

Real-Time Layer-by-Layer Crystal Growth and Etching

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Progress since 1995.

The pace of experimental research can be exhilaratingly fast, and, at times, it can be painfully slow. On the slow end of the scale are the proposals for equipment and personnel, design and construction of experimental apparatus, and training of students, etc. This whole process can often take several years, even for a relatively modest experimental program. On the other hand, the actual collection of data and the discovery of new science often takes only a matter of days. I wrote the first CHESS newsletter article on the “real-time growth initiative” in 1995, just after Joel Brock, Ernie Fontes, and I had received funding from the NSF to construct a new vacuum chamber to perform in-situ X-ray studies of crystal-growth processes. Joel and I and also other collaborators, including Barbara Cooper, had worked towards starting a similar research effort since at least as far back as 1991. 1995 was also a pivotal year, because the Cornell Center for Materials Research allocated funding for a graduate student, Arthur Woll, to work on the growth of thin films in the new vacuum chamber.



Figure 1: The ultra-high vacuum thin film growth chamber set up in the A-2 hutch. The two-theta arm with detector is at the right, and a Si(Li) detector for energy analysis of X-ray fluorescence from the sample is in the left foreground.

The design and construction of the crystal growth chamber took about a year, and we had our first X-ray run at CHESS in December of 1995. At that time it was mainly Arthur and myself doing most of the hands-on work. Stefan Kycia, who was then a postdoc at CHESS joined us for the first run. We successfully studied the nucleation of gallium-nitride on silicon carbide, and discovered several important effects, which would form the basis of our research on nitrides over the next few years. The duration of this first run was three weeks, and the first actual growth simultaneously studied with X-rays was completed at 9 P.M. on December 26th, 1995. This first real-time data set lasted exactly six minutes. A few months later, we published a paper from this experiment, on the nucleation of GaN [1]. The most significant experimental result of this first run was the discovery that the thickness of the film does not increase linearly as a function of time. The observation of this effect helped us to explain why some thin films are composed of discontinuous islands in the early stages of growth, rather than producing a



Arthur Woll moments after completing his PhD thesis defense in September of 1999.

continuous film from the beginning. The GaN growth collaboration has since produced several more publications [2-4].

As an example, Figure 2 shows the effect of different growth conditions on the nucleation of GaN on a sapphire surface. Figure 2(a) shows intensity oscillations characteristic of the layer-by-layer growth mode when ammonia ions are used as the nitrogen source. Figure 2(b) shows that neutral ammonia molecules produce a film that is rough on the atomic scale. Finally, Figure 2(c) shows that pre-treatment of the sapphire surface with ions produces a smoother film than in (b), but not as smooth as in (a). As another example of the results, Figure 3 shows the strain relaxation behavior of a GaN single crystal thin film as it is being grown. The data helped us to understand why some films suddenly get bumpy when the film thickness exceeds one atomic layer. This information is being used by other researchers to perfect their growth techniques in order to make nitride materials for devices such as blue lasers, light-emitting diodes, high-power transistors, and flat-panel displays.

It may seem ironic that years of preparation lead up to experiments where the final data only takes a few minutes (or less) to collect. However, the power of X-ray scattering techniques is that they allow you to see things at the scale of individual atoms that were not possible to see previously. Since we are most interested in what is happening during the growth process, we want each data point to be collected in less than a second in order to get a snapshot of the surface before it changes. Therefore, a facility like CHESS is essential for looking at atomic-scale processes on surfaces, which requires a very high intensity X-ray beam. The high flux wiggler station, A-2, is well suited to this type of experiment because it produces one of the highest intensity high-energy X-ray beams available today, enabling us to study growth processes at 100 millisecond time-resolution. In the summer of 1996, we had our second run. This run was the start of a second ambitious project: to learn about the surfaces of gold crystals. The experiments were closely tied to Cornell’s

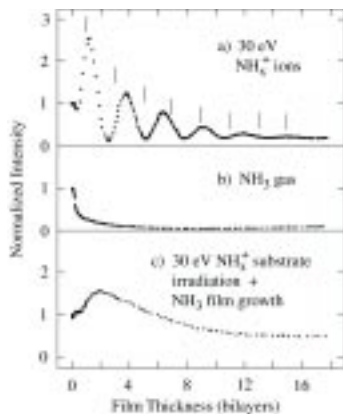
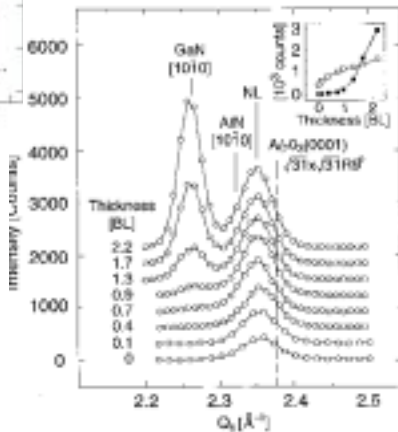


Figure 2: Real-time data during the nucleation of GaN on sapphire. The data show a variety of growth modes.

Figure 3: X-ray diffraction scans during the growth of GaN on sapphire. The data can be interpreted as a sudden relaxation of strain as the thickness exceeds one atomic layer.



“Energetic Beam Deposition” group led by Barbara Cooper and Jim Sethna. One of the first experiments was to study the thermal annealing of a Au(111) surface. This experiment became the subject of Tatyana Curcic’s PhD thesis [5]. A second experiment related to this project was led by Ramana Murty, a postdoctoral research associate in Cornell’s physics department (now on the staff at Argonne National Laboratory). Ramana’s experiments were aimed at understanding the fundamental processes of erosion of metal surface by energetic ions. This project ultimately led to several highly original discoveries [6,7].

One of these discoveries was dubbed persistent layer-by-layer etching [6]. This is a surprising effect since etching normally roughens a surface as a result of removing material in a statistically random way. The experiment showed that in a certain range of temperature and etching rate, the surface can heal itself as the etching is carried out. This result has implications for ion-beam and plasma processes used in semiconductor wafer processing and fabrication of magnetic recording heads. In a related experiment, Ramana showed that it is also possible to form regular patterns on gold surfaces by ion erosion, and he determined an equation that predicts the size of the pattern.

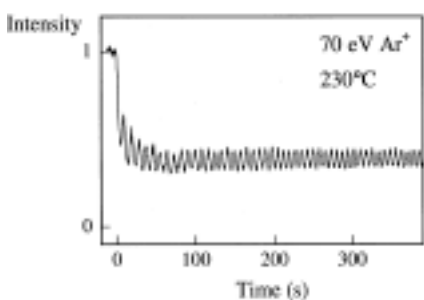


Figure 4: The persistent layer-by-layer etching effect is seen by intensity oscillations where each period corresponds to removal of one atomic layer.



Ramana Murty after discovering the persistent layer-by-layer etching effects.

Future plans

We are now in another construction phase with many laboratory upgrades in progress. One of the most exciting is the new G-line (see article by Bilderback on page 19). One of the three X-ray hutches is planned to be the future full-time home for the thin-film growth apparatus. Several experimental projects related to real-time growth are ongoing, including energetic beam growth of semiconductors, ion etching of metals and glass surfaces, thermal relaxation of surfaces, and formation of nanostructures using energetic beam techniques. Interest in this type of research remains extremely high, and there are many more fascinating scientific discoveries to be made.

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