Real-time crystal growth initiative at CHESS

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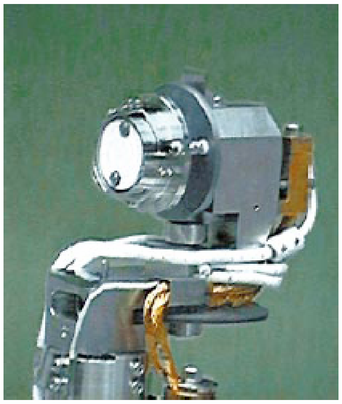
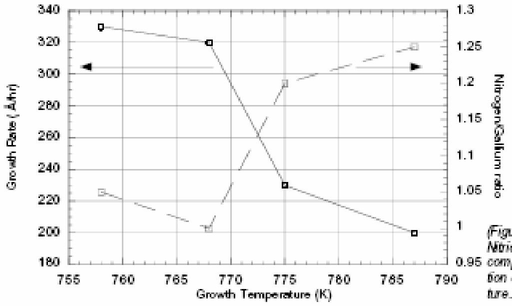
This CHESS initiative to grow thin semiconductor films and study the process in real-time with x-rays gained momentum during the past year with a number of new accomplishments. Although the project began only a little more than a year ago, it has become a major new research initiative at CHESS, with significant participation of faculty members from the Cornell Materials Science community. The accomplishments include constructing an epitaxy system for thin film growth; the award of an equipment grant from the National Science Foundation to build a second growth system for *in-situ* x-ray studies; the design and construction of this new system (still in progress); and funding from the Materials Science Center for a graduate student to work full time in this area.

In August of 1994, we grew our first films of a semiconducting material — gallium nitride. The films were grown by a technique called Metallorganic Molecular Beam Epitaxy, using the epitaxy system built with the help of Cornell undergraduate Young Park. This system consists of a gas delivery system and an ultra-high vacuum compatible growth chamber. Since the project had no direct funding initially, we constructed the chamber largely using borrowed equipment. The gas manifold was built from quarter-inch stainless steel tubing, welded and leak checked at CHESS. The vacuum chamber was salvaged from a piece of x-ray beamline left over from one of the CHESS undulator runs. For pumping, we used a fifty liter-per-second turbopump left over from the experiments of a visiting scientist from several years ago. We borrowed a roughing pump from the Laboratory of Nuclear Studies. Finally, we purchased three automatic gas flow valves and cylinders of ammonia and trimethylgallium for our nitrogen and gallium sources. Once the chamber and gas manifold were finished, we needed a substrate to grow our films on and a way to heat the substrate up to at least 800°C. We found a current regulated power supply that would go up to about 5 amperes, and built a sample holder that would run the current directly through a narrow strip of wafer to heat it up. We used silicon as a substrate material since it is easy to heat and is readily available.

We have now completed a number of growth runs, and have learned to grow GaN films at rates of about 350Å/hr and to vary the composition from 1:1 perfect stoichiometry to 1:1.25 nitrogen rich. Figure 2 shows film growth rates and compositions as a function of temperature, as determined by Rutherford Backscattering Spectrometry. Also, we have done some x-ray studies in which we determined that the films are the hexagonal phase of GaN. One surprising result is that the basal plane of the GaN film is oriented perpendicular to the growth direction, even on Si(111) substrates, where one would expect that, due to the hexagonal symmetry of the substrate surface, the basal plane would lie in the plane of the film. Figure 3 shows an azimuthal scan of the [0002] diffraction intensity in the grazing angle scattering geometry for sample GaN$_{18}$ and shows that the film consists of crystallites with six discrete azimuthal orientations. These early experiments show that our growth system is capable of growing stoichiometric gallium nitride material. The second round of experiments, which will occur this summer will focus on improving the crystallinity of the films and reducing their roughness.



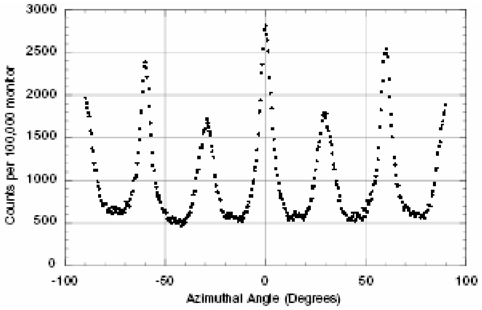
(Figure 1) Photo of the UHV sample manipulator.



(Figure 2) Gallium Nitride growth rate and composition as a function of growth temperature.

Our experiments on GaN come at a time of increasing excitement about GaN as a material for advanced solid state devices. The reason for this excitement is that GaN is a light emitting semiconductor, and, along with its cousins aluminum nitride and indium nitride, have become favorite candidate materials for the fabrication of solid-state lasers that emit blue light. Widely considered to be a critical component for high density optical disks, the blue laser has long been sought by optoelectronics researchers. The current generation of blue lasers are made from zinc-selenide, which, so far, can only survive up to a few hours after turning on. It is not clear whether they can be made reliable enough to go into a real device, such as a CD player, or a mass storage disk for a computer. Within the next few years, there is considerable hope that, once certain materials problems are solved, there will be a new generation of reliable blue lasers based on GaN..

Meanwhile, the film growth project continues, and is taking on a new dimension. Young Park will be working again at CHESS during the summer of 1995, after which he will leave to begin graduate



(Figure 3) Azimuthal scan on the GaN [0002] reflection, showing the polycrystalline structure of a 1650Å thick film grown on an Si(111) substrate.

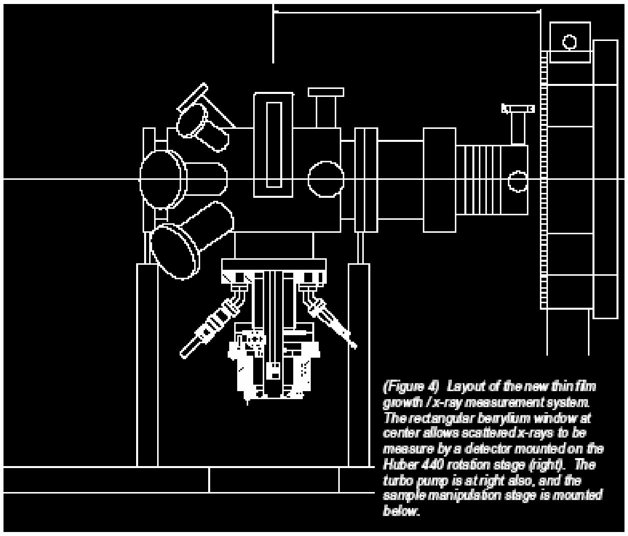
studies in Chemical Engineering at the University of Massachusetts at Amherst. At about the same time that we started working on the film growth project, we began plans to build a growth system that would be capable of doing the film growth with enhanced capabilities and also allow a simultaneous probe of the structure of the film with x-rays from the storage ring. In August a grant was awarded by the National Science Foundation in the amount of $89,000 to build this new system. Randy Headrick is the principal investigator on the grant, along with co-PIs Joel Brock from the Department of Applied and Engineering Physics at Cornell, and Ernie Fontes, a CHESS staff scientist. This was a milestone, not only for the film growth project, but also for CHESS, since this was the first in-house CHESS project started by a staff scientist to receive outside funding.

Since that time a lot of effort has gone into designing the new vacuum system, sample manipulator (see Fig. 1), sample heater, and beryllium windows to get x-rays into and out of the chamber. The experience that we have gained in the study of GaN growth in the epitaxy system has enabled us to design a system that will be optimized for both film growthand *in-situ* measurements.

The new chamber (Fig. 4 and cover photo) will have a sample manipulator with a differentially pumped rotation stage and be pumped by a 450 liter-per-second wide-range turbopump. A Huber 440 rotation stage mounted next to the chamber will hold a detector arm for a NaI counter or position-sensitive detector. We are just beginning to assemble the vacuum system. Initial calibration experiments will begin in the summer of 1995, with a goal of *in situ* experiments in the Fall. In the meantime, we continue to make use of the original epitaxy chamber.

The latest development in the Real Time Growth project is the participation of Cornell's Materials Science Center, in the form of support for a graduate student. Arthur Woll, a student in the Applied and Engineering Physics department has begun working on the new chamber, which will be used initially to study the growth of gallium nitride thin films as a continuation of our early work. Arthur also participated in a run at the CHESS F3 station to analyze the structure of GaN thin films grown in the epitaxy system. In addition to film growth using conventional gas precursors, we are planning to accommodate experiments using ion beam or molecular beam sources. These experiments will be carried out in collaboration with faculty members affiliated with the Materials Science Center.

From our early experiments, we have already begun to explore some of the properties of the films such as the surface roughness, the evolution of crystal quality as the growth proceeds, and variation of the growth rate and composition. Dependence of these features on the substrate temperature, as well as other parameters, is already yielding insight into the growth process. Experiments in our new system will allow us to follow the growth as it occurs, so that a better understanding of the time evolution of the film's structure can be obtained. Monitoring the intensity of surface truncation rods will also yield insight into the layer-by-layer growth process. These experiments represent an entirely new use for Cornell's synchrotron source, and will take full advantage of the higher intensity x-ray beams that will be available after the storage ring upgrades are completed. They also represent a convergence of interests in the important area of Materials Science within the Cornell community.



(Figure 4) Layout of the new thin film growth / x-ray measurement system. The rectangular beryllium window at center allows scattered x-rays to be measure by a detector mounted on the Huber 440 rotation stage (right). The turbo pump is at right also, and the sample manipulation stage is mounted below.