with areas \( A_1 \) to \( A_4 \), and \( (A_1 + A_3) - (A_2 + A_4) = 0 \). In between the first two nodes, there is a maximum in oscillation amplitude (antinode in the envelope function) which corresponds roughly to three simultaneously present domains with the signed area sum, \( A_1 - A_2 + A_4 \), equal to about one third of the total surface area. It follows that the beating period, as measured from
one node to the next, corresponds to the addition of two new domains with equal area. Thus, the beating pattern has a bilayer period in terms of the developing roughness, while the rapid oscillations have a bilayer period in terms of the average film thickness. In the limit of a very rough film, the oscillation amplitude, proportional to \((A_1 + A_2 + A_3 + \cdots) - (A_2 + A_3 + A_6 + \cdots)\), approaches zero by statistical averaging, and the bilayer oscillations fade away.

Figure 3 presents a pictorial description of the model. Perfect layer-by-layer growth is characterized by a film thickness distribution function in the form of a linear slope with a width of 1 ML (standard deviation \(\sigma_0 = 0.289\)), as seen in Fig. 3(a) for average film thickness \(\bar{N} = 0\) ML. As the film grows, this distribution function moves to the right continuously, with each atomic layer being filled sequentially. Roughening causes the slope to broaden, as indicated by the examples in Figs. 3(b) and 3(c) (thick lines, labeled “linear”) for \(\bar{N} = 34\) and 54 ML. A more realistic description of the roughness is to add a Gaussian broadening by convolution to allow rounding of the distribution function (circles in Fig. 3, labeled “linear \(\otimes\) Gaussian”). Also shown for comparison in each case is a cumulative Gaussian distribution function (thin curve) obtained by convolving a step function with a Gaussian of a suitable width. This distribution is what one would normally expect based on the central-limit theorem for continuum random processes [17,18].

The distribution function obtained from convolving a linear slope and a Gaussian is used to model the data in Fig. 2(a). The standard deviation of the linear slope is assumed to increase as a power law for increasing \(\bar{N}\):

\[
\sigma = \sigma_0 = \alpha \bar{N}^\gamma,
\]

where \(\alpha\) and \(\gamma\) are constants. The Gaussian width is assumed to scale similarly. The x-ray intensity is calculated from a layered-sum of the scattering amplitudes [19]

\[
I \propto \left| B + \sum_{N=1}^{\infty} (-1)^{N+1}D(N, \bar{N}) \right|^2,
\]

where \(B\) is the scattering amplitude of the substrate and \(D\) is the film thickness distribution function at average thickness \(\bar{N}\). The results from a least-squares fit (curve) are shown in Fig. 2(a), and the corresponding distribution functions (circles) at \(\bar{N} = 34\) and 54 ML are shown in Figs. 3(b) and 3(c), respectively. Also shown is the linear slope component of the distribution in each case. The two coverages 34 and 54 ML correspond to a node and an antinode, respectively, and the corresponding linear distribution component spans two and three atomic layers, just as expected.

If \(D\) is taken to be a linear slope only, without the Gaussian broadening, the calculated x-ray intensity yields an ideal beating pattern. The added Gaussian diminishes the beating effect. In the continuum stochastic limit, the broadening must be entirely Gaussian in nature. To test this limit, we replace the distribution function \(D\) from the fit by a cumulative Gaussian distribution with the same standard deviation. The resulting functions \(D\) are shown by the thin curves in Fig. 3. The differences from the original distribution functions are quite subtle. If these Gaussian distribution functions are employed to calculate the x-ray intensity, the results, shown in Fig. 2(b), do not exhibit a beating pattern. This analysis demonstrates the extreme sensitivity of the measurement to slight departures of film roughness from the Gaussian limit. The vertical markers in Fig. 2 are separated by 2 ML; they are positioned to correspond to the minima of the x-ray intensity oscillations before the first node. In crossing the first node, the phase of the bilayer oscillations reverses as a result of the domain structure evolution, as seen in Fig. 2(a), but this phase reversal does not happen for the model calculation in Fig. 2(b).

The roughness of the film, defined as the standard deviation of the distribution function, is shown in Fig. 4 as a function of the average film thickness. The components corresponding to the linear slope and Gaussian broadening are also presented. The Gaussian component is almost a constant, while the linear component increases steadily.

FIG. 3 (color online). Film thickness distribution functions for film thicknesses of (a) 0, (b) 34, and (c) 54 ML, respectively. The thick lines are linear distributions, and the circles are the results of convolution of the linear profiles with a Gaussian. The thin curves are cumulative Gaussian distribution functions with the same standard deviation as the convoluted case.
The final roughness of the film, at a total thickness of \( \sim 75 \text{ ML} \), is \( \sim 1.4 \text{ ML} \), which is just \( \sim 1 \text{ ML} \) over the initial ideal value of \( \sigma_0 = 0.289 \). The growth is indeed very smooth, which can be attributed to the facile surface diffusion at the substrate temperature chosen. The deposited material readily finds and attaches to nearby TiN atomic steps. However, there are few TiN step edges available at the initial stage of growth, which can lead to a rapid initial jump in roughness for the first ML as seen in Fig. 4.

Film roughness is driven by randomness inherent in the deposition process. With a very large number (\( \sim 10^{15} \)) of atoms falling on the surface for the growth of each atomic layer, one would normally assume that the resulting roughness must be governed by a nearly ideal stochastic process characterized by a Gaussian distribution. However, ripening of the surface by diffusion and self organization counteracts the effects of the random process. While it can never completely eliminate all fluctuations, it can lead to a measurable departure in the Gaussian statistics. This work shows that x-ray diffraction at an anti-Bragg point is a very sensitive probe of this effect, and nodes and antinodes in the beating pattern can be identified with the development of new growth domains separated by one atomic layer in thickness. The phenomenon reported here should be quite general, and the method of analysis should be broadly applicable. Our finding has significant implications regarding the nature of roughness buildup and may be exploited in designing growth pathways to minimize or control structural imperfections in thin films.

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**FIG. 4.** Roughness, or standard deviation of the film thickness distribution function, as a function of film thickness. The roughness from the fit (curve) and its linear and Gaussian components are indicated.

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[16] X-rays probe all atomic layers in the film, while RHEED probes the top few atomic layers only. The analysis presented in our Letter, based on a sum of scattering amplitudes from all atomic layers, is not applicable to RHEED. The two methods generally yield complementary information.

