

# **Coherent X-ray Scattering Studies of Surface Evolution During Materials Growth and Modification**

A Proposal Submitted for Science at the LCLS:  
Category “A” Letter of Intent

Submitted: June 21, 2004

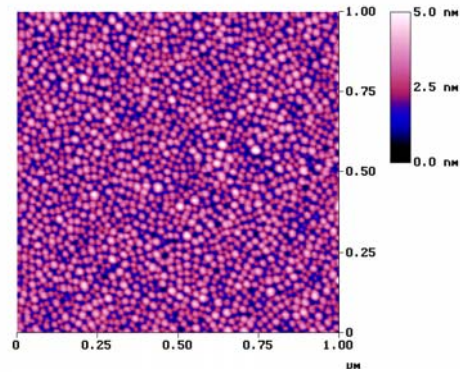
Prof. Randall Headrick  
Department of Physics  
University of Vermont  
Burlington, VT 05405  
(802) 656-0048 (office)  
(802) 656-0817 (FAX)  
rheadrick@uvm.edu

and

Prof. Karl Ludwig  
Department of Physics  
Boston University  
Boston, MA 02215  
(617) 353-9346 (office)  
(617) 353-9393 (FAX)  
ludwig@buphy.bu.edu

## I. Introduction

Advanced materials continue to be at the forefront of science and technology. The formation of these materials requires increasingly sophisticated growth techniques, surface modification regimens, or carefully controlled phase transitions. In many cases, there is the desire to create and control self-organized nanoscale features during growth and processing (as shown from the work of Headrick and collaborators in Fig. 1). Important progress has often been made through heuristic approaches, or on the basis of information obtained from detailed post mortem analysis of materials that have undergone processing. However, in many cases, the realization of these approaches' full potential will require a more detailed understanding of the detailed changes occurring during growth/processing.



**Figure 1** AFM image of self-organized mounds formed on a cobalt (0001) surface by 500 eV Ar<sup>+</sup> sputter etching. Similar methods can be used to form nanometer scale quantum dots on surfaces.

Synchrotron-based real-time x-ray studies offer at least four important advantages in gaining such fundamental insight: penetration of ambient gaseous/liquid environments, ability to vary depth of structural sensitivity, ability to probe structures from 10<sup>-1</sup> - 10<sup>3</sup> nm in length scale, and ease of interpretation. These attributes make *in-situ* x-ray study a uniquely powerful tool. Despite the natural advantages of x-ray photons as experimental probes, and the significant advances in their application to real-time studies of materials growth/modification in the past decade, limited temporal resolution and/or coherence have been major limitations.

The time-scales of relevance to modern materials growth/modification vary widely, but many, such as atomic diffusion or step motion on surfaces, are much less than a second. While existing insertion device beamlines at 2<sup>nd</sup> and 3<sup>rd</sup> generation sources have the brightness to examine associated surface scattering in a traditional, “incoherent” manner, they do not provide the ability to perform coherent scattering studies that could investigate in increased detail surface morphology evolution and step motion. The LCLS provides just such opportunities.

## II. Potential of Coherent Surface-Sensitive X-ray Scattering at the LCLS

While “coherent” x-ray scattering has been developing as a tool for the study of equilibrium fluctuations<sup>1</sup> and phase transition kinetics<sup>2,3,4</sup> in bulk materials, there have thus far been very limited application to surface structure. Our experience, however, suggests that the 10<sup>12</sup> photons in each pulse available from the LCLS, will be sufficient to create surface-sensitive speckle patterns with a typical statistical accuracy of a few percent. There are two different modes in which real-time surface-sensitive coherent scattering experiments can be utilized. First, experiments can be done in a serial manner,

sampling the surface evolution with the 120 Hz frequency of the x-ray pulse. For many cases, this will be sufficient. For those situations which require a higher time resolution, a pump-probe method can be utilized, with, for example, a pulsed laser deposition plume arriving at a set time before the x-ray pulse.

A key question is how such surface speckle patterns can be interpreted to reveal surface evolution during surface growth/modification. In the case of equilibrium fluctuation spectroscopy, where the amplitude of fluctuations is small, the decay of correlations can typically be analyzed within a linear response formalism. In studying growth and/or surface modification, we are often dealing with situations that are far from equilibrium. Thus far, the only theoretical or simulation treatments of speckle evolution in nonequilibrium systems of which we're aware examines coarsening of phase ordered or phase separated domains in bulk materials<sup>5,4,3</sup>. Typically these involve two-time correlations that are not accessible to traditional x-ray measurements of the time-evolving average single-time structure factor  $S(q,t)$ . At this time, no such theories or simulations are available for relevant surface models of growth or processing. However, models of surface evolution typically employ a Langevin formalism (such as, for instance, the Kardar-Parisi-Zhang equation or typical MBE models)<sup>6</sup>, as do the models of phase ordering and separation mentioned above. With the impending availability of surface x-ray speckle data, it is hoped that further theoretical and simulation progress can be made on the surface evolution problem as well.

Another approach to analyzing coherent surface scattering data is to invert it to obtain real-space coarse-grained pictures of the surface evolution. In the hard x-ray regime, the largest effort thus far has focused on inverting data taken near a Bragg peak of a microcrystallite<sup>7</sup>, but the Robinson group has also been making some progress in the surface scattering/reflection regime<sup>8</sup>. We can anticipate that trying to invert data to obtain a coarse-grained image of an evolving sample surface will be even more difficult.

One type of coherent surface-sensitive experiment at the LCLS might use a grazing-incidence small-angle x-ray scattering (GISAXS) geometry with a fixed incident beam and an area detector examining the scattering pattern. In the direction normal to the plane of incidence/specular reflection (which we will call here the "y-direction") the highest wavevectors examined by GISAXS typically correspond to lengths scales of a few nanometers, but the smallest wavevectors examined typically correspond to less than the micron size scale. In the direction along the length of the beam footprint (the "x-direction"), the highest wavevectors correspond to micron length scales. Thus the reconstruction of the surface morphology would be anisotropic – incorporating detailed, nanometer-size features in the y-direction but only large-scale variations in the x-direction. To take advantage of this, crystal steps due to miscuts could be lined parallel to the beam direction, so that the best resolution is obtained in the direction perpendicular to the steps.

Another type of coherent experiment might examine the evolution of the speckle near an anti-Bragg point. Because of the scattering geometry, this would give more nearly similar information in the two orthogonal surface directions. In collaboration with a

group at a CNRS laboratory (LTPCM) in Grenoble, one of the PI's (Ludwig) is currently part of a proposal submitted to develop such experiments at the ESRF (though, of course, without the coherent intensity necessary for real-time measurements).

In sum, then, the detailed interpretation of surface-sensitive coherent x-ray scattering is a topic that still presents challenges, but one on which progress is being made and which offers the possibility of unique insights into surface evolution during growth/modification.

### III. Research Directions:

In this section, we discuss the important contributions that real-time coherent studies at the LCLS might make in several materials growth/modification fields. In several of these fields, self-organized nanoscale features on surfaces can be obtained utilizing, for instance, sputter etching, strain effects, Stranski Krastanov growth, Volmer-Weber growth, or phase separation. Thus these studies form part of a larger effort in the community to create and control nanoscale features during growth and processing.

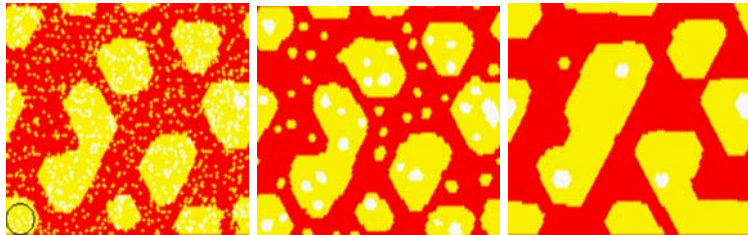
#### III.a Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a thin film deposition technique that has increased in importance over the last decade because of its flexibility and advantages in fabricating thin films of complex materials. Traditional materials systems for PLD include various complex oxides, such as high  $T_c$  superconductors and colossal magnetoresistance materials. However, materials of interest include semiconductors and even metallic films which often require ultra-high vacuum conditions. PLD performed in ultra-high vacuum conditions is referred to as pulsed laser molecular beam epitaxy, or PL-MBE.

One great advantage of PLD is that multi-element materials are deposited with the same composition as the target material, thus greatly simplifying the deposition of thin films of complex materials. Less widely appreciated advantages include: (i) since PLD is at the ultimate limit of non-equilibrium vapor deposition, metastable materials and nanoscale structures may be formed that are difficult or impossible to fabricate by other means, and (ii) the laser plume contains energetic particles that may promote smoothing of surface roughness (interfaces formed by PLD have been reported with  $< 1 \text{ \AA}$  RMS roughness in several cases).

Atomic diffusion on surfaces can occur on picosecond time scales.

Instantaneous pulse      Microsecond time scale      Millisecond time scale



**Figure 2** Kinetic Monte Carlo simulation of pulsed growth on a Cu(111) surface. The three colors correspond to the initial surface and two incomplete monolayers of deposited copper. The images show that the relaxation of the surface after a deposition pulse spans many orders of magnitude in time. The ability to probe these effects in the time domain will open up a new window on thin film growth and surface processes.

However, surfaces may evolve on times scales of seconds, or even longer in many cases. PLD presents an interesting opportunity, since film growth is accomplished by bursts of particle flux (composed of atoms, ions and small clusters) that last a few microseconds. The growth surface then continues to evolve until the next pulse arrives on the order of a second later. The time structure of the growth process thus spans six orders of magnitude.

In Fig. 2, we show an example of pulsed growth on a Cu(111) surface. A kinetic Monte Carlo simulation was performed on a 100 by 100 atom surface at 300K. Deposition in instantaneous pulses of 0.1 ML each are followed by a 100 msec “relaxation”. The figure shows the time evolution after the fourth pulse on an initially flat surface. Upon instantaneous deposition, the surface is covered with many monomers and dimers composed of Cu atoms. Since individual atoms and dimers are highly mobile, they rapidly coalesce into metastable 2D islands of 10-20 atoms. As time goes on, the smaller islands are absorbed into larger islands on the surface. This dynamic process is then repeated again and again during subsequent pulses.

Complex materials are thought to follow a pattern similar to the simple case of Cu(111). However, it has been widely speculated that there is an additional “assembly” step in which the elements composing the material aggregate into small units with the correct composition, which then diffuse around to join up to step edges or large islands.<sup>9</sup> The assembly process probably occurs only at very early time scales, and has thus far not been observed directly.

Although the experiments described above are flux limited experiments, the high coherent brightness of LCLS will bring new experiments into play, such as the study of surface evolution on short time scales with time-correlation spectroscopy.

### **III.b Atomic Layer Deposition**

Atomic layer deposition (ALD) is in some aspects similar to chemical vapor deposition (CVD) in that it utilizes chemical reactions between precursor molecules to deposit new material. However, unlike CVD processes, precursor species are introduced individually, in a pulsed mode. In conjunction with the proper chemistry limiting the adsorption to a single layer of the reactant molecules, this results in a highly controlled process with inherently atomic-layer resolution. Initially, the inherently low growth rates of the technique made it commercially unattractive relative to CVD or physical vapor deposition (PVD) techniques such as sputter, thermal or e-beam deposition. However, with the continued evolution of fabricated structures into the nano-regime, the layer-by-layer growth method characteristic of ALD has come to be seen as a significant advantage. It is now on the International Technology Roadmap for Semiconductors<sup>10</sup> because of future needs for precise nanoscale deposition of high- $k$  dielectrics, diffusion barriers, and electrodes<sup>11</sup>. Other applications are in nanocoating.

In traditional ALD the activation energy for precursor adsorption and reaction comes from the thermal background. In order to decouple reaction kinetics from substrate temperature, and hence avoid sample damage arising from higher temperatures, plasma-enhanced ALD (PE-ALD) is becoming increasingly important. The use of plasmas to

excite molecular hydrogen for the chemical reduction of metal precursors on the sample surface has been particularly promising [12].

The LCLS will enable detailed investigation of the structural evolution of ALD films during both their initial nucleation phase and during their steady state growth phase. Moreover, the millisecond time resolution achievable in many of the x-ray techniques will allow us to examine the surface evolution as the layer of precursor molecules is adsorbed and/or reacts. Key issues accessible to such studies include the evolution of surface morphology (ALD often leads to relatively rough surfaces) and the degree to which absorption and reaction processes are spatially homogeneous or heterogeneous on the surface.

The high brightness of the LCLS beam will increase the chance of unintentionally modifying surface chemistry during ALD. Therefore, an important component of initial studies will be to assess the effect of the x-ray probe on surface properties. Studies involving grazing angle scattering will spread the beam over a relatively large surface area, and thus minimize this type of effect. Since the ALD effect depends so critically on surface chemistry, it is expected to be more sensitive to such effects than most of the other processes described in this proposal.

### **III.c Ion and Plasma Bombardment of Surfaces**

Despite the technological importance of plasma-surface interactions<sup>13</sup> relatively little is known about the structural behavior of surfaces in contact with a plasma environment. Processes utilizing these interactions include deposition, etching, surface passivation, and ion implantation. As the technique has matured the complexity of process application has increased. For example, in state-of-the-art etch processing the delineation of device features is performed on the nanometer-scale and processing must stop on the atomic scale. To compound this complexity, the inherent damage of the plasma exposure must be minimized or, preferably, eliminated. To meet such stringent demands requires a continued transition of plasma process development from a traditionally empirical nature to one based on an understanding of plasma-surface interactions at the atomic level.

A major reason for our limited fundamental understanding of surface behavior in plasma environments is the difficulty of applying traditional surface electron techniques, such as LEED and RHEED, for *in-situ*, real time characterization in the 1-5 mTorr corrosive environment of interest. Far more effort in the field has therefore been placed on characterizing the plasma itself, using methods including electrostatic probe, stimulated and spontaneous optical emission, and mass spectrometry. At best, these methods produce measurable quantities that can be correlated to changes at the exposed surface - for instance, the relative concentration of reactant or product. Far fewer techniques, generally optical in nature, have made direct measurements of the state of the surface during plasma exposure. While the experiments and simulations discussed above have provided considerable insight into the nature of the surface during exposure to the plasma environment, detailed experimental information about the morphological evolution of the surface has been conspicuously absent. In the past several years, a number of experiments in which the PI's have been involved have shown the power of "traditional" surface-sensitive x-ray scattering to probe surface evolution during ion

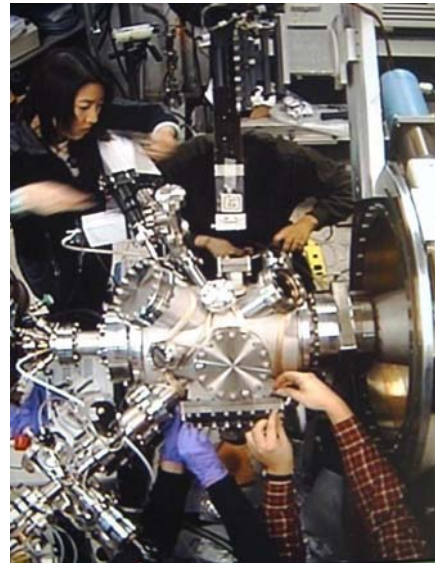
bombardment<sup>14</sup>, including the self-organized formation of nanoscale “dots” as shown in Fig. 1 above. However, surface-sensitive coherent x-ray scattering at the LCLS can provide much more detailed information than has previously been possible.

#### IV. Resources

The two PI’s are just completing the construction of a facility for real-time x-ray studies of materials on the insertion-device beamline X21 at the NSLS. It is funded with approximately \$500k support from NSF Major Research Instrumentation (MRI) and Instrumentation for Materials Research (IMR) grants, as well as matching funds from the PI’s universities. To promote flexibility, the x-ray spectrometer is designed so that modest-sized processing/vacuum chambers can be rolled onto a base diffractometer system. It allows multiple specialized chambers to be constructed, optimized for processing, and then moved onto the diffractometer for x-ray experimentation. This base diffractometer system is also compatible with one on the new insertion-device G-line at CHESS.

Experiments with the facility are initially focusing on, among other things, surface evolution during ion bombardment and plasma processing, growth of novel thin films by PLD and growth of III-V nitrides by MBE. Therefore processing and characterization equipment for these two chambers includes an Oxford Instruments ECR plasma source, an Applied Epi RF plasma source, Applied Epi effusion cells, a magnetron sputter deposition cell, a laser with PLD target, a Balzers mass spectrometer, an Auger system and a RHEED system. It is anticipated that the facility will continue to be run on the NSLS and the NSLS-II, but not all of the materials growth/modification equipment and UHV chambers will be used simultaneously there. Thus it is anticipated that significant sharing of resources might be possible, indeed desirable, between the facility at the NSLS and the one envisioned at the LCLS. Thus experiments at the NSLS facility could focus on those issues resolvable with traditional “incoherent” scattering and prepare the way for directed “coherent” x-ray experiments at the LCLS.

In order to perform such studies, a new surface diffractometer would be required along with some ancillary equipment. Using the design from the NSLS, we anticipate that capital funds of approximately \$300k will be necessary to construct an end-station facility for the proposed coherent x-ray studies of surface evolution during growth/modification. These funds would be sought from the NSF and DOD instrumentation programs, and from the DOE. Operating funds for current work are provided by DOE and NSF (including a new 5-year CAREER grant for Headrick), but on the timescale of the LCLS turn-on, new/renewal funding would need to be established at NSF or DOE.



**Figure 3** Members of the Headrick and Ludwig groups at work on the new real-time materials growth and modification facility at the NSLS.

## V. References

---

1. See, for instance, S. Brauer, G.B. Stephenson, M. Sutton, R. Bruning, E. Dufresne, S.G.J. Mochrie, G. Grubel, J. Als-Nielsen and D.L. Abernathy, *Phys. Rev. Lett.* **74**, 2010 (1995).
2. A. Malik, A.R. Sandy, L.B. Lurio, G.B. Stephenson, S.G.J. Mochrie, I. McNulty and M. Sutton, *Phys. Rev. Lett.* **81**, 5832 (1998); F. Livet, F. Bley, R. Caudron, E. Geissler, D. Abernathy, C. Detlefs, G. Grubel and M. Sutton, *Phys. Rev. E* **63**, 036108 (2001); A. Fluerasu, “*Coherent X-ray Studies of Non-Equilibrium Processes*”, Ph.D. Thesis, McGill University (2003) (to be published shortly with thesis advisor M. Sutton).
3. K.F. Ludwig, F. Livet, F. Bley, J.-P. Simon, R. Caudron, D. Le Bolloc’h and A. Moussaid, “X-ray Intensity Fluctuation Spectroscopy Studies of Ordering Kinetics in Cu-Pd Alloy”, to be submitted shortly to *Physical Review*.
4. L.-M. Stadler, B. Sepiol, R. Weinkamer, M. Hartmann, P. Fratzl, J.W. Kantelhardt, F. Zontone, G. Grübel and G. Vogl, *Phys. Rev. B* **68**, 180101 (2003); L.-M. Stadler, B. Sepiol, J.W. Kantelhardt, I. Zizak, G. Grübel, G. Vogl, *Phys. Rev. B* **69**, 224301 (2004).
5. G. Brown, P.A. Rikvold, M. Sutton and M. Grant, *Phys. Rev. E* **56**, 6601 (1997); *Phys. Rev. E* **60**, 5151 (1999).
6. A. Pimpinelli and J. Villain, *Physics of Crystal Growth* (Cambridge University Press, 1999); A.-L. Barabasi, H.E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, 1995).
7. I.K. Robinson, I.A. Vartanyants, G.J. Williams, M.A. Pfeifer and J.A. Pitney, *Phys. Rev. Lett.* **87**, 195505 (2001); G.J. Williams, M.A. Pfeifer, I.A. Vartanyants and I.K. Robinson, *Phys. Rev. Lett.* **90**, 17 (2003).
8. I.K. Robinson, J.L. Libbert, I.A. Vartanyants, J.A. Pitney, D.M. Smilgies, D.L. Abernathy and G. Grubel, *Phys. Rev. B* **60**, 9965 (1999); J.L. Libbert, R. Pindak, S.B. Dierker and I.K. Robinson, *Phys. Rev. B* **56**, 6454 (1997); I.A. Vartanyants, J.A. Pitney, J.L. Libbert and I.K. Robinson, *Phys. Rev. B* **55**, 13193 (1997).
9. V.S. Achutharaman, N. Chandrasekhar, O.T. Valls, and A.M. Goldman, *Phys. Rev. B* **50**, 8122 (1994)
10. <http://public.itrs.net/Files/2001ITRS/Home.htm> -- see for instance the Interconnect section.
11. For an overview of applications in silicon technology, see H. Kim, IBM Research Report RC22737 (available on the Web at <http://www.research.ibm.com>).
12. S.M. Rossnagel, A. Sherman and F. Turner, *J. Vac. Sci. Tech.* **B18**, 2016 (2000).
13. M.A. Lieberman and A.J. Lichtenbeg, *Principles of Plasma Discharges and Materials Processing* (John Wiley & Sons, New York, NY, 1994).
14. M. Ramana Murty, T. Curcic, A. Judy, B. Cooper, A. Woll, J. Brock, S. Kycia and R. Headrick, *Phys. Rev. Lett.* **80**, 4713 (1998); C.C. Umbach, R.L. Headrick and K.-C.

---

Chang, Phys. Rev. Lett. **87**, 246104 (2001); O. Malis, J.D. Brock, R.L. Headrick, M.-S. Yi and J.M. Pomeroy, Phys. Rev. B **66**, 035408 (2002); K.F. Ludwig, Jr., C.R. Eddy, Jr., O. Malis and R.L. Headrick, Appl. Phys. Lett. **81**, 2770 (2002).