

Pulsed Laser Deposition in G3 Hutch

Aaron Fleet¹ and Darren Dale²

¹Department of Applied and Engineering Physics, Cornell University

²Materials Science & Engineering, Cornell University

G-Line: A Unique Opportunity

In August of 1999, Joel Brock, then Director of Graduate Studies in Cornell's Department of Applied and Engineering Physics, contacted Aaron Fleet to inquire if he wanted to help build a new x-ray beamline at CHESS. As a naive first-year graduate student, the project was sold to him as a way to jump-start his research, learn the intimate details of synchrotron science on a level that few students could, and construct a unique experiment that materials researchers world-wide would envy. Joel's prophetic sales pitch failed to mention sleep deprivation.

Darren Dale had come to Cornell to study thin films of novel materials in Yuri Suzuki's laboratory in the Department of Materials Science and Engineering. Many interesting materials, for example high-temperature superconductors, magnetic oxide materials, and ferroelectrics, possess the perovskite crystal structure, with three or more constituent elements. Pulsed Laser Deposition (PLD) is widely used to grow such materials, primarily due to the similarity of the source and film stoichiometries. Despite its widespread use, researchers know little about the dynamic processes involved in PLD. Yuri, Darren, Joel, and Aaron formed a collaboration between the seemingly disparate fields to study the growth processes operating during PLD.

The G3 PLD initiative operates in the larger context of an Interdisciplinary Research Group (IRG) of the Cornell Center for Materials Research (CCMR). The IRG, composed of roughly one dozen faculty and graduate students from four Cornell departments, focuses on fundamental interactions between thin film growth and energetic particle beams. While researchers have intensively studied the physics of thermal (much less than one eV kinetic energy) deposition techniques (MBE, CVD) over the past sixty years, much less work has targeted understanding the effects of energetic beams (tens of eV) on crystal growth. Such techniques, e.g. PLD, sputter deposition, plasma-assisted deposition, are relative newcomers to the world of thin film growth, yet they have become standard techniques for a variety of materials in both academic and industrial settings. The primary objectives of the G3 PLD project are to determine the effects of the energetic plume on film growth, and to learn how to grow very smooth crystalline films with excellent magnetic and transport properties.

When we first arrived at CHESS, G-line was as incomplete as our grasp of x-ray science. No instrumentation was installed – even the lead shielding for the three hutches was absent. Over the subsequent five years, we participated in every aspect of G-line's construction, from painting the exposed section of tunnel in the vault, to the installation of the station and hutch computer systems, to the eventual commissioning of the x-ray optics. Our first major project was to develop a remote, computer-driven motion-control system (Figure 1). We designed and installed the entire system, comprised of a computer running SPEC, onboard motor indexers, and high-current motor drivers directly in the large G-line hutches. This system utilized much shorter motor cables than the standard CHESS design, reducing noise and current losses. The system, controlled via the networked station computers, continues to operate robustly after two years of synchrotron running.



Fig 1: G-line motion control system. All necessary hardware is located inside the hutch and controlled via the computer network.

While working on the beamline, we also designed and constructed a PLD system to operate in the G3 hutch (Figure 2). As one of only two PLD systems in the world specifically designed for x-ray studies, the system would allow a unique opportunity to investigate materials growth *in-situ*.

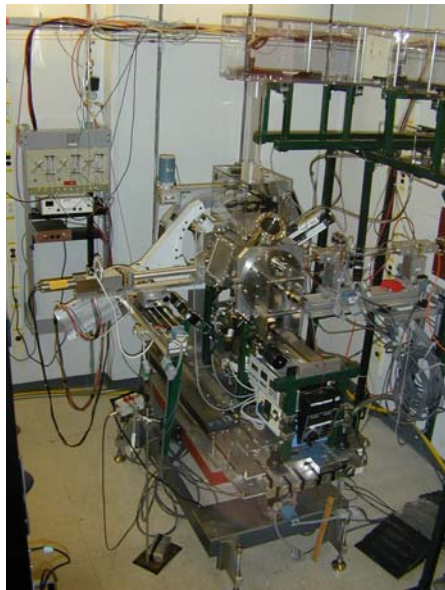


Fig 2a: The G3 hutch. The laser flight path is located 7 feet off the floor [The Eximer laser (not shown) is located to the upper right of the PLD chamber] in order to make room for other equipment. The G3 infrastructure supports toxic gas handling for the laser and film growth.

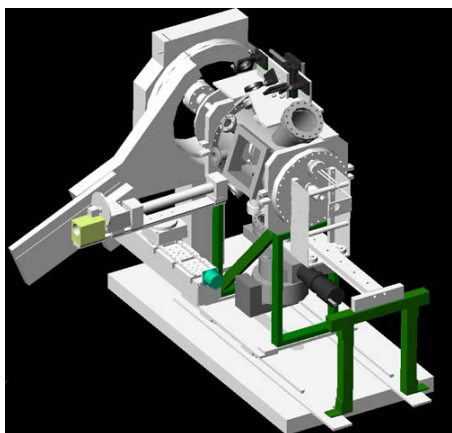


Fig 2b: Auto-Cad rendering of the G3 system. The vacuum chamber is easily removed from the diffractometer to make room for other experiments.

A \$20 Bet: Constructing the PLD System

Conceptually, PLD is one of the easiest thin-film growth methods imaginable. A high-power, focused laser ablates a target material (Figure 3). The plume of ablated material lands on a heated substrate surface, where it can condense to form a film. Multiple targets mounted in a carousel enable growth of multilayer materials.

In contrast, designing a PLD system that allows simultaneous X-ray characterization of the growing film turned out to be quite an undertaking. We required adjustability of the incident and diffracted X-ray beams,

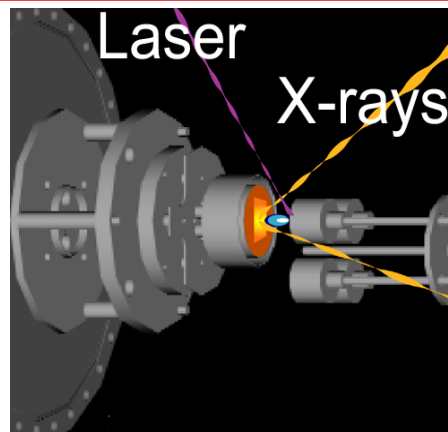


Fig 3: The excimer laser is focused onto a ceramic target which generally has the same composition as that desired in the film. X-rays diffract from the film/substrate system during growth.

and substrate crystallographic axes, with angular resolution of $\sim 0.001^\circ$. The laser had to retain its alignment with the target in different diffractometer positions. Budget restrictions precluded commercial vacuum-compatible sample manipulators. One final complication: the vacuum chamber had to be easily removable from the diffractometer.

We designed a vacuum system and installed it on the diffractometer table that Arthur Woll and Randy Headrick built in 1995 (Figure 2). The diffractometer detector arm was redesigned for a six-circle geometry, to admit both in-plane and out-of-plane scattering. We designed the sample manipulator around a kinematic mount, which we built in the CHESS, Physics, and Materials Science machine shops. The manipulator provides complete angular control of the sample axes, in vacuum, at high temperature. The vacuum chamber rides on a set of rails, for fine adjustment of the sample offset with respect to the incident beam (essential due to thermal expansion of the substrate heater). The rails also allow exchange of vacuum systems. The Engstrom Research Group in the Department of Chemical Engineering has subsequently designed a materials-growth system to utilize the G3 diffractometer for the study of hyperthermal growth processes.

When we had completed the detector arm construction, Joel Brock warned us that its alignment would be a difficult and time-consuming procedure. We arrogantly claimed that we could have the alignment done that afternoon. Joel responded by pinning a \$20 bill to the board and said we could keep it if we were done by the next morning. That afternoon, the G-line refrigerator was stocked with \$20 worth of beer. We have continued this tradition in subsequent synchrotron runs. (The US Surgeon General advises not to operate heavy machinery while under the influence of alcoholic beverages, a policy embraced by CHESS.)

In addition to designing a viable experiment, we had to meet the CHESS safety requirements. We upgraded one of the four gas cabinets in G3 for secondary containment

of the excimer laser's dilute krypton/fluorine supply lines. The laser operates at 26kV, with 600mJ maximum output per 25ns pulse equaling a peak power of roughly 50MW. Because the 248nm wavelength is absorbed by the skin and cornea, we completely enclosed the laser beam in a plexiglass flight path, and interlocked all systems to avoid unsafe laser operation. With a safe, functional apparatus in hand, we prepared for our first set of experiments.

The First Experiments

To commission a new growth system, x-ray beamline, and x-ray hutch, we set modest goals for the first series of experiments, conducted in the fall of 2002: grow smooth films via PLD, and monitor the growth with x-rays. For these experiments, we chose SrTiO₃ as a substrate material. This material is widely used as a template for oxide thin films, and high-quality samples are readily available. For our ablation target, we used the novel material EuTiO₃. This material is lattice-matched to SrTiO₃, and the substitution of europium for strontium allows x-ray fluorescence measurements of deposited material.

In these experiments, we diffracted x-rays of a substrate crystal in the Anti-Bragg (AB) geometry, in which x-rays scattered from adjacent crystalline layers interfere destructively. For 10 keV x-rays, this corresponds to an incidence angle of 4.5 degrees. A simple reciprocal space picture illustrates that scattering at the (00½) position of the specular Crystal Truncation Rod (CTR) is extremely sensitive to surface roughness (Figure 4). As we deposit material onto the initially bare substrate (blue curve), the AB intensity drops, reaching a minimum at half-coverage (green curve). The intensity recovers as the layer completes, so that each AB oscillation should correspond to the deposition of one crystalline monolayer.

This simple description belies the practical difficulties involved in trying to actually observe AB oscillations. We spent our first week of beam simply trying to find the AB position of the bare substrate. This task was complicated enormously by a manual out-of-plane detector arm motion (the motorized detector arm did not exist at the time) that prevented standard rocking curve measurements. Additionally, translating the chamber to compensate for thermal expansion of the substrate heater required multiple trips into and out of the hutch. We spent our "week off" between runs motorizing both of these motions.

Success arrived in the second week when we observed our first AB intensity oscillations. However, typical data (Figure 5) showed two puzzling features: rising oscillation amplitude and baseline. Furthermore, x-ray reflectivity measurements revealed that the EuTiO₃ films were twice as thick as one would predict by simply counting AB oscillations.

Before the week was out, we realized why each AB oscillation corresponded to two deposited monolayers. A careful consideration of the CTR evolution during

heteroepitaxy reveals the presence of Kiessig Fringes due to the electronic contrast between the film and substrate (Figure 6), an effect well documented in the literature.

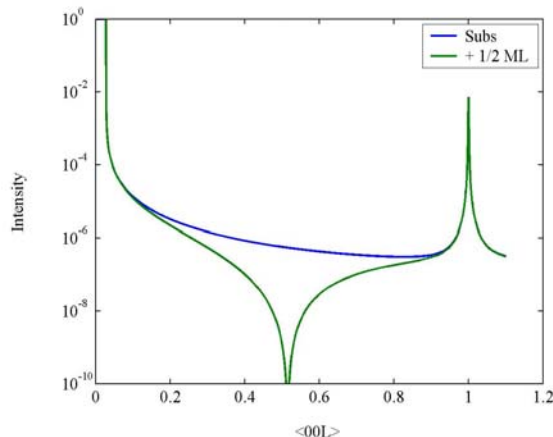


Fig 4: Specular CTR through the (001) peak. Addition of half a monolayer causes complete destructive interference at the <001/2>(anti-Bragg) condition.

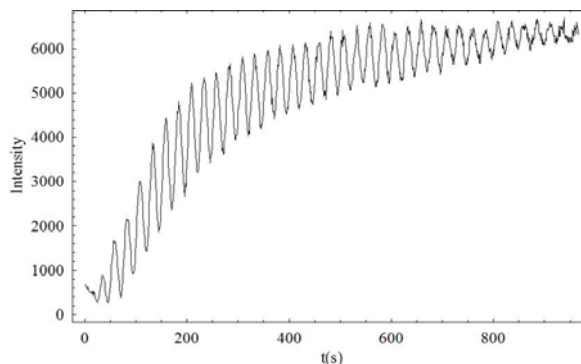


Fig 5: AB oscillations during deposition of ~80 layers of EuTiO₃ on SrTiO₃.

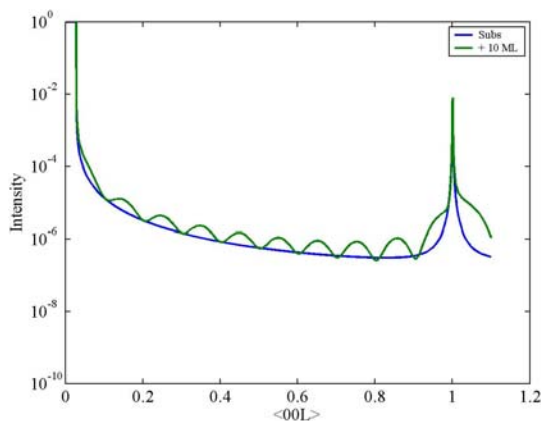


Fig 6: Kiessig Fringes (green curve) due to a 10-layer film. Bare substrate (blue curve) exhibits no fringes.

The number of Kiessig Fringes between Bragg Peaks is equal to the number of deposited layers. An even number of layers produces an AB minimum, while an odd number of layers produces a maximum. Each complete AB oscillation thus corresponds to an addition of two layers of film to the crystal [1]. Later measurements

experimentally confirmed this result (Figure 7).

To determine the origin of the rising amplitude and baseline we developed computer simulations of the experiment. In these simulations, we could control the deposition rate, electronic contrast, film roughness, and numerous other parameters. The simulations indicated that if the film surface was smoother than the initially rough substrate, the oscillation amplitude increased. Additionally, if the film thickness became non-uniform during deposition (on length-scales much greater than the coherence length), the oscillation baseline rose due to contributions to the scattering from different regions of the sample.

This explanation contradicts observations in many other systems, in which surfaces become rough during growth. EuTiO_3 appears to grow very smoothly. Additionally, arresting growth resulted in a decrease in the AB intensity, which could be recovered by resuming growth. In more recent experiments, we have seen pressure-dependent roughening of the SrTiO_3 substrates. SrTiO_3 and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films, at higher pressures, do roughen as they grow, a topic we will address in upcoming papers. To date, we have presented two posters at Materials Research Society meetings, given three talks at American Physical Society meetings, and have several papers in progress.

More Photons, Please

Another two years have elapsed since our first experiments and simulations. The findings that seemed surprising in the Fall of 2002 seem trivial and predictable now. Needless to say, we have learned more x-ray science (and electronics, vacuum technology, materials science etc.) in the last two years than we dreamed possible. In retrospect, Joel Brock had summarized our experience during the first official meeting of the graduate student team: “Welcome to G-line, you’re soaking in it.”

We currently have a long list of PLD experiments waiting for the implementation of the final G-line optics. With an expected $\sim 10^{14}$ photons/second, focused to roughly 1mm^2 , we would boost our intensity at the sample by three orders-of-magnitude. In addition to improved statistics for our current experiments, we anticipate new projects involving time-resolved diffuse scattering, off-specular diffraction, and GISAXS. In particular, we hope to answer long-standing questions regarding the activation of atomistic mechanisms by the energetic ablation plume.

Acknowledgements

We would like to acknowledge the Cornell Center for Materials Research for support, which is in turn supported by the NSF through the MRSEC program. We would like to thank our advisors, Joel Brock and Yuri Suzuki, for their guidance these last five years.

This project is deeply indebted to the CHESS faculty and staff. Ernie Fontes led the X-ray optics upgrades at G-line. This time-consuming project required much effort from the CHESS staff. Jeff White was extremely helpful in addressing safety concerns, writing documentation, and winning approval of the PLD project from the Wilson Lab Safety Committee. Alan Pauling, who designed the G-line front end, also taught us how to use AutoCAD. Dana Richter offered advice on implementation of equipment in G3. We would like to take this opportunity to thank the CHESS staff collectively. We have both been profoundly affected by our time in this lab.

Things have changed over time but the first time Darren was asked to give a talk at the CHESS Journal Club, he responded: “I’m not getting up in front of them, they’re hard-core.”

Footnote:

[1] If the film grows in a layer-by-layer mode, one can observe one AB oscillation per layer due to periodic roughness.

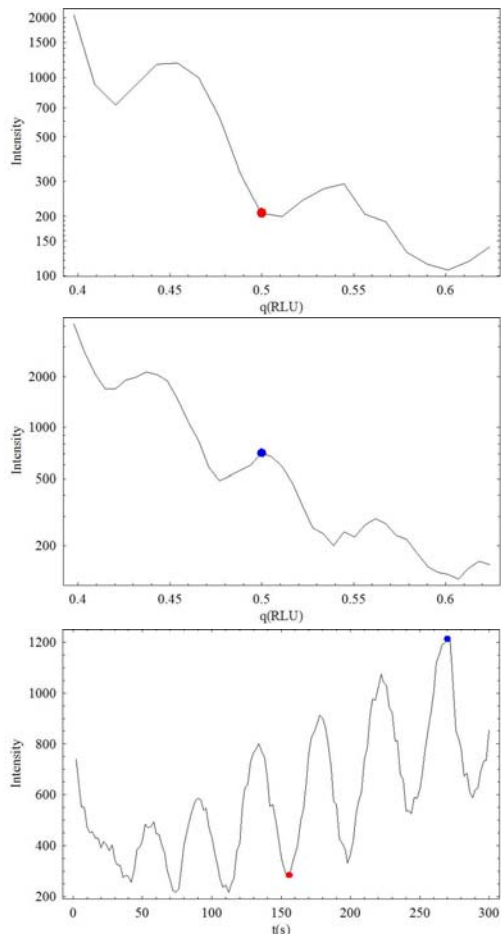


Fig 7: Arresting growth at a minimum in time (red dot, bottom) reveals the AB intensity to be between Kiessig Fringes (red dot, top), while a maximum in time (blue dot, bottom) corresponds to the AB intensity coincident with a Kiessig Fringe peak (blue dot, center).