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Real-time X-ray studies of fundamental surface growth processes

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REAL-TIME X-RAY STUDIES OF
FUNDAMENTAL SURFACE GROWTH PROCESSES

by

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REAL TIME X-RAY STUDIES OF
FUNDAMENTAL SURFACE GROWTH PROCESSES

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ABSTRACT

In this research, some fundamental aspects of surface growth processes are investigated through in-situ synchrotron based x-ray techniques, including a new coherent x-ray technique developed as part of this work, as well as ex-situ Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and simulation. The first part of this dissertation focuses on careful examination of early-time kinetics of indium (In) island growth via real-time Grazing Incidence Small Angle X-ray Scattering (GISAXS) since it is a good example of simple growth systems allowing the results to be directly compared to surface growth theories and also because of its technical relevance for III–V semiconductor deposition. The results are compared with Family-Meakin (FM) droplet growth and coalescence theory through Monte Carlo simulations.

In addition, room temperature deposition of amorphous silicon (a-Si) through DC magnetron sputtering onto a silicon (Si) substrate has been investigated via real-time GISAXS. The deposition conditions are optimized to create an idealized growth environment so that the results can be directly compared to surface growth models. Performing the deposition at room
temperature results in adatoms having limited surface mobility, which causes formation of correlated mound-like structures on the surface at the early stages of the growth. The correlation distance between the mound-like structures is found to grow linearly with time. The results are compared to a ballistic deposition model including self-shadowing and desorption effects.

The second half of this study focuses on investigation of the kinetic roughening dynamics of thin film growth, where the local dynamics are measured after the overall kinetic evolution of the surface roughness reach a steady-state saturation. Coherent X-ray GISAXS (Co-GISAXS) has been developed as a new approach to investigate surface dynamics during thin film deposition. Room temperature deposition of a-Si and amorphous tungsten disilicide (a-WSi$_2$) through DC magnetron sputtering onto respectively Si and SiO$_2$ substrates has been examined. The overall dynamics are complex, but power law behavior is observed for the structure factor and correlation times at the most surface sensitive section of the data. This research demonstrated that Co-GISAXS is a powerful new approach to investigate the correlated dynamics between surface and sub-surface structures.
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LIST OF ABBREVIATIONS

a-Si ................................................................. Amorphous Silicon
a-WSi$_2$ ......................................................... Amorphous Tungsten-di-Silicide
AFM ............................................................... Atomic Force Microscopy
ALD ............................................................... Atomic Layer Deposition
ALE ............................................................... Atomic Layer Epitaxy
APS ............................................................... Advance Photon Source
BA ................................................................. Born Approximation
CDD .............................................................. Charge-coupled Device
Co-GISAXS ... Coherent X-ray Grazing Incidence Small Angle X-ray Scattering
DWBA ......................................................... Distorted Wave Born Approximation
FM ............................................................... Family-Meakin Model
FT ................................................................. Fourier Transform
FWHM ......................................................... Full Width Half Max
In .................................................................. Indium
MC ............................................................... Monte Carlo
NSLS .......................................................... National Synchrotron Light Source
PCS ............................................................. Photon Correlation Spectroscopy
SEM .......................................................... Scanning Electron Microscopy
Si ................................................................. Silicon
SiO$_2$ .......................................................... Silicon-di-Oxide
UHV ............................................................ Ultra high Vacuum
XPCS.............................................................. X-ray Photon Correlation Spectroscopy
XRF ................................................................. X-ray Fluorescence Emission
XRR........................................................................ Specular X-ray Reflectivity
1. Introduction

Today’s technologies demand atomic level engineered materials for successful applications. As a result, detailed understanding of surface growth processes becomes a very essential part of many research fields. In this context, surface studies are addressed by a variety of in-situ and ex-situ techniques. Even though many improvements have been made in the last decades, there are still many fundamental surface and interface issues waiting to be addressed. Increasing our understanding of surface growth modes not only improves deposition techniques but also improves further design and creativity for better quality materials\(^1,2\).

Using synchrotron-based x-ray techniques to study surface growth processes has proven to provide quantitative knowledge where other techniques failed to be successful. Especially in complex growth systems that have more than one competing process happening simultaneously, real time x-ray techniques can be performed without causing any changes in the experimental conditions. X-ray scattering measurements are non-destructive. The weak interaction of hard x-rays with the materials allows us to use a kinematic approximation known as Born Approximation (BA) or its grazing incidence version, the Distorted Wave Born Approximation (DWBA), to model and analyze the experimental results. X-ray experiments can be performed in surface or bulk sensitive geometries and result in information about the measured system from sub-nanometer scales to hundreds of nanometers. Specifically surface sensitive
x-ray scattering techniques have another advantage over qualitative imaging techniques by providing statistical average information over several square millimeters area. A comprehensive temporal record of surface growth dynamics can be achieved by performing real-time studies. Real-time measurements not only remove concerns about possible changes during the time between deposition and measurement but also can give records of post-deposition relaxation processes\textsuperscript{3,4}.

Though growth processes are unique to the particular materials involved, i.e. the particular growth techniques and conditions, from a statistical mechanics point of view they all share universal aspects that have encouraged attempts to model the surface evolution by generic models\textsuperscript{5}. The major part of this thesis research is dedicated to investigation of both early time kinetics and late time steady state local dynamics of amorphous thin film growth via room temperature DC magnetron sputter deposition. Though sputter deposition has been around for multiple decades and has been widely used in the industry for thin film growth, many new questions related to the this growth process have been arising as a result of new technological demands for ultrathin film thicknesses and for well-controlled thin film morphologies. The remaining part of this research uses thermal evaporation to focus on early time growth dynamics of indium island formation because of its technical relevance to III–V semiconductor growth and improving our understanding of early-time Volmer-Weber growth processes.
In Chapter 2, four synchrotron based X-ray characterization techniques are presented. Generic models of fundamental surface growth processes are presented in Chapter 3. Chapter 4 focuses on real-time X-ray studies of Indium island growth kinetics. In Chapter 5, real-time studies of early time room temperature deposition of silicon via DC magnetron sputtering are presented. Chapter 6 discusses Co-GISAXS as a new technique to investigate surface growth dynamics and Chapter 7 presents observation of heterodyne and homodyne mixing in X-ray photon correlation spectroscopy during thin film deposition. Chapter 8 is dedicated to Conclusion and discussion of possible future work.
2. In-situ Synchrotron Based X-ray Techniques

The real-time x-ray scattering studies of early-time kinetics processes during thin film deposition are performed in a custom-built ultrahigh vacuum (UHV) chamber with a base pressure of $10^{-8}$ Torr installed onto a surface diffractometer on beamline X21 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Figure 1). The incoming x-ray beam with photon energy changing between 10keV and 12keV is focused to a dimension of $1000 \times 500 \ \mu m^2$, and the scattered beam is recorded at 30-second or 60-second intervals with a 0.1-second readout by a 487x195-pixel PILATUS detector from Dectris Inc. located 814 mm away from the sample with $172 \times 172 \ \mu m^2$ pixel size. Additionally, real time XRF measurements during In island growth are recorded every second by a SII NanoTechnology Vortex point detector which is located along the surface normal of the substrate.

Real-time x-ray scattering studies of late-time steady-state local surface dynamics during amorphous thin film growth are performed in a custom-built ultrahigh vacuum (UHV) chamber with a base pressure of $3 \times 10^{-8}$ Torr capable of holding a DC magnetron sputter deposition source. The deposition chamber is installed onto a diffractometer on beamline 8-ID-I of the Advanced Photon Source (APS) located at Argonne National Laboratory (Figure 2). Incoming partially coherent x-rays with 7.38 keV photon energy are focused to a beam of dimension of $20 \times 4 \ \mu m^2$ at the sample position to improve speckle contrast. A two-dimensional Princeton Instruments direct illumination CCD camera, which is
located 4067 mm away from the sample, is set to measure the scattered intensity with two-second intervals with a readout time of 1 second and pixel size of $20 \times 20 \, \mu m^2$.

In all the GISAXS experiments (Figure 3) we take the z-direction to be along the sample normal, the x-direction to be the projected direction of the incident beam onto the sample plane and the y-direction to be the perpendicular to the x-direction in the sample plane. Specifically for GISAXS measurements, the measured wavevector transfer decomposes into two components: perpendicular to and parallel with the surface, $q_z$ and $q_{\parallel}$ respectively. The $q_{\parallel}$ includes both $q_x$ and $q_y$ components. However, since $q_x \ll q_y$ as a result of the small incidence and exit angles, and because the surfaces are isotropic, $q_y$ can be approximated as simply $q_{\parallel}$.

**Figure 1.** Growth chamber installed at NSLS X21. (a) shows the Pilatus detector from Dectris Inc. and (b) indicates Vortex Fluorescence detector. The path of the incoming and scattered x-rays is shown by blue arrows.
Figure 2. Growth chamber installed at APS 8-ID-I. The sputtering source is at the top, and the Beryllium windows are covered with red caps. The last collimating slit is visible on the right side of the image, and the beginning of the detector flight path at the left.

2.1. Grazing Incidence Small Angle X-ray (GISAXS)

Grazing Incidence Small Angle X-ray Scattering (GISAXS) has been developed as a powerful technique to investigate the surface morphology of continuous thin films, nanoparticles embedded in a matrix or well-defined nanostructures on the surface. GISAXS has its power by being surface sensitive, non-destructive, and applicable to a wide range of growth and experimental
environments. It is a highly surface sensitive technique because it uses incidence or exit angles close to the critical angle of the total external reflection, $\alpha_c \sim (0.1–0.5^\circ)$.

**Figure 3.** A schematic of GISAXS experiment geometry.

Generally, x-rays belong to the high frequency limit of the electromagnetic spectrum. In this limit, the real part of the refractive index is less than one, and interaction of x-rays with the electrons is very weak except for the case of perfect crystals. Therefore, multiple scattering effects for x-ray scattering experiments can be ignored and the scattering theory can be simplified to a single-scattering approximation; this is known as the kinematical approximation in the x-ray community. In quantum mechanics, the scattered x-rays are modeled by applying first order perturbation to the incidence beam where the Born Approximation (BA) is valid. In other words, the intensity of the scattered beam is proportional to the square modulus of the Fourier Transform (FT) of the electron density in the material\textsuperscript{3, 4}.

In the GISAXS regime, the Born Approximation for the x-ray scattering simplifies to the square modulus of the FT of the surface height (i.e. the height –
height structure factor $S(q_x,q_y)$ in 2-D reciprocal space) in the low roughness limit where $q_z h(x,y) << 1$. When the incident or exit beam is near or below the critical angle for total reflection, the Distorted-Wave Born Approximation (DWBA) provides a more accurate description of the scattering. On a disordered surface, however, the scattering remains proportional to the height-height structure factor in the limit that $q_z' h(x,y) << 1$, where $q_z'$ is the z-component of the change in the scattered wavevector inside the material.

2.2. Specular X-ray Reflectivity (XRR)

In-situ specular x-ray reflectivity measurements of the samples are performed before and after each surface treatment and thin-film growth to determine the suitability of starting substrate, the thin film thickness and the surface roughness. These scans were done by rotation of both detector and sample to keep entrance and exit angles equal. The in-plane wavevector transfer is kept at zero and only the intensity along $q_z$ is explored. XRR is only sensitive to the average perpendicular electron density due to its nature. If the reflection is not coming only from a homogenous substrate, the reflectivity data have oscillations (Kiessig Fringes), which are the result of interference between reflected beams from the layer/layer, substrate/layer and layer/vacuum interfaces (Figure 4). The roughness on the surfaces causes a decrease in the intensity of the overall reflected beam. For the ideal smooth surface case, the XRR data can be modeled as Fresnel Reflectivity due to the homogenous structure of the
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**Figure 4.** Scattering model. \(R_1\) and \(R_2\) are the specularly reflected rays. \(S_1\) and \(S_2\) are the scattered rays. \(\phi_1\) is the incident angle \(\phi_2\) is the reflected angle and \(\Delta\phi_1\) and \(\Delta\phi_2\) are the scattered angles. The indices of refraction for the air and film, respectively, are \(n_1\) and \(n_2\) and the thickness of the film is \(d^9\).

### 2.3. X-ray Fluorescence Emission (XRF)

During the GISAXS experiments, part of the incident x-rays are absorbed by the material which allows us to monitor the x-ray fluorescence from the surfaces during the growth. The energy absorbed from an x-ray photon knocks out an electron from the inner shells, leaving the atoms in an ionized state (Figure 5(a)). When an electron is expelled from the inner shell, it leaves a hole behind that is filled by an outer shell electron resulting in excess energy that can take two forms: fluorescence X-ray emission or Auger electron emission. The first process, fluorescence X-ray emission is depicted in Figure 5(b); the hole is filled by one of the outer shell electrons resulting in emission of a photon with a
specific energy equal to the energy difference between the two atomic shells that are involved in the decay process. In the Auger electron emission, the hole is filled with an outer shell electron and the excess energy is used to knock out one of outer shell electrons (Figure 5(c)). Both processes occur simultaneously as a result of photoelectric absorption and they are element specific. Depending on the Z number of the atoms involved and energy of the incoming x-rays, one of the processes is more favorable and results in higher yield\(^4\). In our system, we are measuring the fluorescence X-ray emission during Indium deposition to monitor their absorption and desorption on the surface.

**Figure 5.** The schematic energy levels diagrams on atoms that only shows the lowest three shells for clarity. (a) The Photoelectric absorption Process. (b)
Fluorescent X-ray Emission. The electron comes from L and M shell to fill the inner shell hole. (c) Auger Electron emission.

2.4. X-ray Photon Correlation Spectroscopy (XPCS): Co-GISAXS

As the result of continued improvement in coherent flux from high brilliance synchrotrons and free-electron lasers, X-ray Photon Correlation Spectroscopy (XPCS) offers new possibilities of measuring local dynamic processes in equilibrium and nonequilibrium systems. XPCS shares physical principles with other Photon Correlation Spectroscopy (PCS) techniques. When coherent light illuminates any material with disorder (static or dynamic), it gives rise to a speckle pattern that depends on the phase differences of the scattered wave from different parts of the sample. As the measured system undergoes changes, the speckle intensities fluctuate in time. XPCS is based on measuring speckle correlation, typically via the intensity autocorrelation function $g_2(t)$. In this study we show that XPCS offers a powerful new way to probe local surface dynamic processes during thin film deposition using coherent x-rays in a Grazing Incidence Small Angle X-ray Scattering geometry, i.e. via Co-GISAXS.

In general XPCS experiments can be run in homodyne or heterodyne modes. In homodyne experiments the intensity fluctuation of the scattered x-rays from the feature of interest alone is measured. On the other hand, in heterodyne experiments the scattered beam is made to interfere with a static or quasi-static reference and the intensity fluctuations of the resulting beam are studied. Under conditions in which significant scattering from the bulk film is observed, we
have discovered that heterodyning can occur between the bulk and surface signals during Co-GISAXS studies of thin film growth\textsuperscript{26}. However, we focus here on experimental conditions giving homodyne behavior. The quantity typically evaluated in XPCS studies is the intensity autocorrelation function:

\begin{equation}
    g_2(q, t) = \frac{\langle l(q,t')l(q,t'+t) \rangle}{\langle l(q,t') \rangle^2} \quad (1)
\end{equation}

where $l(q,t')$ is the intensity at time $t'$ at wavevector $q$. Angle brackets indicate a time averaging over $t'$. Scattered intensity is a second-order function of the electric fields and consequently $g_2(q, t)$ is fourth order in the fields. The electric fields are proportional to the FT of electron density. In a system with a scattered electric field that is a Gaussian random variable having zero mean, $g_2(q, t)$ can be decomposed into a simpler product of the autocorrelation function of the scattered electric field as given by the Siegert relation\textsuperscript{10,13}:

\begin{equation}
    g_2(q, t) = 1 + \beta(q)|g_1(q, t)|^2 \quad (2)
\end{equation}

where:

\begin{equation}
    g_1(q, t) = \frac{\langle E(q,t')E(q,t'+t) \rangle}{\langle E(q,t') \rangle^2}. \quad (3)
\end{equation}

$\beta(q)$ is a contrast term with a value between zero and one which depends on the experimental setup and the coherence of the incidence beam.

It is often reported that the $g_2(q, t)$ function can be well fit with Kohlrausch-Williams-Watts form\textsuperscript{27}:
\[ g_2(q, t) = 1 + \beta(q) e^{-\left(\frac{t}{\tau(q)}\right)^n} \] (4)

where \( \tau(q) \) is the \( q \)-dependent correlation time and \( n \) is an exponent that is specific to a materials process. If the system dynamics obeys a linear theory \( n \) takes a value of one, so that \( g_2(q, t) \) becomes a simple exponential function. An example is a simple diffusive system where individual atoms undergo Brownian Motion. In this specific case of Fickian diffusion, the correlation time function is \( \tau(q) = \frac{1}{Dq^2} \) where \( D \) is the diffusion constant\textsuperscript{10–13}. If the exponent \( n \) takes a value larger or smaller than one, then dynamic processes cannot be explained by simple linear theory. The system then exhibits stretched exponential \( (n < 1) \) or compressed exponential \( (n > 1) \) behavior\textsuperscript{28}. 
3. Fundamental Surface Growth Processes

3.1. Amorphous Thin Film Growth

It is a well-known fact that structural properties of the thin films are strongly dependent on the deposition conditions, specifically the mobility of the adatoms on the surface. The energy of the adatoms is provided by thermal effects, ionic bombardment and chemical reaction to the substrate\textsuperscript{29}. The Structure Zone Model (SZM) had been developed over the years to explain the microstructure of thin films during growth resulting from these three mechanisms mentioned above. Growth zones for thin film deposition had been suggested for the first time by Movchan and Demchisshim in 1969. They established that microstructure of metallic thin films is strictly related to the ratio of substrate temperature ($T_s$) to the melting temperature ($T_m$), $T_s / T_m$, of the material deposited and these films have three well-defined zones\textsuperscript{30}. The thin films are formed by small and elongated grains creating columnar structures with porous morphology and weakly binding grains in the first zone ($T_s / T_m < 0.3$). The columnar structure is formed as a result of low surface diffusion, low adatom mobility and self-shadowing effects. In the second zone, $0.3 < T_s / T_m < 0.45$, as a result of increased temperature the adatom mobility increases so thus surface diffusion; more bonds between the columns occur resulting in denser films. The third zone occurs when $T_s / T_m > 0.45$, so that not only the atoms at the surface but also those within the bulk have enough energy to diffuse. As a result bigger grains form and recrystallization occurs. In 1974, Thorton refined the zone model
by elaborating the importance of the working pressure and putting it into the SZM. The working gas pressure can both change the energy of the ions that arrive onto the surface and change the length of mean free path of the incoming particles consequently kinetic energy of adatoms on the surface. Additionally, Thorton’s version of the SZM includes an additional transition zone (T Zone) between first and second zones. In the T zone, the surface of the films is smoother than Zone 1 and 2 and the microstructure of the thin film is denser\textsuperscript{31}. Additionally, Messier and Giri showed that the border between Zone 1 and the T zone is not linear and depends on the biased voltage on the substrate during the deposition\textsuperscript{32}.

3.2. Family-Vicsek Scaling Equation

Room temperature deposition via DC magnetron sputter deposition leads to nonequilibrium growth dynamics where surfaces lack thermal energy to restructure themselves to find the lowest energy configuration. However, surfaces still go through local relaxation mechanisms that presumably depend on details of the local environment such as the curvature of the surface, leading to correlated surface growth. Following the initial stages of growth and increasing roughness surface correlations typically saturate at some cross-over time $t_\star$ so that roughening mechanisms become balanced by smoothening processes. Kinetic roughening is often discussed through dynamical scaling relationships which connect spatial and temporal correlations and are independent of many
system details. A key surface growth scaling relation is the Family-Vicsek\textsuperscript{33,34} scaling equation:

\[ w(L, t) \sim L^a f \left( \frac{L}{L^z} \right) \] (5)

where \( w(L, t) \) is the roughness of the interface or interface width, \( L \) is the lateral length scale, \( z \) is the dynamic growth exponent and \( \alpha \) is the roughness exponent. \( f \left( \frac{L}{L^z} \right) \) is a scaling function. For \( u \ll 1 \), \( f(u) \) behaves as a power law \( f(u) \rightarrow u^\beta \), and for \( u \rightarrow \infty \), the scaling function approaches a constant value so that \( w(L, t) \sim L^\alpha \). Therefore the surface width approaches a steady state value within the range of length scales studied. The crossover time between power law growth to a constant roughness scales with lateral length scale: \( t \sim L^z \).

Within the Family-Vicsek scaling relation, when evolution of the surface structure reaches a dynamical steady state the structure factor behaves as a power law: \( S(q) \sim q_m^{-m} \). Since the structure factor is directly proportional to the square of the interface width, \( m \) is related to \( \alpha \) as \( m = 2 + 2\alpha \). Additionally the autocorrelation function of surface heights can be related to the dynamic exponent \( z \textsuperscript{35} \):

\[ < h(q, t_1)h(q, t_2) > \sim g_{ss}(q^z|t_1 - t_2|) \] (6)

By solving Eq (4) using Eq (6), the correlation time \( \tau(q) \) is found to be related to length scale \( L \), or equivalently to wavenumber \( q \sim 2\pi/L \), as \( \tau(q) \sim q_m^{-z} \). Therefore the dynamic scaling exponent \( z \) can be extracted directly from Co-GISAXS data.
under steady-state growth conditions. The ability to extract both $\alpha$ and $z$ from the same data set is very powerful. Since the remaining scaling exponent $\beta$ can also be recovered from $\beta = \alpha/z$, Co-GISAXS can be used to fully characterize the dynamics of a growing surface.

3.3. Edward-Wilkinson Model (EW)

In general, the randomly deposited atoms undergo some kind of relaxation mechanism. One of the simplest growth models with a relaxation mechanism is where the randomly deposited atoms are allowed to move on the surface within a limited distance until they find a location with the lowest height among neighboring sites. Then, the atom attaches itself permanently to the site. Limited surface diffusion introduces a non-trivial surface correlation. A model using a Langevin equation for surface growth with limited surface diffusion first was proposed by Edwards and Wilkinson for a Granular Aggregate, so the equation is known as Edwards-Wilkinson (EW) model in the literature. The equation reads

$$\frac{\partial h(x,t)}{\partial t} = \nu \nabla^2 h + \eta(x,t)$$

where $\nu$ is related to the surface tension or finite diffusion coefficient and the first term on the right side of the equation represents the surface relaxation. The random deposition noise $\eta(x,t)$ is usually modeled as Gaussian with average equal to zero. The surface relaxation mechanism depends on the surface structures and the equation is taken to be valid under the small gradient
approximation ($\nabla h << 1$). Since the equation is linear, the EW equation can be solved for structure factors on the surface by using a Fourier Transform. The scaling exponents for the EW model are $\alpha=0$ and $z=2$. The solution predicts exponential growth or exponential relaxation for all length scales depending on whether the surface is stable or unstable at that length scale. If $\nu$ is positive, then the surface is stable, and the surface roughening saturates and approaches a limit which depends on the surface size for deposition at long times.

### 3.4. Kadar-Parisi-Zhang Equation (KPZ)

Kardar, Parisi and Zhang$^{5,38}$ (KPZ) suggested including the first nonlinear extension of the EW equation to have a more comprehensive growth equation that accounts for lateral growth. After adding the nonlinear correction term $\sqrt{1 + (\nabla h)^2}$, which simplifies to $(\nabla h)^2$ in the limit of $|\nabla h| \ll 1$, to the EW model, the KPZ equation is

$$\frac{\partial h(x,t)}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(x,t) \quad (8)$$

Surface correlations reach saturation at a level determined partially by the nonlinear term $(\nabla h)^2$, which has $\lambda$ as a coefficient. There is no exact solution for scaling exponents for the KPZ equation in dimensions beyond 1+1 but many simulations and mathematical models have been used to prediction the exponents. For a 2+1 dimensional system, accepted values of $\alpha$ and $z$ from the literature are $\alpha \approx 0.4$ and $z \approx 1.6$. The $(\nabla h)^2$ nonlinear term determines the
scaling exponents at long times and long wavelengths even if additional linear terms or nonlinear terms such as $\nabla^2(\nabla h)^2$ are added to Eq. 8. Indeed, a key attribute of the KPZ scaling is that more sophisticated growth models, such as ballistic growth models, exhibit similar scaling at long length scales and times.

3.5. Family-Meakin Model (FM)

The Family-Meakin model with homogenous nucleation captures the essential dynamics of three-dimensional (3-D) droplet formation on a two-dimensional (2-D) substrate through vapor phase deposition techniques. FM assumes that there is no diffusion between the droplets and all the evolution is deposition driven. New arriving atoms to the surface serve as new nuclei sites or they join one of the already exist droplets. As they touch each other or they overlap, these droplets coalesce at the center of the mass of two original droplets. The homogenous nucleation can happen any time and any where on the substrate as the deposition continues. The resulting size distribution of the droplets is a superposition of polydisperse small droplets with monodisperse large droplets. For 3-D droplets on a 2-D substrate with homogenous nucleation, the model predicts linear temporal evolution of the characteristic length scale ($R = 2\pi/q_{\text{max}}$ where $q_{\text{max}}$ is the in-plane correlation peak location), which is the distance between the larger monodisperse droplets. Moreover, the in-plane correlation peak height $S_{\text{max}}$ is related to the correlated droplet positions and it is proportional to $\sim MNn^2$ where $M$ is average number of correlated
neighbors around each droplet. $N$ is the total number of larger size droplets that contributes the correlated x-ray scattering and $n$ is total number of atoms in each droplet. The mean droplet radius is proportional to the in-plane correlation distance $R$ and consequently the number of atoms in each droplet is proportional to $R^3$ since the droplets are 3-D. Additionally, the total number of larger droplets should be decreasing as the droplets coalesce $N \sim R^{-2}$. $M$ can be considered constant due to the self-similarity of the droplet distribution evolution. Consequently, the in-plane correlation peak intensity $S_{\text{max}}$ evolves as $\sim (R^4)^{40}$. 
4. Real-time X-ray Studies of Indium Island Growth Kinetics

4.1. Introduction

The surface and interface properties of materials often govern their behavior in modern devices. As these devices become smaller, an understanding of the properties of materials on a nanometer scale continues to grow in importance. The physics governing thin films and their growth therefore remains an active area of investigation. One area of particular interest is nanoscale In and Ga island/droplet kinetics during growth of group-III nitrides. Because the presence of In and Ga on the surface enhances adatom mobility, optimal growth typically occurs just below the metal droplet formation regime. Moreover, the techniques of migration enhanced epitaxy (MEE) and metal-modulated epitaxy (MME) rely on temporarily growing in excess metal flux so that issues of nanoscale droplet formation are relevant in the kinetics\textsuperscript{41–43}. Here we have investigated the kinetics of nanoscale In island growth by vapor phase deposition on sapphire substrates. During growth, the processes of droplet formation, growth, impingement and coalescence have previously been described through theory and simulation by Family and Meakin, who showed that these processes lead to a dynamical self-similarity and scaling of the droplet size distribution\textsuperscript{39}. While the Family-Meakin (FM) model was designed for droplet kinetics, it should be still be useful description for rapidly coalescing solid islands. The FM model assumes that when two growing droplets/islands begin to impinge, they immediately coalesce into a larger droplet of similar shape. In
practice, the new droplet/island should preserve the total volume and center of mass of its parent droplets/islands. This model of morphological evolution produces a droplet distribution consisting of polydisperse small droplets/islands situated between a set of monodisperse larger droplets. The FM model does not take into account evaporation from the surface, diffusion of droplets on the surface, or Ostwald ripening due to diffusion of atoms between droplets.

4.2. Experimental

In order to investigate the kinetics of In nanoscale island evolution, we used real-time Grazing-Incidence Small Angle X-ray Scattering (GISAXS) to examine morphology evolution and x-ray fluorescence (XRF) to monitor the total deposited material. These were performed at the National Synchrotron Light Source at Brookhaven National Laboratory, at the Beamline X21 Facility for Real-Time Studies of Surface Processes. This facility used a vacuum chamber fitted with 250 micron thick beryllium windows and mounted onto a diffractometer table within the path of the x-ray beam, making it possible to grow films in-situ during x-ray scattering experiments and measure surface morphology evolution in real time. In this study, the vacuum chamber base pressure was roughly $10^{-8}$ Torr. For these experiments, an effusion cell operating at 660°C was used for the thermal deposition of In films on c-plane sapphire substrates. Prior to growth, the substrates were annealed at a temperature of 600°C for 10 minutes to remove any adsorbed water molecules. In order to simplify the kinetics by reducing evaporation, island motion and Ostwald coarsening, experiments were performed
at relatively low temperature. Substrates were not actively heated during film deposition, but due to their proximity to the effusion cell the substrate temperature was sustained at approximately 40° C. In order to facilitate data interpretation and compare with theory, Monte Carlo simulations of the FM model were performed using a square lattice of $0.325 \text{nm} \times 0.325 \text{nm}$ cells. As discussed below, to agree with the experimental behavior observed, an initial FM island radius of $r_0 = 1.08 \text{nm}$ was used with a contact angle near 90°.

The growth rates used here were very low in order to facilitate the careful examination of early-stage kinetics. Estimates based on the GISAXS results presented below, post facto AFM and SEM, and comparison with simulations suggest that the growth rate for an effusion cell temperature of 660° C was approximately 0.026 nm/min. The GISAXS measurements during deposition used 12 keV photons with an incident flux of approximately $10^{11} \text{s}^{-1}$. The incident beam was approximately 1x1 mm$^2$; at the grazing incidence angle used, this produced a footprint on the sample that is 1 mm high along the 10 mm length of the sample. The GISAXS experiments used a Pilatus 100K area detector repeatedly recording images every 50 seconds. The scattering geometry for the experiments consisted of an incident x-ray angle of 0.8° and the area detector positioned with a slit system to cover exit angles in the range of 0.05°–0.57°. The GISAXS data discussed below was generated by isolating a 1D region of the area detector corresponding to the Yoneda wing at an exit angle of
approximately 0.19°. To interpret the x-ray scattering in the Born approximation, the diffuse scattering cross section is:

\[
I(q_x, q_y, q_z) \propto \frac{1}{q_z} \int \int dx dy \, e^{i(q_x x + q_y y + q_z h(x,y))} \left| \right|^2
\]  

(9)

where \( q_x \) and \( q_y \) are the in-plane momentum transfers and the out-of-plane momentum transfer is \( q_z = 1.1 \, \text{nm}^{-1} \) for the geometry used in this study\(^7\). When the value of the quantity \((q_z \cdot z)\) is much less than unity, referred to as the low roughness condition, the scattering cross section simply reduces to the modulus squared of the Fourier transform of the film height. However, this condition will only apply at the very earliest stages of growth, and the non-zero value of \( q_z \) must be considered when quantitatively interpreting or attempting to simulate the majority of the GISAXS data. Furthermore, since an angle near the angle of total reflection is used for the exit angle, dynamical effects can also enter the scattering cross section. Consequently, all GISAXS simulations in this study were calculated within the framework of the Distorted-Wave Born Approximation (DWBA), as described by Lazzari\(^{45}\). Figure 6(a) shows the GISAXS pattern seen on the area detector following 50 minutes of indium deposition. A corresponding film was simulated according to the Family-Meakin model, and the expected GISAXS pattern from such a film, calculated using the DWBA, is displayed in Figure 6(b). The location of the Yoneda wing on the area detector, i.e. the horizontal region for which the scattering intensity is greatest, corresponds to a
scattering exit angle equal to the critical angle for total external reflection of the substrate. Both the area detector and simulation-generated images show peaks along the Yoneda wing corresponding to a characteristic distance between structures on the substrate surface.

Figure 6. (a) The GISAXS pattern of indium islands grown for 50 minutes with 0.026nm/min deposition rate on c-plane sapphire substrate at 40°C. (b) Calculated GISAXS pattern for indium islands under the same experimental conditions by Monte Carlo Simulation using DWBA.

4.3. Results and Discussion

X-ray fluorescence (XRF), measured with an energy-dispersive SII NanoTechnology Vortex point detector, was used during In deposition to monitor the relative rate of the film growth. Figure 7 shows that, upon the opening of the effusion cell shutter at 0 seconds, there is a short transient feature and then the fluorescent yield increases linearly with time until the shutter is closed again at
102 minutes, indicating that the rate of In deposition onto the substrate remained constant over the course of the experiment. It is also worth noting that the fluorescent yield remains constant after the effusion cell shutter is closed, so we can assume any desorption of indium atoms from the substrate is negligible, at least on the order of the several minutes observed. Solid lines, overlaying the fluorescence data, have been added to Fig. 7 to act as a guide to the eye.

![Fluorescence Yield vs. Time](image)

**Figure 7.** X-ray Fluorescence (XRF) data taken before, during and after the indium deposition.

Figure 8 shows a typical evolution of the GISAXS pattern observed during the deposition of indium on sapphire. The background pattern present before deposition has been subtracted from the data. The data clearly show the formation of a peak due to the growth of correlated nanoscale structures during deposition. As deposition continues, the position of this peak decreases in wave number, indicating an increase in the characteristic length scale of the growing system of islands, while the intensity of the peak increases. In order to
quantitatively interpret the evolution of the real-time GISAXS, Lorentzian line shapes were fit to the data. The peak positions $q_{\text{max}}$ and the peak heights $S_{\text{max}}$ could then be extracted from the fits. Figure 8 also shows several minutes' worth of GISAXS patterns, measured after the effusion cell shutter was closed, which show that there is very little surface evolution when new material is no longer being deposited on the sample. The inset of Fig. 8 shows the characteristic in-plane length scale $R = \frac{2\pi}{q_{\text{max}}}$ as a function of time. The characteristic length scale can be seen to increase linearly with time for much of the deposition. This manner of coarsening in the system is predicted by the FM model and is the primary motivation for interpreting the data in the context of that model. A vertical dotted line has been added to the inset figure to mark the time at which the effusion cell shutter was closed, and the characteristic length scale can be seen to increase very slightly after this point. However, while there are clearly some kinetics present in the sample that are not driven by the deposition of new material, their effect is minor compared to the influence of deposition-driven processes, and Family-Meakin remains a viable model for describing the data.
Figure 8. In-situ GISAXS data of indium deposition on a sapphire substrate. The graph shows linear plot of correlation peak evolution. The scattering before the deposition was subtracted from the data and the peaks were fitted to Lorentzian line shapes for quantitative analysis. Inset plot displays characteristic in-plane length scale $R=2\pi/q_{\text{max}}$ as a function of time.

Figure 9. Real-time scan of interface fringes (Kiessig Fringes) of In island deposition presented at two different exit angle with calculated fits through Monte
Although x-ray fluorescence, as discussed above, gives a signal that is proportional to the total deposited In atoms on the surface, it does not provide an absolute measure of the film thickness. To establish the actual thickness at a given point in time, we can examine the Kiessig fringes. X-rays scattered from the surface of the film and from the surface of the substrate beneath the film together produce an interference pattern along the off-specular reflection direction on the area detector, and the resulting scattering intensity evolution can be used to determine the rate of increase of film thickness. For a continuous film, the optical path difference for x-rays through the film is easy to calculate for a given scattering geometry, but for a broad distribution of hemispherical islands an analytical solution is less forthcoming. Consequently, the Monte Carlo simulation that modeled the island growth and coalescence was used also to estimate the interference behavior. Figure 9 shows a comparison between the actual intensity oscillations seen during film growth and the simulated results. The two scattering exit angles represented in the data, 0.26° and 0.55°, span most of the range available on the area detector for these measurements. Selecting an indium deposition rate of 0.026 nanometers per minute produces the agreement between experiment and simulation seen in Fig. 9. A dotted line has been added to Fig. 9 to designate the time at which the effusion cell shutter was opened. A brief time elapses between the opening of the shutter and the
beginning of the oscillatory behavior characteristic of the scattering intensity, due perhaps to the formation of a wetting layer on the substrate before island formation begins. Additionally, the method used to simulate the oscillations ignored the phase shift that results from reflections at the film-substrate interface, and a shift of roughly a quarter of the period was added to the calculated result to produce the final agreement. However, even in the absence of such corrections, the frequency itself of the observed oscillations should be directly related to the rate of deposition. A more complete picture of the Kiessig fringe behavior is presented in Fig. 10, which simply shows how the period of the intensity oscillation varies with exit angle. The relationship between intensity oscillation period and exit angle is well-reproduced by the simulation for a range of exit angles, and we can proceed with confidence in our estimation of the indium deposition rate.

![Figure 10](image)

**Figure 10.** The oscillation period of Kiessig Fringes as a function of exit angle of x-rays.
Figure 11 presents the GISAXS patterns discussed above, shown now on a logarithmic scale, along with the calculated structure factors generated by the FM simulation. Good agreement is seen between experiment and theory for the positions of the correlation peaks and to a large extent for the overall line-shapes of the structure factors themselves. As discussed in the original FM paper\textsuperscript{38}, simulations with the FM model produce a monodisperse set of large islands/droplets with a polydisperse power-law distribution of smaller islands/droplets located between them. Our simulations observe the same island size distributions as reported in Ref. 39; calculations with the simulation results show that only the monodisperse large islands contribute significantly to the GISAXS structure factor. Of particular note in Fig. 11 is that both the simulated and measured structure factors tend toward the same power-law behavior for high wave-vectors, made more apparent by the use of a logarithmic scale. For a system of nanostructures such as this, the high wave-vector scattering intensity derives primarily from the shape of the nanostructures rather than from their spatial distribution\textsuperscript{40}. This agreement in asymptotic behavior indicates that the choice of a hemispherical island, rather than another type of structure, was well-founded for our simulations. To provide a contrast, the inset of Fig. 11 shows the GISAXS for 0.9 nm of indium growth compared to the result of a simulation using cylindrical, rather than hemispherical, islands. These cylindrical islands have a height-to-radius ratio $H/r = 1$, and all other simulation parameters are unchanged. In this case, although there is some agreement near the correlation
peak, the simulated and measured structure factors noticeably diverge at higher wave-vector, where agreement is otherwise seen in the main figure. The structure factors for hemispheres and cylinders display different asymptotic power-law behaviors, and it is the former that better reproduces our data. There is some noticeable systematic disagreement, however, that must be investigated further.

Figure 11. Logarithmic plot of in-situ GISAXS data with FM simulation fits. Monte Carlo simulations used hemispherical droplet shape with nearly 90° contact angle. The subsequent scans are offset for clarity. Inset figure displays the same data fitted with FM simulation of cylindrical droplets.

Figure 12 shows the evolution of the characteristic in-plane length scale as a function of film thickness. A curve showing the evolution of the characteristic length scale for our system of simulated islands is also displayed. We have already seen in Fig. 11 that the measured and calculated structure factors agree
well in terms of the correlation peak position, so it is not surprising that the two curves in Fig. 12 show similar trends as well. Extrapolating the data back to zero film thickness, we can see that, even at the very beginning of the deposition, there is a non-zero value for the characteristic length scale for the film. This value, approximately 4.4 $nm$, should reflect the initial inter-island distance. Simulations suggest that the distance between islands at the very start of growth should be about twice the distance the initial adatoms are able to migrate. We can estimate then that the distance over which adatoms may move on the surface to join existing islands or to nucleate new ones is approximately 2.2 $nm$, which is consistent with the initial island radius $r_0 = 1.08 nm$ chosen for the FM simulations.

**Figure 12.** Correlation length as a function of average film thickness.

The evolution of the peak height $S_{max}$ should also result directly from the correlation between island positions. If a given representative island is surrounded by $M$ correlated islands, then $S_{max} \propto (M \cdot n) \cdot (N \cdot n)$, where $n$ is the
number of atoms in each island and $N$ is the total number of islands illuminated by the x-ray beam. Naturally, $n \sim R^3$ and $N \sim R^{-2}$, while $M$ can be considered a constant due to the scaling that is characteristic of the FM model\cite{44}. Therefore, the peak height should increase like the fourth power of the characteristic length scale, i.e. $S_{\text{max}} \sim R^4$, as long as the low roughness condition continues to be satisfied. Consequently, the peak heights extracted from the measured and simulated structure factors are plotted as a function of $R^4$ in figure 13. $S_{\text{max}}$, being linear in $R^4$, should be easily recognized as a straight line when displayed on this scale. However, as growth continues, and the coalescing islands increase in size, the low roughness condition is no longer satisfied, and $S_{\text{max}}$ quickly begins to deviate from this “linear” behavior. Furthermore, the rate of this deviation should provide insight into the shape of the growing islands. To illustrate this, Fig. 13 also shows the results of FM simulations for two other island shapes, a round cap with contact angle 75° and a half-capsule shape with a height-to-radius ratio of 1.2 (where a ratio of unity would represent a hemisphere). These shapes were chosen because, although they represent only slight perturbations to a simple hemisphere, there is already a noticeable difference in the behavior of $S_{\text{max}}$. For the round cap, $S_{\text{max}}$ deviates from the expected low-roughness behavior less readily than the data, while the results islands with a half-capsule shape clearly deviate sooner and more drastically. The FM simulation considering hemispherical islands, of course, shows the largest degree of agreement with the experimental data, strongly suggesting that
this is an accurate reflection of the indium grown during this study.

![GISAXS data and FM simulation comparison via $S_{\text{max}}$ vs $R^4$ plot.](image)

**Figure 13.** GISAXS data and FM simulation comparison via $S_{\text{max}}$ vs $R^4$ plot. Simulation had a good agreement with the data for hemispherical droplet shape. Early in the deposition, the linear behavior is observed.

*Post-facto, ex-situ* AFM and SEM were performed for several samples with different growth times. Figure 14(a) shows the results of AFM for 102 minutes of indium deposition with an accompanying image 14(b) generated from the FM simulation for a corresponding average film thickness, based on the growth rate discussed earlier. The AFM image clearly shows the expected pattern of small islands interspersed between larger islands that are characteristic of the FM theory. It should be noted that the limited resolution of the AFM technique for lateral sizes smaller than 20nm results in underrepresentation of the smaller islands on the surface when compared to the FM simulation result. Sharper presentation of In islands' distribution can be seen in the SEM image of 290 minutes In island deposition in Fig. 14(c) where the
smaller size islands are distributed among relatively monodisperse larger size islands as the FM model suggested.

**Figure 14.** (a) AFM image of 102 minute deposited of indium with 0.026 nm/min rate, (b) Calculated FM simulation surface for same average film thickness, and (c) SEM image of 290 minute deposited of In with 0.026nm/min rate.

### 4.4. Conclusion

In conclusion, the early stages of growth for indium on sapphire have been investigated and appear to be characterized by the nucleation, growth, and coalescence of hemispherical islands. Simulations of the Family-Meakin model have been performed which agree with the results of both real-time GISAXS and *post-facto* AFM and SEM. Previous studies have found good agreement with the FM model for Al island kinetics\(^{40}\). Thus the current work adds further support to the conjecture that the FM could have wide applicability for the early stage thin film Volmer-Weber growth processes of island formation, impingement and coalescence.
5. Real-time X-ray Studies of Early-time Amorphous Silicon Thin-film Growth via DC Magnetron Sputtering

5.1. Introduction

Today’s technologies demand atomic level engineered materials for successful applications. As a result, detailed understanding of surface growth processes becomes an essential part of many research fields. In this context, surface studies are addressed by a variety of in-situ and ex-situ techniques. Although many improvements have been made in the last decades, there are still many fundamental surface and interface issues waiting to be addressed. Increasing our understanding of surface growth modes not only improves deposition techniques but also improves further design and creativity for better quality materials. Even though sputter deposition is a very well established technique that has been used widely in industry for thin film deposition, the technological need for the ultra thin films with controlled surface morphologies challenges our understanding and control over the deposition processes. Therefore, this study carefully examines the early time kinetic processes during room temperature deposition of amorphous silicon (a-Si) thin films by DC magnetron sputtering. The fundamentals of surface growth processes are investigated mainly through real-time Grazing Incidence Small Angle X-ray Scattering (GISAXS) that is a good candidate to examine surface morphology evolution with unprecedented detail. GISAXS has its power by being surface sensitive, non-destructive, applicable to different growth and experimental
environments and providing statistical information over several square millimeters area.

This study is intended to carefully look at the early time kinetics of thin film growth where growth conditions are optimized to create a very simple environment. Room temperature deposition of amorphous silicon (a-Si) through DC magnetron sputtering onto an amorphized Si substrate provides us the very basic growth environment where crystallinity, grain boundaries and substrate mismatch should have no impact. Silicon substrates were amorphized before deposition to minimize effects related to surface tension and to remove the native oxide. Performing the growth at room temperature results in adatoms having limited surface mobility. Ex-situ Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM) studies provide information complementary to the GISAXS results.

GISAXS is a highly surface sensitive technique because it uses incidence and exit angles close to the critical angle of the total external reflection ($\alpha_c \approx 0.1$-$0.5^\circ$). The angle of incidence for these GISAXS experiments was $0.165^\circ$, which is equal to the critical angle of the a-Si thin films at this specific x-ray energy used and this specific thin film density. The critical angles of the total external reflection of the a-Si thin films were measured by Specular X-ray Reflectivity after the deposition of the thin film was completed. As can be seen in Figure 3, during GISAXS experiments, the surface normal is taken as the z-direction and the in-plane x- and y-directions are defined respectively as being parallel and
perpendicular to the projection of the incident x-ray beam on the sample surface. Additionally, the low roughness limit was satisfied during these experiments by having low effective $q_z$ and low average surface roughness as discussed in Chapter 2.1. In the GISAXS geometry the wavenumber transfer in the x-direction, $q_x$, is very small due to the small incidence and exit angles, so that the y-direction on the detector closely represents $q_y$ which we can approximate as simply the wavenumber transfer parallel to the sample surface and designate $q_\parallel$.

5.2. Experimental

All the real-time x-ray scattering studies are performed in a custom-built ultrahigh vacuum (UHV) chamber with a base pressure of $10^{-7}$ Torr installed onto a surface diffractometer on beamline X21 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. An x-ray beam with 10keV photon energy was used, and the scattered beam was recorded by a 487 x 195-pixel PILATUS detector from Dectris Inc. located 818 mm away from the sample with 172-micron pixel size.

The area detector simultaneously measures in-plane scattering at a range of exit angles ($\alpha_{\text{out}}$) positions in the GISAXS geometry. The range of measurements for in-plane scattering is $0.2 \text{ nm}^{-1} < q_\parallel < 4.77 \text{ nm}^{-1}$ at exit angles between $0.16^\circ$ and $0.17^\circ$. As a result our GISAXS experimental setting is sensitive to the changes on the surface in the one-nanometer to the thirty-nanometer range. The in-plane diffuse scattering information was obtained from the detector images by integrating, at each $q_\parallel$ value, pixels at five adjacent $\alpha_{\text{out}}$
positions around the Yoneda wing (with average of 0.165°) to have better surface sensitivity and count rate.

DC Magnetron sputtering deposition of a-Si thin films was performed at room temperature. Growth substrates were 1 x 1 cm$^2$ silicon pieces cut from a 600 μm thick Silicon (111) wafer. The substrate surfaces were cleaned and amorphized by normal-incidence 2 keV Ar+ ion bombardment with 5.4 x 10$^{15}$ cm$^{-2}$ fluence using a Perker-Elmer Phi sputter gun before deposition. A DC Magnetron sputter source and 99.999% purity argon gas for the plasma were used. Argon gas pressure was set to 15 mTorr and 20 Watt was used for applied power.

5.3. Results and Discussion

The scattered x-rays at the Yoneda wing position are analyzed and temporal evolution of structure factor during DC magnetron sputtering of Si is presented in Figure 15. The average deposition rate was calculated as 0.85 nm/min from the XRR data taken after deposition stopped. The structure factor stops evolving as soon as the deposition stops suggesting that kinetics of the surface growth is deposition driven. The initial background scattering before the deposition started is carefully subtracted from the scans that are taken during the deposition. The GISAXS data shows a correlation peak forming and growing after the deposition started, suggesting correlated nanostructure formation and growth on the surface. The correlation peaks measured at different times are fit to Eq 10 to get the peak position $q_{max}$ and peak intensity $S_{max}$ where $y_0$ is a
constant offset value, \( A \) is the total area under the peak, \( \omega \) is a FWHM of the peak and \( q_{\text{peak}} \) is the peak center. As can be seen clearly from the figure itself, the correlation peak intensity increases as deposition continues and the peak position moves to lower \( q_{\parallel} \) values. This behavior suggests that correlated nanostructures are growing and coarsening as more material is deposited on the surface.

**Figure 15.** (a) In-situ GISAXS data of a-Si thin film deposition on a Si substrate via DC Magnetron Sputtering. The graph shows correlation peak evolution. The scattering before the deposition was subtracted from the data and the peaks were fitted to weighted Lorentzian equation (Eq 10) to analyze peak positions, widths and heights, (b) Calculated structure factor from Monte Carlo simulations of Ballistic deposition model. The correlation peak is forming and moving to lower wavenumbers as the monolayer numbers increase.
\[ I(q_{||}) = q_{||} \times \left( y_0 + \frac{A}{\pi} \times \frac{\omega^2}{4(q_{||}-q_{\text{peak}})^2 + \omega^2} \right) \] (10)

Temporal evolution of the correlation distance \((R=2\pi/q_{\text{max}}\text{, where } q_{\text{max}} \text{ is the in-plane correlation peak location})\) between the nanostructures for a-Si surface structures is linear as can be seen from Figure 16. According to the GISAXS data the initial average nanostructure size is 5.4 nm in diameter, which can be interpreted as the diffusion length for a-Si atoms on the surface. The intensities of the correlation peaks are plotted against time in Fig. 17. The temporal evolution of \(S_{\text{max}}\) is linear with time suggesting the correlation of the surface structures gets stronger as their sizes grow. Experimentally, scaling of the individual structure factor patterns at different times by \(q_{\text{peak}}\) in the x axis, and \(S_{\text{max}}\) in the y-axis makes all patterns collapse to a single one (Figure 18 (a)). This suggests the a-Si surface structures are self-similar.

Furthermore, SEM images taken at different times of the deposition are presented in Figure 19 (a)–(g). SEM images show mound-like structures forming and growing in size over time, and these structures are sitting on a continuous film. SEM results support the GISAXS data by showing the evolution of the mound-like structures on the surface.
Figure 16. Correlation length as a function of average film thickness (a) Obtained from GISAXS data (b) Deduced from results Monte Carlo simulations of ballistic deposition model.

Figure 17. Temporal Evolution of peak intensity is linear with time (a) GISAXS data (b) Monte Carlo simulation of ballistic deposition model.
In order to model the growth system, a ballistic deposition model with self-shadowing and desorption mechanisms\textsuperscript{47,48} has been developed. A ballistic deposition model has been chosen for this specific system because the nanostructures are self-similar and correlated as can be seen in fractal-like growth which can be result of ballistic deposition \textit{without} surface relaxation. In this model, deposition atoms leave from a randomly chosen location with a cosine angular distribution with respect to the z-direction and move until they hit an occupied site on a 512 x 512 lattice. The deposition atom either sticks to the arriving location or is re-emitted with an outgoing angle that is a cosine distribution around the local surface normal. The probability of an atom undergoing re-emission depends on a sticking coefficient parameter. If an atom is re-emitted from the first site and hits on an occupied lattice site, it sticks to the second lattice position; otherwise the bounced atom leaves the simulation. When an atom sticks to any place, the random relaxation process starts. During the relaxation process, a given number of atoms are randomly chosen around the sticking atom within a given diameter. The chosen atom may relax to a new location within its second nearest neighbor distance. The movement of a chosen atom depends on the total number of bonds for the current and possible new atom position. Since using a cosine distribution to choose the trajectory of incoming or bouncing atoms increases the probability of an atom sticking on a higher surface site than just lower positions, this results in self-shadowing mechanisms\textsuperscript{47,48}. When the ballistic deposition model is run with 0.6 sticking
45 coefficient, 60 relaxation steps with relaxation radius of 10 neighbors after each atom deposition, and when the relaxing atom is forced to move only if it can go to a site with more bonding, a good agreement with the data has been reached.

Figure 18. Structure factors scaled by $q_{\text{peak}}$ in x-axis and $S_{\text{max}}$ in y-axis showing collapse onto a common lineshape. (a) GISAXS data (b) Monte Carlo simulation of a ballistic deposition model.

Figure 15(b) shows the calculated structure factors from the Monte Carlo simulation of ballistic deposition model. In order to compare the simulation results with the data, a simulation unit is taken to be equal to 0.22 nm in real space length. A correlation peak forms and moves in to smaller wavelengths as the numbers of monolayers are increased. The overall behaviors of the structure factors are shown in Figure 15 are very similar to each other. Additionally, the correlation peak positions and heights at different simulation times are deduced by fitting simulation results to a Gaussian line shape. It can clearly be seen from
Figure 16 (b) and 17(b), both peak intensity and position have linear temporal evolution in agreement with GISAXS data. Furthermore, the correlation peaks calculated from Monte Carlo simulations also exhibit dynamic scaling behavior (Figure 18 (b)).

**Figure 19.** SEM images of early-time a-Si at different thicknesses (a-g) and calculated surfaces from a ballistic deposition model at different numbers of monolayers (h-k). The temporal size evolution of the surface structures is in agreement between SEM images and simulations((h) 25 ML (5.5 nm), (i) 50ML (11.0 nm), (j) 75 ML (16.5 nm), (k) 100ML (22.0 nm)).
Some images of simulated surfaces by a ballistic deposition model for different total monolayers are also presented in Figure 19 (h)–(k). The simulated surfaces have mound-like structures and they grow over time similar to what the SEM results suggested.

5.4. Conclusion

Real-time GISAXS studies of early stage kinetics of amorphous silicon thin film growth by DC Magnetron sputtering was performed in order to develop a better understanding of the growth kinetics for room temperature deposition. Correlated nanostructure formation and coarsening on top of a continuous a-Si film are found to be the primary growth mechanisms occurring under these specific deposition conditions. The correlation peak position and intensity evolution are determined from fitting the measured structure factors to Eq 10. The temporal evolution of the correlation distance and total amount of correlation between the self-similar nanostructures is linear with film thickness. We do not know of any applicable analytic models which reproduce these features. However, the kinetic Monte Carlo simulations of a ballistic deposition model with self-shadowing and desorption mechanism shows very good agreement with the x-ray data and SEM studies.
6. Co-GISAXS as a New Technique to Investigate Surface Growth Dynamics

6.1. Introduction

As the result of continued improvement in coherent flux from high brilliance synchrotrons and free-electron lasers, X-ray Photon Correlation Spectroscopy (XPCS) offers new possibilities of measuring local dynamic processes in equilibrium and nonequilibrium systems. XPCS shares physical principles with other Photon Correlation Spectroscopy (PCS) techniques. When coherent light illuminates any material with disorder (static or dynamic), it gives rise to a speckle pattern that depends on the phase differences of the scattered wave from different parts of the sample. As the measured system undergoes changes, the speckle intensities fluctuate in time. XPCS is based on measuring speckle correlation, typically via the intensity autocorrelation function $g_2(t)$. In this study we show that XPCS offers a powerful new way to probe local surface dynamic processes during thin film deposition using coherent x-rays in a Grazing Incidence Small Angle X-ray Scattering geometry (Figure 20), i.e. via Co-GISAXS. GISAXS has its power by being surface sensitive, non-destructive, and applicable to a wide range of growth and experimental environments. Consequently the Co-GISAXS approach gives unprecedented ability to measure dynamic evolution of the surface as a function of length scale. Previously, the dynamics of polymer systems and fluctuations of capillary waves on water surfaces have been studied using Co-GISAXS. However, to the best of our
knowledge, this is the first time that Co-GISAXS is used to study fundamental surface dynamics during thin film growth.

Figure 20. Schematic diagram of Co-GISAXS measurements during sputter deposition of Si and WSi$_2$.

The interpretation of the speckle correlation from a nonequilibrium growth system can in general be very complicated. Therefore this study carefully examines the late time dynamic process of kinetic roughening during amorphous thin film growth after the surface roughness reaches a dynamic steady state. Kinetic roughening is a ubiquitous process but, despite much discussion, the extent to which actual systems obey simple models remains controversial. To optimize the scattering signal for these proof-of-concept experiments, we have deliberately chosen growth conditions which lead to relatively rough surfaces. Room temperature deposition of amorphous silicon (a-Si) and amorphous tungsten disilicide (WSi$_2$) through DC magnetron sputtering onto silicon (Si) and silicon dioxide (SiO$_2$) substrates respectively provides the basic growth
environment in which crystallinity, grain boundaries and lattice mismatch with the substrate should have no impact. However, for growth at room temperature adatoms have limited surface mobility, resulting in complex surface and internal structures.

6.2. Experimental

Real-time x-ray scattering studies are performed in a custom-built ultrahigh vacuum (UHV) chamber with a base pressure of $3 \times 10^{-8}$ Torr capable of holding a DC magnetron sputter deposition source. The deposition chamber is installed onto a diffractometer on beamline 8-ID-I of the Advanced Photon Source (APS) located at Argonne National Laboratory. Incoming partially coherent x-rays with 7.38 keV photon energy are focused to a beam of dimension of $20 \times 4 \mu m^2$ at the sample position to improve speckle contrast. Grazing incidence angles of x-ray beam are chosen to be less than or equal to the critical angle of total external reflection ($\alpha_c$) of the deposited materials to decrease the bulk scattering and to improve surface sensitivity. A two-dimensional Princeton Instruments direct illumination CCD camera, which is located 4067 mm away from the sample, is set to measure the scattered intensity with two-second intervals with a readout time of 1 second and pixel size of $20 \times 20 \mu m^2$. In order to record a wider region of $q_{\parallel}$ space, the detector location is periodically moved horizontally while keeping the detector-to-sample distance constant. Each detector location shares 20 mm of overlap with the previous one to guarantee continuity of the data. The scattered x-rays are recorded around the
Yoneda wing position\textsuperscript{43}, which is where enhanced surface scattering occurs when the exit angle of the scattered x-rays $\alpha_{out} = \alpha_c$. When $\alpha_{out}$ is higher than $\alpha_c$, the scattering becomes less surface sensitive and starts to have more bulk scattering component. On the other hand, the scattering becomes more surface sensitive when $\alpha_{out} < \alpha_c$ but less intense. In order to check the effect of exit angle on $S(q||)$ and $g_z(q||, t)$, the recorded data is analyzed at three different $q_z$ locations: 0.1° above the exit critical angle, 0.1° below the exit critical angle and at the Yoneda wing position itself (i.e. at the exit critical angle).

The temporal evolution of scattered intensity was used to determine when the surface roughening process reached a steady state. In general, the scattering at higher wavenumbers saturates sooner than at smaller ones. The steady state conditions for all length scales examined were reached within 8000 seconds after the deposition started. All other data presented in this study only includes results taken after steady state conditions were satisfied.

The deposition of a-Si and a-WSi$_2$ thin films is performed using DC magnetron sputtering at room temperature. Argon gas of 99.999% purity is used for the plasma. The sputtering targets are pre-sputtered for an hour with shutter closed to remove any contamination and oxide layers before deposition starts. The substrates have 1 × 2 cm$^2$ dimensions and are solution cleaned before being put into the vacuum chamber. The a-Si thin films are deposited on the 600\textmu m thick Si (111) wafers with Ar gas pressure of 10 mTorr. Two different deposition powers (20W and 40W) are used to investigate effects of the deposition rate on
surface dynamics. The a-WSi$_2$ thin films are grown onto 200$\mu$m thick SiO$_2$ templates with 25W deposition power and with 10mTorr Ar gas pressure.

Post-growth specular X-ray reflectivity investigations of the a-Si and a-WSi$_2$ thin films are performed to measure $\alpha_c$ and the density of the films after each deposition is completed. The critical angle of the a-Si thin films is measured as 0.21° which is 0.03° less than the critical angle of crystalline Si at this energy. The calculated density of the a-Si thin films using these critical angle measurements as well as ex-situ SEM micrographs and microbalance results, suggests that the grown films have 70% of the density of crystalline silicon. The measured critical angle for a-WSi$_2$ thin films is the same as expected for crystalline WSi$_2$, 0.45°, suggesting that the films have the same density as crystalline WSi$_2$.

6.3. Results

6.3.1. a-Si Thin Film Deposition

During the Co-GISAXS measurements, the incidence angle for incoming x-rays is set to 0.16° which is well below the $\alpha_c$ of the films to emphasize scattering from the surface and near-surface (< 5 nm) layers. The values of in-plane reciprocal space accessed were 0.005 Å$^{-1}$ < $q_{||}$ < 0.121 Å$^{-1}$, corresponding to lateral length scales of $2\pi/q_{||}$ ~ 50-1250 Å. Exit angles measured on the area detector were 0.028° < $\alpha_{out}$ < 0.394°.
Figure 21. Steady-state GISAXS intensities measured at exit angles below, at, and above the Yoneda wing during a-Si thin film growth. The intensities are fit by a heuristic equation containing a Gaussian function and power law as discussed in the text. Fit parameters are given in Table 1.

Figure 21 shows the GISAXS intensity, which is proportional to the structure factor $S(q_{||})$, measured after the surface roughness evolution reached a steady state. The structure factors measured at the three distinct exit angles all behave as a power law at low $q_{||}$ but there is increased scattering with a shoulder at the higher wavenumbers. The amount of increased scattering at high $q_{||}$ and the exact exponent of the power law at low $q_{||}$ change with exit angle. The more pronounced bump at higher exit angle suggests that the extra scattering is coming from the near-surface layers.
Figure 22. Ratio of Power Law to Gaussian component of the structure factor at $q\parallel = 0.02 \text{ Å}^{-1}$ as a function of exit angle for growth of a-Si and a-WSi$_2$. The ratio grows significantly below the critical angles for the two films.

All structure factors are fit by a heuristic equation which is the sum of a Gaussian function and a power law:

$$I(q\parallel) = I_p q\parallel^{-m} + I_g e^{-q^2/2\sigma^2} \quad (II)$$

The fit results for each structure factor (above, at, and below the Yoneda wing) can be found in Table 1. The results of the fits are generally consistent, though the exponent of the power law increases slightly as the exit angle increases. The width of the Gaussian function indicates that near-surface scattering is coming from structures approximately 100 Å in lateral size. Figure 22 shows the ratio of the power-law to Gaussian components at $q = 0.02 \text{ Å}^{-1}$ as a function of exit angle. It is seen that the power-law component increases rapidly relative to the
Gaussian component as the exit angle decreases below the critical angle. This suggests that the power-law component of the scattering comes from the surface itself while the Gaussian component comes from the near-surface region.

<table>
<thead>
<tr>
<th>Label</th>
<th>Incidence Angle</th>
<th>Exit Angle</th>
<th>Power Law Exponent (± 0.25)</th>
<th>Gaussian Width (σ)</th>
<th>Correlation size (2π/σ)</th>
</tr>
</thead>
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<tr>
<td>Below Yoneda</td>
<td>0.16°</td>
<td>0.11°</td>
<td>2.45</td>
<td>0.061 Å⁻¹</td>
<td>103 Å</td>
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<tr>
<td>Above Yoneda</td>
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<td>0.31°</td>
<td>2.90</td>
<td>0.068 Å⁻¹</td>
<td>92 Å</td>
</tr>
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Table 1. The results of the heuristic function fits of the structure factors of the a-Si thin films during steady state growth.

After the scattering reaches a steady state, the dynamics are investigated through the intensity autocorrelation function $g_2(q_{||}, t)$. Since scattering at exit angles above the Yoneda peak shows increased contributions from near-surface scattering which can lead to interference between surface and near-surface scattered waves, we focus on the scattered intensity at the Yoneda wing and below it. The $g_2(q_{||}, t)$ results are fitted with Eq. 4 to yield the correlation times $\tau(q_{||})$ and exponents $n(q_{||})$. As Fig. 23 shows, the $g_2(q_{||}, t)$ functions clearly show compressed exponential behavior. The fit correlation times are presented in Fig. 24. At long time scales the beamline optics may not be stable, so the longest correlation times should be interpreted cautiously. At both the Yoneda wing location and below, $\tau(q_{||})$ decreases approximately as a power law and then
decreases more slowly at larger $q_{\parallel}$ (i.e. for real-space correlations < 80 nm). The modest $\tau(q_{\parallel})$ regions displaying power law behavior are fit and the resulting exponents are $z \sim 1.24$ at the Yoneda position and $z \sim 1.05$ for the exit angle below it.

**Figure 23.** Typical homodyne $g_2(t)$ intensity autocorrelation function for steady-state growth of a-Si and a-WSi$_2$. The correlation decay follows a compressed exponential.
Figure 24. Correlation times for a-Si thin film growth measured at exit angles below and at the Yoneda wing.

Figure 25. Compressed exponents from the $g_2(t)$ fits for exit angles below and at the Yoneda wing for a-Si growth.
Figure 25 shows the measured exponents $n(q_{||})$ from the $g_2(q_{||},t)$ fits as a function of wavenumber. Their behavior is complex. In general the compressed exponents stay less than 1.5 for $q_{||} < 0.02\text{Å}^{-1}$ at all exit angles but then increase to approximately 2.

**Figure 26.** Comparison of a-Si deposition at 20W and 40W. a) GISAXS intensity b) correlation time and c) compressed exponent.

In order to investigate the effects of the deposition rate on the surface dynamics, the deposition power is increased from 20W to 40W and the GISAXS scattering is examined at a single detector position. Deposition studies have shown that the deposition rate is approximately linearly proportional to deposition
power. As the deposition rate is doubled, the structure factor remains unchanged (Fig. 26a). On the other hand, the values of $\tau(q_{||})$ decrease by the factor of 1.8 at a given wavenumber as the deposition rate is doubled (Fig. 26b). This confirms that the time scales for dynamics at the surface are only driven by the deposition itself, not by equilibrium thermal effects. We have also found that the surface dynamics cease entirely when the deposition is halted (not shown). The compressed exponents remain unchanged (Fig. 26c).

**Figure 27.** Cross-section SEM image of a-Si thin film.

*Ex-situ* cross-sectional SEM study of the a-Si thin film shows highly elongated structural domains within the film that are aligned parallel to the surface normal (Fig. 27). Each domain has a width of approximately 3000 Å and a height that can be as large as the total film thickness. The domains are separated from each other by narrow, deep valleys. In contrast, the Gaussian-components of the x-ray results are the result of near-surface structures with only a 100Å size scale. Though it is more difficult to see these finer structures from
the SEM image, the existence of finer structures within these structural domains has been reported in the literature\textsuperscript{32,49}. Therefore, it seems likely that the 3000Å wide structural domains observed in SEM are formed of smaller structures, which cause the near-surface x-ray scattering observed.

6.3.2. a-WSi\textsubscript{2} Thin Film Deposition

![Figure 28](image.png)

**Figure 28.** Steady-state GISAXS intensities measured at exit angles below, at, and above the Yoneda wing during a-WSi\textsubscript{2} thin film growth. The fits are to a heuristic equation containing a Gaussian function and power law; results are given in Table 2.

The experimental geometry was chosen to enhance the surface sensitivity while maintaining sufficient signal-to noise-ratio. The incidence angle for incoming x-rays was set to $0.40^\circ$, which is lower than the critical angle for total external reflection for a-WSi\textsubscript{2} thin films, and the scattered x-rays were recorded at exit angles between $0.36^\circ$ and $0.7^\circ$. The in-plane scattering was examined over a similar range as for the a-Si growth.
Figure 29. Correlation times for a-WSi$_2$ thin film growth measured at exit angles below and at the Yoneda wing.

Figure 28 shows the GISAXS intensities of a-WSi$_2$ thin films after the surface growth reached a dynamic steady state. Similarly to the a-Si thin film results, all the intensities exhibit two regions: a power law region at low $q_\parallel$ and a region of increased scattering with a shoulder at high $q_\parallel$. The shape of the structure factor curves barely changes between different exit angles. As before, all the structure factors are fit by power-law and Gaussian components as given by Eq. 11; the fit results for each structure factor can be found in Table 2. As shown in Fig. 22, the ratio of power-law to Gaussian behavior increases sharply as the exit angle goes below the critical angle, again suggesting that the power-law behavior is associated with the surface itself and the Gaussian with the near-surface region. The exponent of the power law decreases slightly as the exit angle of the x-rays increases. The width of the Gaussian function suggests that
near-surface scattering is coming from structures which are approximately 90 Å in lateral size.

<table>
<thead>
<tr>
<th>Label</th>
<th>Incidence Angle</th>
<th>Exit Angle</th>
<th>Power Law Exponent (± 0.2)</th>
<th>Gaussian Width (σ)</th>
<th>Correlation size (2π/σ)</th>
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</thead>
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<tr>
<td>Below Yoneda</td>
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<td>Yoneda</td>
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<td>94 Å</td>
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<td>Above Yoneda</td>
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<td>0.55°</td>
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<td>67 Å</td>
</tr>
</tbody>
</table>

Table 2. The results of the heuristic function fits of the structure factor of the a-WSi2 thin films during steady state growth.

The local surface dynamics of the a-WSi₂ films was studied via the intensity autocorrelation function $g_2(q_\parallel, t)$, and correlation times $\tau(q_\parallel)$ and exponents $n(q_\parallel)$ were extracted similarly to the a-Si thin film case. Figure 29 shows how the correlation times depend on wavenumber for exit angles at the Yoneda wing and below. The stability of the beamline at long time scales (affecting the low $q_\parallel$ correlation times) and contribution from the near-surface scattering at high $q_\parallel$ caused $\tau(q_\parallel)$ to behave as a power law in very limited region for both exit angles. In this region $\tau(q_\parallel)$ varies as $\tau \sim q_\parallel^{-2.00}$ at the Yoneda wing and $\tau \sim q_\parallel^{-1.67}$ below it. The exponents $n(q_\parallel)$ obtained from fits of the $g_2(q_\parallel, t)$ function for a-WSi₂ films are plotted in Fig. 30; the compressed exponents are between 1.2 and 2, roughly comparable to what was found for the a-Si growth.
Figure 30. Compressed exponents from the $g_2(t)$ fits for exit angles below and at the Yoneda wing for a-WSi$_2$ growth.

The deposited a-WSi$_2$ thin films were studied by \textit{ex-situ} cross-sectional SEM (Fig. 31) to have a better understanding of structures within the film. Similar to the a-Si thin films, there are highly elongated structures within the a-WSi$_2$ thin films. By comparison to cross-sectional SEM images of a-Si thin films, it can be concluded that the structural domains in a-WSi$_2$ are narrower and still very tall. The finer structures (~200Å) are more pronounced than in the a-Si SEM image. The near-surface layer x-ray scattering is presumably from these finer structures sitting under the surface.
6.4. Discussion and Conclusions

The results for sputter deposited growth of a-Si and a-WSi$_2$ show similar systematic behaviors, allowing more general conclusions to be drawn. The x-ray scattering and SEM micrographs show that both film structures are complex. Post-facto AFM analysis shows that surface roughness is $\sim 5$ nm for the a-Si films and $\sim 2$ nm for the a-WSi$_2$ films. These are comparable to the sampling depth of the x-rays, so the results here should be considered as sampling the width of the film-vacuum interface. While surface scattering is consistent with power law spatial correlations on the longest length scales examined here, the structure at shorter length scales appears to be dominated by near-surface structures – possibly nano-columns that have been reported in earlier literature$^{32,49}$. 

![Figure 31. Cross-sectional SEM image of a-WSi$_2$ thin film.](image-url)
The Co-GISAXS technique has allowed us to examine the steady-state dynamics of kinetic roughening for the first time. Increasing the deposition rate shows that the dynamics are driven by the deposition process itself under the conditions studied here. However, just as the real-space structure of these films is complex, so is their dynamics complex as well. All $g_2(q_{||},t)$ functions exhibit compressed exponential relaxation, which is not consistent with linear models such as EW. Compressed exponents have been previously measured in wide variety of soft materials\textsuperscript{28,50-54} (gels, sponges, clays and emulsions), in magnetic and in electronic\textsuperscript{55-57} systems. Moreover, simulations of the KPZ model show that nonlinearities can produce compressed exponents, and the exponents measured here could be indicative of the nonlinear surface growth dynamics\textsuperscript{58}. However the particular wavenumber dependence of $n(q_{||})$ seen in these experiments is, to our knowledge, unique.

The measured correlation times are consistent with a power law behavior at the lower wavenumbers accessible but show a marked flattening toward the higher wavenumbers. This could be associated with the presence of near-surface structure seen in the scattered intensity itself. While simplified models such as KPZ may capture some of the essential physics of the surface growth dynamics over a limited range of length scales, additional mechanisms may be equally important at other length scales. In particular, continuum models such as KPZ make the basic assumption that the local surface growth velocity is uniquely determined through a specific function of the local surface gradient $\nabla h$. Such
models neglect important interactions between surface and near surfaces features (e.g. through relaxation of strain), as well as neglecting other nonlocal effects such as shadowing.

Within structure factor and correlation time power law regimes, exponents measured here vary but are clearly inconsistent with predictions of the linear EW model. They are rather closer to those predicted by the nonlinear KPZ model, but a detailed understanding of the compressed exponents of the $g_2(q_{\parallel},t)$ function predicted by the model does not yet exist. Now that such detailed experimental information about surface dynamics is available from Co-GISAXS, it’s clear that a more detailed dialogue of experiment with theory/modelling modeling of amorphous growth is warranted.
7. Using Coherent X-rays to Directly Measure the Propagation Velocity of Defects during Thin Film Deposition

7.1. Introduction

A key objective for understanding surface dynamics during thin film growth is the ability to monitor nanometer-scale surface fluctuation dynamics in real time\(^{13,23,59}\). These fluctuations of roughness and density occur on timescales that rarely exceed a few seconds, and take place in environments that are inaccessible to most high spatial resolution probes. For example, scanning probe microscopy is widely used to study interfacial reactivity in non-vacuum environments\(^{60}\), but is limited by inability to probe surfaces in real time during deposition; electron microscopy is mainly limited to high vacuum environments and low magnetic fields\(^{61,62}\). X-rays have the potential to overcome these challenges due to their highly penetrating nature and sensitivity to nanometer-scale features. Observation of subsurface structures in real time during film growth appears to be even more challenging, and has rarely been attempted\(^{63}\). Bulk signals are sometimes observed as unwanted background in grazing incidence surface X-ray scattering experiments, but there have been few attempts to quantitatively understand the features responsible for such signals\(^{64,65}\).

Interaction of surfaces with nanometer-scale buried defects and formation of bulk defects at a growing surface are integral to many industrial processes. For example, misfit dislocations nucleate at free surfaces and buried interfaces in...
strained layer epitaxial growth of layers for photonic devices\textsuperscript{66}, motion and ordering of oxygen vacancies in complex oxide materials for ferroelectric memory depend on the surface conditions during growth\textsuperscript{67-69}, and voids in electrochemically deposited layers used for interconnects in electronic circuits are introduced by surface processes during deposition\textsuperscript{70}.

The use of X-ray scattering techniques to probe \textit{in situ} real-time processes has largely been restricted to well-ordered crystalline structures and to statistical averages of disorder due to limitations in the spectral brightness of X-ray sources. A fundamental limitation in this regard is the coherence length of X-rays, usually <1 µm, which imposes an averaging over many coherence volumes contained within X-ray beams of typical dimensions\textsuperscript{4,7,71}. However, recent advances in high spectral brightness sources, along with parallel advances in X-ray area detectors has led to a new frontier in X-ray scattering through techniques such as X-ray photon correlation spectroscopy (XPCS)\textsuperscript{11,18,72-76} that can follow the natural thermal fluctuations in condensed matter systems\textsuperscript{4,77}.

Here, we describe a new application of coherent X-rays that extends scattering studies to observation of local fluctuation dynamics during film growth via XPCS, and also provides a sensitive measure of the relative propagation velocity of surface and subsurface features. This technique opens up possibilities for studies of surfaces\textsuperscript{71}, interfaces\textsuperscript{78,79}, and bulk defects\textsuperscript{64,65}, such as for crystal growth in the step-flow mode, where monolayer steps propagate with a well-defined velocity and direction\textsuperscript{80,81}. 
When a coherent beam of light falls on an object with any type of disorder, static or dynamic, the scattered light forms a speckle pattern composed of an apparently random array of bright spots (Fig 32a). If the different parts of the object fluctuate in time, the speckle pattern also fluctuates on the same timescale due to the changing pattern of interference between the scattered waves. In this case where dynamics are present, XPCS can characterize fluctuation time scales as a function of length scale via the X-ray wave vector transfer $q$. XPCS has previously been utilized for studies of thermal fluctuations on surfaces such as capillary waves on liquid surfaces and polymer film surfaces$^{13, 17, 23}$. Employing heterodyne measurements by mixing in a reference signal can increase the signal-to-noise ratio and also opens the possibility of obtaining phase information. Heterodyne mixing from bulk samples has been observed up to a wave vector transfer of $q \sim 0.02 \text{ Å}^{-1}$ using an external random scatterer as a static reference$^{82}$. Heterodyne mixing of surface scattering has been observed at relatively small values of the in-plane wave vector transfer, $q_{||}$, on the order of $10^{-6} - 10^{-5} \text{ Å}^{-1}$ (i.e. rather large length scales) due to a fortuitous overlap between the tails of the specular reflected beam and the non-specular surface scattering. However, coherent mixing of surface scattering with a reference wave at larger scattering vector (smaller length scales) has not been demonstrated. Here, we report the observation of a new phenomenon -- coherent mixing of the bulk and surface waves (Fig. 32b,c) -- that provides access to the relative phases of the scattered signals up to $q_{||} \sim 0.12 \text{ Å}^{-1}$. The strategy that we employ is to use the
surface advancing at a constant growth velocity to produce a quasi-static reference wave in order to deduce whether bulk defects propagate along with the surface as they form (homodyne mixing case) or whether they form localized features that do not propagate (heterodyne mixing case).

Figure 32. Schematic of the experiment and coherent mixing effects. (a) X-rays from the synchrotron source are focused by a compound refractive lens (CRL) and a collimating slit system into an ultra-high vacuum sample enclosure. An amorphous thin film is deposited, which causes the surface to advance at the growth velocity, and also induces random fluctuations in the surface roughness. Scattered coherent X-rays form a speckle pattern that corresponds to the
detailed configuration of the surface, which is recorded versus time by a high-resolution photon sensitive X-ray area detector. (b) In addition to scattering from the surface (green lines and equation), the X-rays penetrate beneath the surface and may be scattered by density variations in the bulk of the film (blue). The functions $g_s^{(1)}(\Delta t)$ and $g_b^{(1)}(\Delta t)$ correspond to the intermediate scattering functions for surface and bulk contributions respectively. (c) The two signals interfere coherently creating temporal correlations in the speckle pattern that can oscillate if the frequencies $\omega_s$ and $\omega_b$ of the two components differ. Note that the surface component $g_s^{(1)}(\Delta t)$ advances in phase with a frequency $\omega_s$ that is determined by the film growth velocity, and the bulk component $g_b^{(1)}(\Delta t)$ may be in-phase with the surface (homodyne mixing mode) or advance with a different phase (heterodyne mode), depending on the nature of the features responsible for the bulk scattering. The second order correlation function $g^{(2)}(\Delta t)$ can be extracted directly from intensity data, as described in the main text.

7.2. Results

We apply this novel approach to studies of amorphous thin films during magnetron sputter deposition by monitoring the grazing incidence small angle X-ray scattering (GISAXS) speckle pattern in real time (Fig. 32). The angle of incidence is chosen to be close to the critical angle for total external reflection, or slightly above it so that the signal escape depth can be varied over a wide range by changing the exit angle between the surface and the detected X-rays. Before
discussing the results in detail, we describe three principles of the measurement technique: (i) preparing a steady-state growth surface, (ii) extracting correlation decay lineshapes from a sequence of images, and (iii) varying the degree of mixing between surface and bulk waves by varying the exit angle.

An important aspect of this measurement is that the surface is prepared in a state of stationary surface dynamics where the average properties of the surface such as roughness are unchanging but local fluctuations occur as long as the deposition continues. We find that amorphous surfaces often obey the Family-Vicsek scaling relation for surface growth\textsuperscript{33,34}:

\[ w(L, t) \sim L^\alpha f \left( \frac{t}{L^z} \right) \]  \hspace{1cm} (5)

where \( w(L,t) \) is the interface width due to roughness, \( L \) is the system size or lateral length scale, \( z \) is the dynamic growth exponent and \( \alpha \) is the roughness exponent. The scaling function \( f(u) \) satisfies \( f(u) \to 1 \) for \( u \to \infty \), and so the surface width approaches a steady state value within the range of length scales accessible to the experiment. This is verified by monitoring the static GISAXS intensity averaged over the speckles (Fig. 33 and Supplementary Figs. 39 and 40). Information about local fluctuations is contained in the time-time correlation function\textsuperscript{35},

\[ < h(q_{||}, t_1) h(q_{||}, t_2) > \sim g_{ss}(q_{||}^z |t_1 - t_2|) \]  \hspace{1cm} (6)

where \( h(q_{||}, t) \) is the Fourier component of the surface amplitude at wave vector \( q_{||} \) and time \( t \). This expression is valid for \( t_1, t_2 \to \infty \) and \( |t_1 - t_2| \) finite, i.e. the so-
called steady-state regime. Also, \( \lim_{x \to \infty} g_{SS}(x) = 0 \), so Equation 6 implies that the correlations decay with a time constant \( \tau_s(q_{||}) \sim q_{||}^{-z} \). We find that for thin film growth with conditions used in this work, the surface time constants are relatively long (compared to, e.g. the expected timescales for surfaces during epitaxial growth), \( \sim 100 \) seconds or larger (Fig. 34).

A second important aspect of this method is the evaluation of the surface correlation decay time constant \( \tau_s(q_{||}) \) from experimental data and comparison to theoretical models. We utilize standard data reduction methods of XPCS by relating the measured intensity versus time \( I(q, t) \) to the intensity autocorrelation function

\[
g^{(2)}(q, t) = \frac{\langle I(q, t')I(q, t' + t) \rangle}{\langle I(q) \rangle^2} \quad (1)
\]

The above equation can be decomposed into a simpler product of correlation functions of electric fields rather than intensities

\[
g^{(2)}(q, t) = 1 + \beta(q)|F(q, t)|^2 \quad (2)
\]

where \( F(q, t) = g^{(1)}(q, t)/g^{(1)}(q, 0) \) is the normalized intermediate scattering function with \( g^{(1)}(q, t) \sim \langle E(q, t')E^*(q, t' + t) \rangle \), and \( \beta(q) \) is the optical contrast factor. The intermediate scattering function is related to density-density variations in the sample, and in the case of GISAXS the surface scattering is related to variations in the height of the surface through \( g_s^{(1)}(q, t) \sim \langle h(q_{||}, t')h^*(q_{||}, t' + t) \rangle \). It follows from our discussion of the statistical
properties of growing surfaces that the intermediate scattering function takes the form

\[ g_s^{(1)}(\mathbf{q}, t) \sim \exp\{i \omega_s t - \left[ \tau_s(q_{||}) t \right]^{\gamma} \} \quad (12) \]

where \( \omega_s = q_z v \) is the product of the component of the momentum transfer perpendicular to the growing surface and the growth velocity \( v \), and \( \Gamma_s(q_{||}) = 1/\tau_s(q_{||}) \). This form matches closely to the form describing capillary waves on liquid surfaces \(^{30}\), except that capillary waves propagate in the plane of the surface and so the phase depends on the in-plane component of the wave vector transfer, while in the case of surface growth the velocity is normal to the surface.

The stretching exponent \( \gamma \) takes into account the possibility that the equation of motion of the surface is non-linear, i.e. that it may include terms such as \((\nabla h)^2\), in which case the decay of the correlations does not have to be a simple exponential. In the absence of any optical mixing, i.e. neglecting the bulk contribution to the scattering, the theoretical expression for the intensity autocorrelation function becomes

\[ g_s^{(2)}(\mathbf{q}, t) = 1 + \beta(\mathbf{q}) \exp\{-2\left[ \tau_s(q_{||}) t \right]^{\gamma} \} \quad (13) \]
Note that the phase information is lost in the single-wave homodyne detection scheme. This mode is achievable in GISAXS by varying the incidence and detection angles $\alpha_i$ and $\alpha_f$ of the X-rays with respect to the surface. Fig. 34a illustrates a case where the incidence and exit angles are both less than the critical angle for total external reflection $\alpha_c$, and the decay of the correlations is consistent with Equation 13. Curve fitting results show that surface correlations decay with $\gamma \approx 1.2 - 1.7$, indicating a compressed exponential line shape (Supplementary Tables 3 and 4).

**Figure 33.** Static intensities during steady state growth. Data averaged over speckles for exit angles $\alpha_f$ above and below $\alpha_c$, the critical angle for total external reflection as a function of the in-plane component of the scattering vector $q$. Two
sets of curves are shown: for a Silicon film (squares) and a WSi$_2$ film (circles).
The intensity at angles below the critical angle is lower because the X-ray escape depth is greatly reduced, and the difference between the intensities at the two different exit angles gives a qualitative indication of the bulk contribution. Note that the critical angles measured for WSi$_2$ and Si with 7.35 keV X-rays are approximately $\alpha_c = 0.40^\circ$ and $0.21^\circ$ respectively. The incidence angles are $\alpha_i = 0.39^\circ$ and $\alpha_i = 0.26^\circ$ respectively.

The third, and most novel aspect of this method is heterodyne mixing. We vary the incidence or exit angle to control the X-ray penetration and escape depths in order to control the amount of mixing between the surface and bulk waves. Note that the bulk signal is not assumed to be entirely static, since features formed at or just beneath a growing surface will no longer contribute to the signal after they become deeply buried. In contrast, previous heterodyne mode XPCS methods have relied on a perfectly static reference wave$^{11,13,17,82,83}$. Our approach here is that it is not necessary to have a perfectly static reference wave, rather we have a symmetric situation where either wave can be considered to be the reference. This does somewhat complicate the analysis and fitting since in general there are more unknown parameters to determine. However, tuning the mixing ratio by varying the X-ray penetration and escape depths over a wide range provides a powerful method for decoupling the two signals or mixing them in almost any ratio desired. Following the discussion of
surface correlations above, our trial form for the intermediate scattering function for the bulk wave is

\[ g_b^{(1)}(\mathbf{q}, t) \sim \exp\{i\omega_b t - \Gamma_b t\} \quad (14) \]

If we assume that randomly distributed bulk features do not segregate to the surface, then for a given angle of incidence the maximum time constant at large exit angles should be \( \tau_{b,\text{max}} \approx \Lambda/\nu \), where \( \Lambda \) is the penetration depth of the incident X-rays and \( \nu \) is the growth velocity. For example in the case of a Silicon surface with 7.35 keV X-rays incident at 0.21°, the penetration depth is about 1500 Å, so that with a growth velocity of 0.57 Å/s, we estimate \( \tau_{b,\text{max}} \approx 2500 \) s (Fig. 36b). Moreover, the assumption that the bulk features do not segregate also implies that they have zero velocity, so that \( \omega_b = 0 \).

The intensity autocorrelation function for coherent mixing of two waves with intensities \( I_s \) and \( I_b \) evaluates to

\[
\langle I(\mathbf{q}, t')I(\mathbf{q}, t' + t) \rangle - \langle I(\mathbf{q}) \rangle^2 = I_s^2 \left[ g_s^{(2)}(\mathbf{q}, t) - 1 \right] + I_b^2 \left[ g_b^{(2)}(\mathbf{q}, t) - 1 \right] + 2\beta I_b I_s \text{Re} \left[ g_s^{(1)}(\mathbf{q}, t) g_b^{(1)*}(\mathbf{q}, t) \right] \quad (15)
\]

Note that we can recover the form for a static reference wave by setting one of the \( g^{(1)}(\mathbf{q}, t) \) functions in Equation 15 to unity and the corresponding \( g^{(2)}(\mathbf{q}, t) \) equal to \( 1 + \beta \). Upon inserting the intermediate scattering functions for both waves from Equations 12 and 14, we have
\( \langle I(q,t')I(q, t+t) \rangle \sim 1 + I_0^2 \exp\left[-2 \left[ \Gamma_s(q_{||}) t \right]^v \right] + I_b^2 \exp(-2 \Gamma_b t) \)
\( + 2I_bI_s \cos((\omega_s - \omega_b) t) \exp\left[-\left[ \Gamma_s(q_{||}) t \right]^v - \Gamma_b t \right] \) \hspace{1cm} (16)

Equation 16 is our master equation that can describe the correlations of any combination of surface and bulk waves with different intensities, time constants, and growth velocities. Note that the phase information is included in the last term, and that in the special case \( \omega_b = 0 \), heterodyning is observed and the correlation function oscillates with a period
\[ T_{HD} = \frac{2\pi}{q_z v} \] \hspace{1cm} (17)
while for the case \( \omega_b = \omega_s \) there will be no oscillations. We refer to the latter case as homodyne mixing to distinguish it from single-wave homodyne. Fig. 32c illustrates both heterodyne and homodyne mixing.

The measurements discussed above were carried out over a range of \( q_{||} \) up to 0.12 Å\(^{-1}\) and \( q_z \) up to \( \sim 0.03 \) Å\(^{-1}\) for two different amorphous thin film systems, WSi\(_2\) and Silicon. We confirmed that the averaged intensity was unchanging \( \sim 2000 \) s after the start of each deposition (Supplementary Figs. 39 and 40). Post-growth atomic force microscopy measurements showed surface roughness of 4-6 nm under the conditions used here. Fig. 33 shows evidence for bulk scattering since the speckle-averaged intensity for exit angles above the critical angle is larger than for below the critical angle. The bulk signal also converges to a steady state during the deposition due to the limited penetration
depth of the X-rays at the grazing angles used in the experiment, as discussed above.

Figure 34. Identification of heterodyne and homodyne mixing. Examples of temporal correlation data and fitting results for (a-c) WSi$_2$ and (d-f) Si are shown. The surface component dominates at grazing exit angles below the critical angle and the heterodyne curve calculated from Equation 16 is almost indistinguishable from the surface homodyne curve calculated from Equation 13 (a and d). In contrast, the bulk component becomes significant enough to produce a strong heterodyne effect for exit angles above the critical angle (b and e). At larger $q_{||}$, the bulk component becomes dominant, but no heterodyne oscillations are observed for any exit angle (c and f show results for high $q_{||}$ and large exit angle). This is interpreted as the bulk and surface contributions having the same frequency, i.e. $\omega_b = \omega_s$, in the 2-wave homodyne mixing mode.
Correlation curves were calculated from the x-ray data using Equation 1, and were fitted using Equation 16 for each dynamic $q_{||}-q_z$ mask region. The resulting correlation curves (Fig. 34) exhibit strong heterodyne mixing at low $q_{||}$, up to about 0.05 Å$^{-1}$ in both cases, but only for exit angles above the critical angle (Fig. 34b,e). Fig. 35 shows the heterodyne period extracted from the fitting results. In order to calculate $q_z' = k(\sin \alpha_f' + \sin \alpha_i')$, we use corrected incidence and exit angles $\alpha_i' = (\alpha_i^2 - \alpha_e^2)^{1/2}$ and $\alpha_f' = (\alpha_f^2 - \alpha_e^2)^{1/2}$. Fig. 35 shows that the heterodyne period varies linearly with $1/q_z'$, and does not vary systematically with $q_{||}$. Moreover, both growth velocities are in agreement with quartz crystal microbalance (QCM) calibration and post-deposition cross sectional Scanning Electron Microscopy measurements of film thickness within 20%. In order to make the QCM results agree with the measured growth velocities perfectly, we need to assume that the actual film density is less than the nominal bulk density (2.33 and 9.30 g/cm$^3$ for Si and WSi$_2$, respectively). This is not unreasonable under the conditions used. For example, there have been reports of a density deficit, which increases with sputtering pressure in amorphous metal and semiconductor films$^{84}$. It is notable that many transmission electron microscopy studies have been carried out that show $\sim$100 Å voids in a broad range of thin films deposited by various methods, such as sputter deposition, thermal evaporation, and electroplating$^{70}$. In addition, there have been reports of diffuse scattering in small angle electron diffraction patterns of amorphous Si thin films.
that were attributed to voids\textsuperscript{85}. Thus voids or other defects are natural bulk scatterers to provide heterodyne interference.

**Figure 35.** Measurement of the surface velocity from the heterodyne period. (a) Examples of heterodyne oscillations for Si at several $q_z'$ with $q_\parallel = 0.011$ Å\textsuperscript{-1}. The red lines are fitted curves using the heterodyne model. Each curve is displaced from the one underneath it by 0.2. (b) The heterodyne period is found to be linear with $1/q_z'$, and independent of the in-plane component of $\mathbf{q}$. Data points are for several values of $q_\parallel$ between 0.006 - 0.026 Å\textsuperscript{-1} and 0.022 - 0.042 Å\textsuperscript{-1} for Si and WSi\textsubscript{2} respectively. Lines are the calculated heterodyne periods for the surface growth velocities indicated in the figure.
Figure 36. Control of the homodyne mixing ratio by varying the exit angle. (a-c) Summary of Silicon fitting at $q_\parallel = 0.1$ Å$^{-1}$. (a) Correlation versus delay time at $\alpha_i = 0.21^\circ$. The optical mixing is modeled as homodyne in this region of $q_\parallel$ due the complete absence of heterodyne oscillations. Note that at this particular combination of $q_\parallel$ and exit angle the surface and bulk wave intensity factors ($I_s$ and $I_b$ in Equation 16) are nearly equal. (b) Time constants of surface and bulk contributions averaged over $q_\parallel = 0.10$ to 0.12 Å$^{-1}$. The bulk and surface components are distinguishable since they have significantly different time constants. (c) Variation of surface and bulk wave intensities with exit angle. The surface component dominates below the critical angle, while the bulk component dominates above it. (d) Surface and bulk wave intensities for WSi$_2$ averaged over $q_\parallel = 0.08$ to 0.10 Å$^{-1}$. The intensities cross at a higher angle compared to (c) because the critical angle is larger for WSi$_2$ than for Si.

The picture described above is appealing, but incomplete since we observe that the heterodyne oscillations disappear for $q_\parallel > 0.05$ Å$^{-1}$ although it is clear from Fig. 33 that the bulk signal is still present at the highest $q_\parallel$. Fig. 36 shows that there are still two components present in the correlation decay plot at high $q_\parallel$, and they can be distinguished in two ways: (i) the surface and bulk
signals have different time constants, and (ii) surface and bulk wave intensities vary in a systematic way as a function of exit angle. The results show unambiguously that there are still two waves undergoing optical mixing. The lack of heterodyne oscillations suggests that there is a population of defects with very different characteristics (e.g. propagation or segregation velocity) compared to the features that produce the heterodyne signal at lower $q_{||}$.

We model this phenomenon as a bulk wave with a phase that advances with the surface so that $\omega_b = \omega_s$. In this case, the heterodyne term in Equation 16 is still present, but it does not vary with time and so there are no oscillations; this is the homodyne mixing mode. The behavior of this second population of defects is consistent with elongated three-dimensional features that grow with the surface. It is known that a wide variety of thin films (both amorphous and crystalline) form in a columnar morphology\textsuperscript{30}. These features are readily observed with scanning electron microscopy, and for our films the column widths are several thousand angstroms (Supplementary Fig. 41). However, this is much too large to explain the bulk signal that we observe. Scanning tunneling microscopy experiments on Si sputter deposited onto highly oriented pyrolytic graphite have found bundles of much smaller nanowires with diameters in the range of 30 – 70 Å and at least 1000 Å long\textsuperscript{38}, which is in good agreement with our results. Moreover, we note that a much earlier small-angle X-ray scattering study found evidence for highly anisotropic rodlike features with similar dimensions in amorphous Germanium films\textsuperscript{86}. This type of nanocolumnar
structure with the long axis of the nanocolumns oriented perpendicular to the film surface has been suggested to be generally present in thin films prepared under low mobility conditions independent of the method of vapor deposition used to prepare the film. These features should naturally produce scattering with a phase that advances with the surface. In this picture, the ‘surface’ signal corresponds to the tops of the nanocolumns, while the ‘bulk’ signal corresponds to the sides of the nanocolumns.

7.3 Conclusions

Coherent mixing of surface and bulk X-ray scattering waves provides a powerful way to recover relative phase information during thin film deposition. We have applied the effect to measure the dynamics of nanoscale surface and sub-surface features that are not readily distinguishable from each other in conventional X-ray scattering. The results reveal surprisingly rich insights into thin film growth dynamics and defect formation. We conclude that there are two defect populations: compact void-like features forming near the surface that are buried during deposition, and a second population of elongated column-like features. The void scattering mixes with the surface scattering to produce a heterodyne signal, with oscillations arising from the relative motion of the growing surface with respect to the defects. The oscillation frequency corresponds well with the surface growth velocity, implying that the voids do not segregate \( v_b = 0 \). In contrast, the scattering from the sides of the nanocolumns mixes with the surface scattering to produce a two-wave homodyne signal, since these features
propagate upward in coincidence with the surface. A highly surface sensitive mode is also demonstrated, where the surface dynamics itself is accessed independently of the subsurface structure. The ability to monitor these fundamental processes using Coherent GISAXS represents an important step forward in elucidating the nanoscale mechanisms underlying thin film deposition processes.

7.4. Methods

The experiments were carried out at beamline 8-ID-I at the Advanced Photon Source (APS) at Argonne National Laboratory. An X-ray wavelength of 1.69 Å (E = 7.35 keV) was selected using a double bounce Ge(111) monochromator with a bandwidth of $\Delta \lambda / \lambda \sim 3 \times 10^{-4}$. The X-ray beam was focused to 20 μm (H) by 4 μm (V) at the sample through a compound refractive lens and collimating slits, with a flux of $\sim 7 \times 10^{10}$ ph/s. A direct detection charge-coupled-device with 20 μm pixels (Princeton Instruments LCX-1300) was placed 4 m from the sample.

A custom stainless steel vacuum chamber with Beryllium windows was constructed for this experiment. The chamber is pumped via a turbo-molecular pump with magnetically levitated bearings (Edwards STP-301), with a 65 lb. vibration isolator installed on the backing line, and backed by a scroll pump. The sample is held on a sample stage in vertical reflection geometry with no in-vacuum motions. The entire chamber is rotated about an axis that passes
through the sample surface via a 2-circle segment (Huber 5203), which is part of the standard beamline setup. See Fig. 2 for a photograph of the system installed at APS 8-ID-I.

A downward facing water-cooled sputter gun (Meivac) capable of holding 2" diameter targets is used as the deposition source. It is placed at a distance of 100 mm above the substrate surface in normal incidence. WSi$_2$ and Si sputtering targets purchased from Kurt Lesker Corp. are bonded to copper backing plates. Substrates are either pieces of Silicon wafers (for the Si depositions) or Silicon wafers with a 500 nm thermal oxide (for the WSi$_2$ depositions). A sputtering power of 20 W (for the Si depositions) or 25W (for the WSi$_2$ depositions) is produced by a DC power supply (Advanced Energy MDX500). The Argon pressure during sputtering is between 10 and 16 mTorr. This pressure range is chosen because it is above the roughening transition pressure for WSi$_2$ (~6 mTorr)$^{87}$. The sample stage was replaced with a quartz crystal microbalance for calibration of deposition rates. Calibration runs were done in the same chamber both before and after the X-ray experiments, and were found to be reproducible within 3%, which indicates that changes in the deposition rates during the experiments due to erosion of the targets or other factors was minimal. Several post-deposition measurements were performed on the films, including Atomic Force Microscopy to characterize the surface roughness and cross-section Scanning Electron Microscopy to image the microstructure in the bulk of the films.
Data collection scans are performed at a fixed angle of incidence. The detector intercepts a total range of $q_\parallel \sim 0.025 \, \text{Å}^{-1}$ during each scan, so 6 overlapping regions were used to reach the full range of $q_\parallel$, 0.003 to 0.12 Å$^{-1}$. We define $q_\parallel$ as being the component of the wave vector transfer $q = k_f - k_i$ in the plane of the surface, while the perpendicular component is denoted as $q_z$. All scans are performed on each sample during a single long continuous deposition in order to ensure that the sample surface is maintained in steady-state conditions. Each scan consists of 50 dark images, followed by 1024 images with 2 seconds integration. Note that the first scan for each sample during the transient period of surface development is not used for the steady-state analysis. See Supplementary Figs. 39 and 40 for examples of the transient behavior.

XPCSGUI is a custom MATLAB based analysis package for XPCS data sets. XPCSGUI was used to define $q_\parallel$-$q_z$ mask regions and to compute intensity autocorrelations and two-time correlations. Fitting of $g^{(2)}(t)$ intensity autocorrelation curves is accomplished with a least-squares Levenberg-Marquardt minimization with a fitting function based on Equation 16. See Supplementary Tables 3 and 4 for detailed fitting results.
7.2. Supplementary Information

7.2.1. Heterodyne and homodyne analysis of WSi$_2$ deposition at 16 mTorr Argon pressure.

Figure 37. Summary of $g^{(2)}$ correlations for three different values of $q$, with fitted curves for the heterodyne model (a and d), and the homodyne model (b, c, e, f). Note that (a), (d), and (f) are reproduced in Fig. 34 of the main text. The fitting equation is based on Equation 16 in the main text.

This document shows analysis with 20 dynamic regions of exit angle, each 50 pixels high and 18 regions of $q$. Note that there 6 scans per sample and so there are $20 \times 18 \times 6 = 2160$ fitted curves like the ones in Fig. 37 above. Each curve is normalized using static intensity derived from a mask with 60 regions in exit angle and 90 regions in $q$. 
### Data parameters

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**Table 3** Summary of fit parameters for the temporal correlation results shown in Fig. 37. Column labels marked by an asterisk indicate parameters that were held constant, and individual parameters marked by an asterisk are at a limiting value. The heterodyne period $T$ is not relevant for the homodyne fitting, and so these parameters are marked with NA. The main fitting parameters are: surface intensity factor $I_s$, surface time constant $\tau_1$, stretching exponent $\gamma_1$, heterodyne period $T$, bulk intensity factor $I_b$, and bulk time constant $\tau_2$. Note that the contrast factor $\beta$ is folded into the intensity factors $I_s$ and $I_b$. 

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**Note:**
- $q_\parallel$: Parallel component of the scattering vector.
- $\varphi_f$: Phase of the incident wave.
- Baseline*: Baseline value for the fit.
- $I_s$: Surface intensity factor.
- $\alpha_1$: Surface time constant.
- $\alpha_1^*$: Surface time constant with an asterisk (limiting value).
- $T$: Heterodyne period.
- $I_b$: Bulk intensity factor.
- $\alpha_2$: Bulk time constant.
7.2.1.1. Start of deposition

The deposition was started at 14 mTorr and the pressure drifted up to 16 mTorr during the first two scans. The angle of incidence was nominally 0.45 degrees, and the exit angle ranged from about 0.3 degrees to as much as 0.65 degrees from the bottom of the detector to the top. The in-plane component of $q$ ranges from 0.021 A$^{-1}$ to 0.044 A$^{-1}$ for the “Sq2” scans.

![Figure 38](image)

**Figure 38.** Total scattered intensity at 0.5 deg exit angle at the beginning of the deposition (left). Two-time correlation plot for the same data (right).

The deposition is started at frame 20 of scan Sq2_001. The effect is noticeable in both the two-time plots as well as one-time $g^{(2)}$ plots. Images were collected every 2 s, so that frame 20 corresponds to 40 s of elapsed time.

The total diffuse intensity, above left, increase by an order of magnitude when the deposition is started. Then there are a few oscillations that damp out by about 500 seconds. That corresponds to about 460 seconds of deposition at 0.18 nm/sec, which is about 80 nm. This can be compared to the penetration
depth -- which is a little over 100 nm. It makes sense that the oscillations are from interference between scattering from the top surface and the interface. These oscillations in the diffuse scattering are analogous to oscillations in the specular that are known as Kiessig fringes. But diffuse Kiessig fringes should only happen in special circumstances where the interface and surface structures are correlated. That would appear to be the case here. One easy way for this to happen is if the film is not continuous. Then the part of the interface that is exposed is "different" than the part that is covered, and this will lead to diffuse scattering that can interfere with the scattering from the top surface of the film.

The plot on the right is the two-time correlation plot for the same scan. It is made with the "top" detector mask, which is a 300-pixel mask positioned just above the critical angle and covering about 0.08 degrees of exit angle. The main correlation streak is very uniform, but there are noticeable additional streaks that are away from the main diagonal. These streaks correspond to a time-displaced correlation, which is related to the growth velocity of the surface. The peak marks the time delay for the scattering from the surface at a later time to come back into correlation with itself from an earlier time. It is interesting that the effect appears almost immediately after the growth is started while Kiessig fringes are present, and then seems to damp out as the intensity oscillations damp out. Then, the effect gets stronger again near 700 sec and keeps going until the end of the scan.
Figure 39. Total intensity (left). Two-time correlation plot showing that the heterodyne effect is well established during steady state deposition (right). The film is thick enough that the substrate/film interface no longer plays a role.

The second scan is in the same q range and immediately follows the first 2048 sec scan with the deposition continuing throughout. It shows the same effect, which seems to get even stronger, even showing the second order beat clearly. The first scan started at 14.4 mTorr and ended at 15, while the third scan started at 15.8 mTorr.

Note that in subsequent data analysis it was found that the 300 pixel high mask is too large, since it tends to wash out higher order fringes. All other plots in this document use narrower mask regions.
7.2.2. Heterodyne and homodyne analysis of Si Deposition at 10mTorr 20W

0.26deg incidence

Figure 40 Summary of $g^{(2)}$ correlations for three different values of $q$, with fitted curves for the heterodyne model (a and d), and the homodyne model (b, c, e, f). The fitting equation is based on Equation 16 in the main text.

With the angle of incidence above the critical angle of 0.21 degrees, scattering from the bulk and near surface region are very noticeable. By varying the exit angle, we can distinguish surface scattering from these contributions.
Table 4. Summary of fit parameters for the temporal correlation results shown in Fig. 40. Column labels marked by an asterisk indicate parameters that were held constant, and individual parameters marked by an asterisk are at a limiting value. The heterodyne period $T$ is not relevant for the homodyne fitting, and so these parameters are marked with NA. The main fitting parameters are: surface intensity factor $I_s$, surface time constant $\tau_1$, stretching exponent $\gamma_1$, heterodyne period $T$, bulk intensity factor $I_b$, and bulk time constant $\tau_2$. Note that the contrast factor $\beta$ is folded into the intensity factors $I_s$ and $I_b$. 

<table>
<thead>
<tr>
<th>Data parameters</th>
<th>Fit parameters</th>
</tr>
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<tbody>
<tr>
<td>$q_\parallel$ (Å$^{-1}$)</td>
<td>Baseline*</td>
</tr>
<tr>
<td>0.011</td>
<td>0.15</td>
</tr>
<tr>
<td>0.052</td>
<td>0.15</td>
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<tr>
<td>0.110</td>
<td>0.15</td>
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<td>0.011</td>
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<td>0.38</td>
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<tr>
<td>0.110</td>
<td>0.38</td>
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</table>
7.2.2.1 Scanning Electron Microscopy

The columns observed near the top surface of the sample have a width of several hundred nm.

Figure 41. SEM cross section for Silicon Sample 3.
8. Conclusion

Controlling surface growth processes during material deposition is a key to growing materials for today’s technologies with predicted properties. Therefore real-time x-ray scattering techniques have been used to investigate surface growth processes with unprecedented detail during thin film deposition to expand our fundamental understanding not only for improving the quality of existing materials but also improving designs for future materials. Conventional GISAXS is a powerful tool to investigate early-time kinetic evolution of the surfaces, so it is used to investigate early stages of indium island growth and early-time a-Si thin film growth. However, regular GISAXS is not sensitive to distinguish the late-time dynamical behaviors known as kinetic roughening where the spectrum of average surface roughness remains unchanged but local dynamics processes continuous to evolve. Moreover, the final structure of the thin films is usually defined by the processes during the kinetic roughening regime. Coherent-x-ray GISAXS (Co-GISAXS) has been developed as a powerful tool to investigate the steady-state dynamics of kinetic roughening during thin film growth. All the x-ray scattering results are supported by ex-situ AFM and ex-situ SEM (Table 5).

The early stages of growth for indium on sapphire have been investigated via real-time GISAXS, and the effective surface growth processes are found to be a nucleation, growth, and coalescence of hemispherical islands in complete agreement with Family-Meakin model. The findings of this work strengthen the idea of using the FM model to describe early time thin film Volmer-Weber growth
processes of island formation, impingement and coalescence. Furthermore, real-time GISAXS studies of early stage kinetics of amorphous silicon thin film growth by DC Magnetron sputtering were performed in order to develop a better understanding of the growth kinetics for room temperature deposition. GISAXS data showed that correlated mound-like nanostructures are forming and coarsening on the surface and their overall kinetic evolution has strong similarities to fractal-like growth. Additionally, ex-situ SEM images show that the mound-like structures are sitting on a continuous a-Si thin film and the structure sizes grow with time. The x-ray results have been compared to Monte Carlo simulation of a ballistic deposition model with self-shadowing and desorption mechanisms and a good agreement has been achieved.

Real-time Co-GISAXS investigation of steady-state local surface dynamics of room temperature deposition of a-Si and a-WSi$_2$ via DC magnetron sputtering has been performed. Growth conditions are optimized to create an idealized kinetic roughening growth environment. Using incidence angles smaller than the critical angle of total external reflection, the x-ray sampling depths are kept within the surface roughness measured by post-facto AFM so the results are considered as sampling the width of the film-vacuum interface. While surface scattering is consistent with power law spatial correlations on the longest lengthscales examined here, the scattering at shorter length scales appears to be dominated by near-surface structures. Post-facto SEM studies showed that the structure of these films is complex, so is their dynamics. It has been shown
that within structure factor and correlation time power law regimes, exponents measured here vary but are clearly inconsistent with predictions of the linear EW model. They are rather closer to those predicted by the nonlinear KPZ model, but a detailed understanding of the compressed exponents of the $g_2(q_{||},t)$ function predicted by the model does not yet exist. Now that such detailed experimental information about surface dynamics is available from Co-GISAXS, it’s clear that a more detailed dialogue of experiment with theory/modeling modeling of amorphous growth is warranted.

<table>
<thead>
<tr>
<th>Chapter Number</th>
<th>Measurement Technique</th>
<th>Material</th>
<th>Deposition Technique</th>
<th>Investigated Stage</th>
<th>Substrate Temperature</th>
<th>Argon Pressure</th>
<th>Effusion Cell Temp. or Dep. Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Real-Time GISAXS</td>
<td>Indium</td>
<td>Thermal Evaporation</td>
<td>Early-time</td>
<td>40°C</td>
<td>NAN</td>
<td>600°C</td>
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<tr>
<td>5</td>
<td>Real-time GISAXS</td>
<td>Silicon</td>
<td>DC Magnetron Sputtering</td>
<td>Early-time</td>
<td>Room Temperature</td>
<td>15 mTorr</td>
<td>20 W</td>
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<tr>
<td>6</td>
<td>Real-time Co-GISAXS</td>
<td>a-Si a-WSi$_2$</td>
<td>DC Magnetron Sputtering</td>
<td>Steady-state Roughening</td>
<td>Room Temperature</td>
<td>10 mTorr-40 W-25 W</td>
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<tr>
<td>7</td>
<td>Real-time Co-GISAXS</td>
<td>a-Si a-WSi$_2$</td>
<td>DC Magnetron Sputtering</td>
<td>Steady-State</td>
<td>Room Temperature</td>
<td>10mTorr-16 mTorr</td>
<td>20 W</td>
</tr>
</tbody>
</table>

**Table 5.** Summary of the experimental details for different chapters
Furthermore, we have shown that Co-GISAXS also offers a powerful new tool to investigate correlations between surface and subsurface structures by coherent mixing of surface and bulk x-ray scattering. Real-time Co-GISAXS investigation of the dynamics of nanoscale surface and sub-surface features during room temperature sputter deposition of a-Si and a-WSi$_2$ has been done. The results suggest that there are two types of defects existing within the thin films: compact void-like features forming near the surface that are buried during deposition, and a second population of elongated column-like features. It is shown that the void scattering mixes with the surface scattering to produce a heterodyne signal, with oscillations arising from the relative motion of the growing surface with respect to the defects. In contrast, the scattering from the sides of the nanocolumns mixes with the surface scattering to produce a two-wave homodyne signal, since these features propagate upward in coincidence with the surface. The ability to monitor these fundamental processes using Coherent GISAXS represents an important step forward in elucidating the nanoscale mechanisms underlying thin film deposition processes.

8.1. Future Work

The power of Co-GISAXS has been shown as a new approach to investigate steady-state kinetic roughening dynamics of surfaces and subsurface defects. Many unanswered questions and issues related to fundamental surface growth processes can start to be addressed. However, improvements are needed in the experimental apparatus. First, Co-GISAXS investigation of the
steady-state kinetic roughening dynamics of amorphous thin films was limited by
the experimental chamber which does not allow sample cooling or heating. The
power law nature includes a wide range of timescales, so studying the dynamical
scaling carefully requires a wide dynamical range. In the current set up, the
shorter time scales are limited by the deposition rate and the longer time scales
are limited by beamline stability. If a cooling system can be implemented to the
current set-up, the deposition rate can be increased without adding extra thermal
energy to the system, and consequently the shorter time boundary could be
expanded allowing the investigation of dynamic scaling with more certainty.
Additionally, the dynamics of thermal relaxation during growth can be
investigated if the sample heating is implemented allowing definitive testing of
existing surface growth models to actual surface growth processes.

The Co-GISAXS technique can also be developed further to resolve the
problems in the epitaxial growth of oxide and nitrites. Existing characterization
techniques can only monitor early-time local surface dynamics during epitaxial
growth, which causes problems if the nature of the growth changes i.e. from
layer-by-layer growth to mounded-like growth. Co-GISAXS can offer crucial
additional information relevant to models of growing islands and mounds on the
surfaces. Likewise, studying new promising deposition techniques, such as
Atomic Layer Deposition (ALD) / Atomic Layer Epitaxy (ALE), through Co-
GISAXS would reveal new insight to the dynamics of the growth steps which
eventually can enable near-atomic level control of both stoichiometry and
thickness of nitrides or other materials. Furthermore, the Co-GISAXS technique has a potential to become a unique tool to investigate the heterogeneous dynamics during thin film growth such as discontinuous stress relaxation and 3-D Volmer Weber island formation, growth and coalescence.
**List of Journal Abbreviations**

<table>
<thead>
<tr>
<th>Journal Title</th>
<th>Abbreviation</th>
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<tr>
<td>Acta Crystallographica Section A</td>
<td>Acta Crystallogr. Sect. A</td>
</tr>
<tr>
<td>Current Opinion in Colloid &amp; Interface Science</td>
<td>Curr. Opin. Colloid. In.</td>
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<td>Current Science</td>
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<td>J. Vac. Sci. Tech. A</td>
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<td>Nano Letters</td>
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9. References


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Matter 24, 445006 (2012).


[58] M. Mokhtarzadeh, private communication.


Curriculum Vitae

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EDUCATION

Boston University College of Engineering
PhD and Master of Science, Materials Science and Engineering 2015

Sabanci University
Bachelor of Science, Materials Science and Engineering, Minor: Physics  June 2010

RESEARCH EXPERIENCE

BU Materials Science and Engineering  Boston, MA
Doctoral Research: “Real Time X-ray Studies of Fundamental Surface Growth Processes”

- Designed experimental setups, built vacuum chamber components, prepared experimental plans in advance with high precision, troubleshoot the any technical problems, and learn to operate highly sophisticated x-ray setups and UHV systems to perform in-situ deposition experiments at the synchrotron x-ray sources at Brookhaven National Laboratory (Upton, NY) and Argonne National Laboratory (Lemont, IL) during to the limited awarded measurement time (usually around one week per quarter).

- Studied surface processes during RF sputter deposition of amorphous silicon and tungsten-di-silicide thin films to have an atomic level control over material structures through in-situ Grazing Incidence Small Angle X-ray Scattering (GISASX), X-ray Photon Correlation Spectroscopy (XPCS) and ex-situ Specular X-ray Reflectivity (XRR), AFM, SEM and XRD.

- Investigated nucleation, coalescence and growth phenomenon during indium and gallium island deposition via Molecular Beam Epitaxy (MBE) to have better quality III-V semiconductor materials by using in-situ GISAXS and ex-situ XRD, XRR, AFM and SEM.
• Analyzed in-situ x-ray data: modeled and simulated complex surface growth processes.

**BU Materials Science and Engineering**

*Graduate Researcher*  
Boston, MA  
Fall 2010

• Designed and fabricated amorphous silicon thin film solar cells prototype to improve the light harvesting efficiency by using metal evaporator, DC magnetron sputtering, photolithography and chemical etching.

• Investigated effects of material growth techniques and growth conditions on photovoltaic properties of the devices through UV-visible absorption spectroscopy, FT-IR and I-V measurements.

**Sabanci University**

*Istanbul, Turkey*

*Undergraduate Research Assistant*  
2007-2010

• Investigated controlled assembly and crystal formation mechanisms through synthesis of colloidal gold and ZnO nanoparticles.

• Performed optical and structural characterization techniques (UV-visible absorption spectroscopy, Dynamic Light Scattering (DLS), FT-IR, C-NMR, H-NMR, PL Spectrometer); analyzed results, and wrote and defended an undergraduate thesis.

**Swiss Federal Institute of Technology Zurich (ETH-Z)**  
*Zurich, Switzerland*

*Undergraduate Research Intern*  
Summer 2009

• Synthesized metal nanoparticles by non-aqueous sol-gel method to employ them in various applications such as active material for CO$_2$ sensors, as catalyst in polymerization of various alcohols, and as coating material for laser detection process.

• Performed optical and structural characterization techniques (XRD, C-NMR, H-NMR, SEM); analyzed results, and wrote and presented project report.

**SKILLS**

**Technical Skills:** UHV systems, RF-Sputter Deposition, MBE, ALD, XRD, SEM, AFM, TEM, Ion Etching, Grazing Incidence Small Angle X-ray Scattering (GISAXS), X-ray Photon Correlation Spectroscopy (XPCS), Specular X-ray
Reflectivity (XRR), X-ray Fluorescence Emission (XRF), Photolithography, UV- visible absorption spectroscopy, Dynamic Light Scattering (DLS), FT-IR, C-NMR, H-NMR, PL Spectrometer.

**Software skills**: Matlab, Origin, MS Office, MAC, PC, SPEC, IsGISAXS, ImageJ & Inkscape.

**PUBLICATIONS**


**PRESENTATIONS**

