

**Development of High Quantum Efficiency UV/Blue Photocathode Epitaxial Semiconductor
Heterostructures for Scintillation and Cherenkov Radiation Detection**

Summary of Research

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Overview, Significance, and Impact of Research

Enormous technological breakthroughs have been made in a variety of optoelectronic devices through the use of advanced heteroepitaxial-semiconductor crystal growth techniques such as molecular beam epitaxy (MBE). The primary goal of this research project was to further extend this technology and to demonstrate significant gains in UV/blue photonic detection by designing and fabricating atomically-tailored heteroepitaxial GaAlN/GaInN photocathode device structures. Although a simple activated p-type single layer GaN structure can deliver 10 to 20% quantum efficiency, a more complex design is required to achieve the higher levels that our research is targeting. Band gap engineering concepts are being employed in the photocathode structures that we have fabricated by MBE. The high level of sophistication and complexity of our approach required some further effort in the basic optimization before completed devices could be evaluated. No other approach has the same potential to reach the high quantum efficiencies (in excess of 50%) that we are targeting in the UV/blue waveband.

This NASA Explorer technology research program has focused on the development of photocathodes for Cherenkov and scintillation radiation detection. Support from the program allowed us to enhance our MBE system to include a nitrogen plasma source and a magnetic bearing turbomolecular pump for delivery and removal of high purity atomic nitrogen during GaAlN/GaInN film growth. Under this program we have also designed, built and incorporated a cesium activation stage. In addition, a connected UHV chamber with photocathode transfer/positioner components as well as a hybrid phototube stage was designed and built to make in-situ quantum efficiency measurements without ever having to remove the photocathodes from UHV conditions. Thus we have constructed a system with the capability to couple atomically-tailored MBE-grown photocathode heterostructures with real high gain readout devices for single photon detection evaluation. Complete GaN/InGaN photocathodes have been designed and fabricated on up to 2-inch diameter sapphire substrates by MBE (Fig. 1). The structural, optical, and electronic properties of these films have indicated very good quality material. We have activated photocathode surfaces with cesium and measured the photoelectron emission quantum efficiency and spectral response.

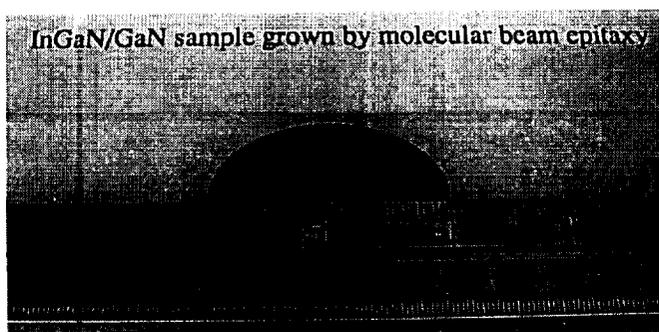


Figure 1: A two inch diameter graded GaN/InGaN wafer grown by molecular beam epitaxy.

By alloying with In, we have extended the response of GaN photocathodes into the visible band. Enhanced sensitivity to blue light should enable a new generation of photomultiplier tubes for scintillation light detection in X-ray detectors, active shields for X-ray experiments, and scintillating fiber detectors. Optical monitors fabricated using such photocathodes are likely components in future wide field X-ray experiments. High efficiency photocathodes with extended wavelength coverage, based on AlGaIn/InGaIn are expected to supplement developments in high-resolution readouts and will provide a powerful element of future generations of UV instruments.

Photocathode Design, Epitaxial Growth, and Material Quality

Our research on high quantum efficiency photocathodes involved the design and fabrication of precisely-tailored heteroepitaxial semiconductor structures that have sensitivity in the UV/blue spectral range. We selected the AlGaIn/InGaIn system mainly because the band gap can be tailored over an energy range from 1.9 to 6.2 eV and epitaxial thin film layers can be grown directly on optically transparent sapphire substrates. All of the AlN/GaN/InGaIn heterostructures discussed in our work have been fabricated by MBE.

The use of MBE for crystal growth makes it possible to control film composition on an atomic scale and to fabricate abrupt heteroepitaxial interfaces. This ultra-high-vacuum technique allows for very quick on/off switching of atomic and molecular beams through the use of shutters in front of each thermal or electron beam source. The system we are using for GaAlN/GaInN is equipped with an RF plasma source to deliver atomic nitrogen to the substrate for growth, as well as an oil-free magnetic bearing turbomolecular pump for removing excess molecular nitrogen from the ultra-high vacuum chamber. Standard MBE effusion sources are used for both Ga and In as well as the Mg p-type dopant. Electron beam sources are used for the Al flux and Si n-type dopant.

A reflection high-energy electron diffraction (RHEED) system mounted inside the vacuum chamber allows the surface crystal quality to be monitored during growth as individual atomic layers are added to the surface one at a time by examining surface reconstruction diffraction patterns. This feedback provides the absolute finest control of the heteroepitaxial crystal growth process, thereby making possible precise fabrication of semiconductor layered structures for fabricating high quantum efficiency photocathode devices. Figure 2 shows typical RHEED patterns from GaN grown on sapphire substrates in our MBE system. The streaked pattern shown on the left indicates an atomically-smooth growth front. We have found that the RHEED pattern is very sensitive to the ratio of Ga to N flux during growth in that Ga-rich conditions lead to a highly streaked diffraction pattern while N-rich conditions produce a more spotted diffraction pattern as shown on the right side of Fig. 2. However a high flux ratio can also lead to Ga precipitation on the surface. The best films are produced when the ratio of Ga to N flux is close to one.



Figure 2: Left: RHEED pattern of GaN captured during the growth process with Ga/N flux ratio near one. Right: RHEED pattern for a GaN layer later during growth with Ga/N flux less than one.

The potential to increase the quantum efficiency of these photocathodes relies on a couple of key design features that can be incorporated in our heteroepitaxial layers. Examples of this are shown in Fig. 3 where conduction and valence band edge energy spatial profiles are displayed for two possible photocathode designs. This diagram is a rough schematic plot of band gap versus depth into the photocathode structure. For clarity the thickness of individual layers shown in Fig.3 are not drawn to scale.

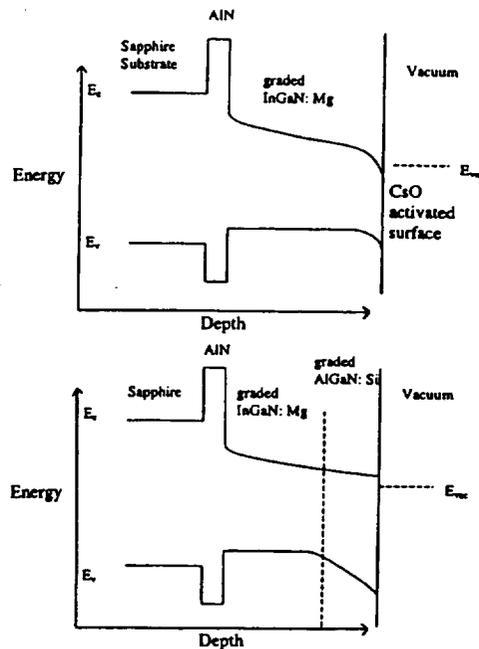


Figure 3: Spatial profiles of conduction and valence band edge energies, E_c and E_v respectively, for composition variations versus depth in two different photocathode heterostructures shown at the top and bottom. E_{vac} is the vacuum energy near the photocathode surface.

All of the GaN/GaInN heterostructures used in our studies were grown on single-crystal sapphire substrates. The mechanical strength and UV/visible optical transparency properties of sapphire make it an excellent choice as a window material for photocathode structures. An AlN optical antireflection layer can be inserted between the sapphire and the AlGaInN photocathode region, as shown in Fig. 3, to serve as a wide-band-gap barrier to prevent electronic back diffusion into the substrate interfacial region where defect densities are expected to be higher and nonradiative recombination of photoexcited electrons larger. Inserting this wide band gap AlN buffer layer in the structure ensures that photoexcited electrons do not diffuse back toward the sapphire substrate interface, but instead are reflected toward the photocathode emission surface. We can also grade the alloy composition in the photocathode region to tailor the conduction and valence band profiles in a manner which will enhance photoelectron transport to the surface. Examples of this are shown in Fig. 3, where conduction and valence band-edge energy spatial profiles, E_c and E_v , respectively, are displayed for two photocathode designs. In Fig. 3 the GaInN alloy composition spatial profile is graded not only to optimize the electronic transport to the front surface but also to extend the optical absorption to longer wavelength. The energy gap of GaN in the wurtzite crystal structure is 3.39 eV at room temperature [1]. This can be adjusted to lower energies through the addition of In to the alloy

It is known that an electric field applied inside a semiconductor photocathode layer drives electrons toward the emitting surface and in so doing can increase the quantum efficiency by as much as a factor of two [2]. As shown at the top of Fig. 3 we have been exploring a design to create these internal fields in the photocathode layer by grading the alloy composition, which tilts the conduction and valence band edges. As the In content in the alloy layer increases the energy gap between valence band and conduction band decreases, resulting in a sloping of the band edges. Although the fractional amount of change in the conduction and valence bands are different, the overall effect is to tilt the conduction band since the p-type dopant incorporated throughout the layer allows mobile hole charge carriers to diffuse in a manner that minimizes the energy, leaving the valence band profile flat. The tilted conduction band drives photoelectrons toward the surface, increasing their escape probability and thus the quantum efficiency. Finally, an activation layer of Cs on the surface bends the bands to achieve a negative electron affinity (NEA) condition, which is vital for having a high photoelectron escape probability. We have also been considering novel means of activating the photocathode emitting surface in order to achieve the NEA condition. Since AlN and AlGaInN with high Al concentration have an intrinsic NEA surface, we suggest the possibility of ending the epitaxial layers with a Si-doped AlGaInN surface in order to achieve an NEA condition without the need for post-growth Cs activation. This design is shown at the bottom of Fig. 3.

Adding In as an alloy component to the GaN epitaxial layer does induce strain due to the lattice mismatch between GaN and InN. It can also lead to elemental phase segregation in the alloy layer. This puts some limits on the epitaxy and also narrows the growth parameter window. In spite of these constraints we have come up with a method that appears to work and allows grading of the alloy with good crystal quality. X-ray diffraction and TEM lattice image studies show good registry of epitaxial GaN and InGaInN layers with the c-plane oriented, single-crystal sapphire substrates (see Figs.4, 5, and 6).

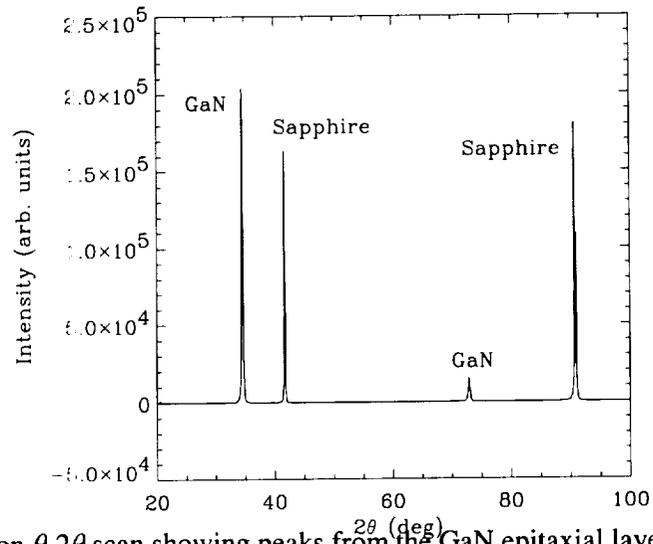


Figure 4: X-ray diffraction θ - 2θ scan showing peaks from the GaN epitaxial layer grown on a single-crystal c-plane sapphire substrate.

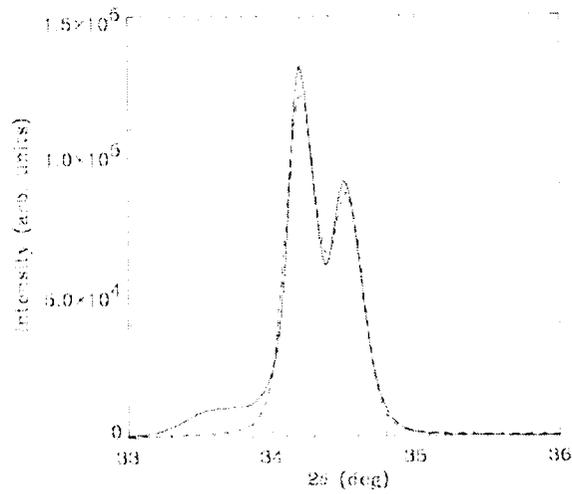


Figure 5: X-ray diffraction θ - 2θ scan and Voigt function fit for an epitaxial GaN/InGaN heterostructure showing a double peak structure, indicative of the c-plane lattice spacing differences between the two layers resulting from lattice expansion in the alloy layer.



Figure 6: Transmission electron microscopy cross sectional image of a GaN/InGaN structure grown on a sapphire substrate showing parallel c-plane oriented lattice planes.

We have also developed a method to fit x-ray peaks using Voigt functions. By removing instrumental broadening contributions we can evaluate defect density correlations with x-ray peak widths. We can also fit several peaks arising from multilayered GaN/InGaN heterostructures to extract lattice strain profiles (Fig. 5). The FWHM of the GaN (0002) X-ray peak is approximately 400 arc seconds for a 0.5 μm -thick film, which indicates high-quality for such thin epitaxial GaN on sapphire. Optical absorption measurements of our GaN and InGaN samples confirm the expected band gap shift with increasing In concentration as shown in Fig. 7.

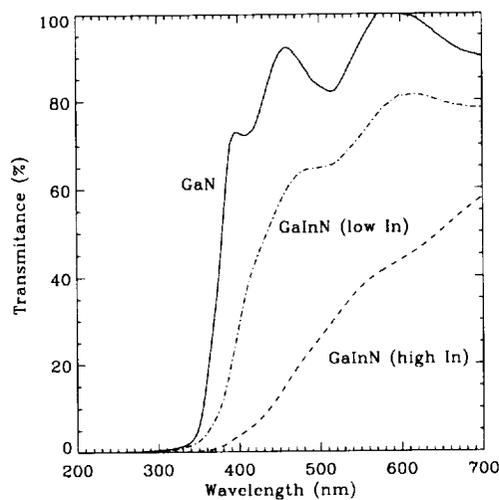


Figure 7: Optical transmission as a function of wavelength for GaN and InGaN samples showing the band-edge shifting at higher In concentrations.

Another very important component of our photocathode development has been the ability to achieve high p-type doping levels in the active InGaN layer. Typically Mg is used as a p-type dopant in GaN. It is difficult to get highly p-type GaN epitaxial material in part due to the large intrinsic background n-type carrier concentration, as well as the large ionization energy of the Mg p-type acceptor level [3]. We had success with Mg by first reducing the n-type background by growing under slightly N-rich conditions and also by growing on the Ga-face, which is achieved by exposing the sapphire surface to a nitrogen plasma prior to growth [4]. Hall measurements, using the Van der Pauw technique, resulted in p-type carrier concentrations near 10^{18} cm^{-3} . We found this to be adequate for fabricating semiconducting photocathode layers with negative electron affinity (NEA) surfaces.

Photocathode Quantum Efficiency

During this research program we have developed a sophisticated system for determining the absolute photon conversion efficiency and spectral response of our photocathode detectors using a photon counting system and differential measurements with respect to a calibrated absolute reference. This system is not sensitive to intrinsic gain of the photocathode or to other systematic uncertainties such as lamp drift, pedestal variations, alignment or charge-collection efficiency.

As mentioned earlier, the MBE system is comprised of three primary components: the growth chamber, sample introduction and Cesium activation chamber, and the quantum efficiency chamber (see Fig. 8). The photocathode wafer can be transferred from the growth chamber to a carousel for activation in the sample introduction chamber. Thereafter, the carousel can be translated back and forth between the activation chamber and the quantum efficiency chamber. This system makes possible *in-situ* measurements of quantum efficiency and spectral response without breaking vacuum, providing the best feedback for optimizing wafer growth and surface activation.

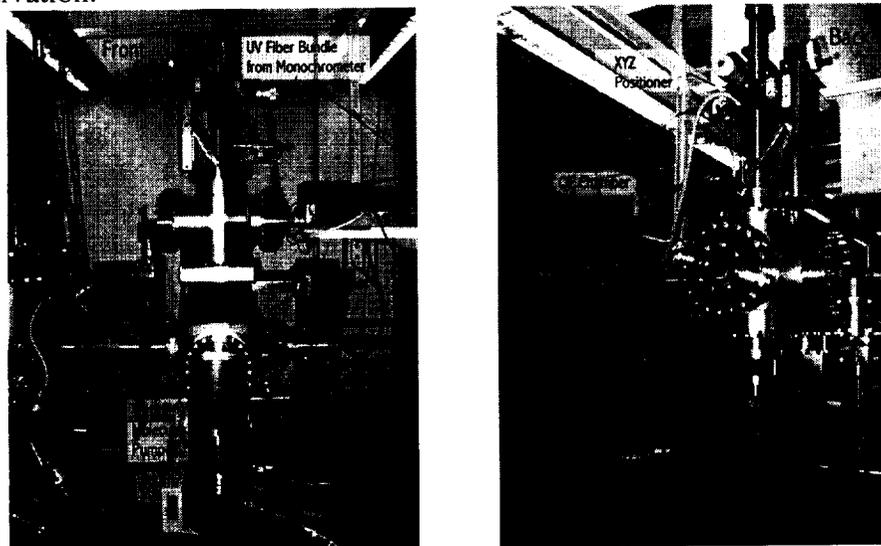


Figure 8. Front and back views of our custom-built photocathode quantum efficiency measurement system connected to the MBE vacuum chamber.

A monochromatic, pulsed light source has been installed on a small optical bench near the quantum efficiency chamber (see Fig. 8). The optical system consists of a pulsed Xe flash-lamp followed by a monochromator under computer control. A custom-made bifurcated fiber bundle consisting of 14 interleaved UV transparent fused-silica fibers is formatted onto the output slit of the monochromator to evenly split the light into two paths each consisting of a close-packed bundle of 7 fibers. One fiber bundle delivers light to a UV-enhanced silicon photodiode reference detector located in a shielded enclosure on the optical bench. The other branch of the fiber bundle goes to a focusing beam probe held by an XY positioner above a window of the vacuum chamber. Light is focused on one end of a fused-silica fiber mounted in the vacuum chamber. This fiber is terminated with a small collimating lens that illuminates the photocathode surface (Fig. 9).

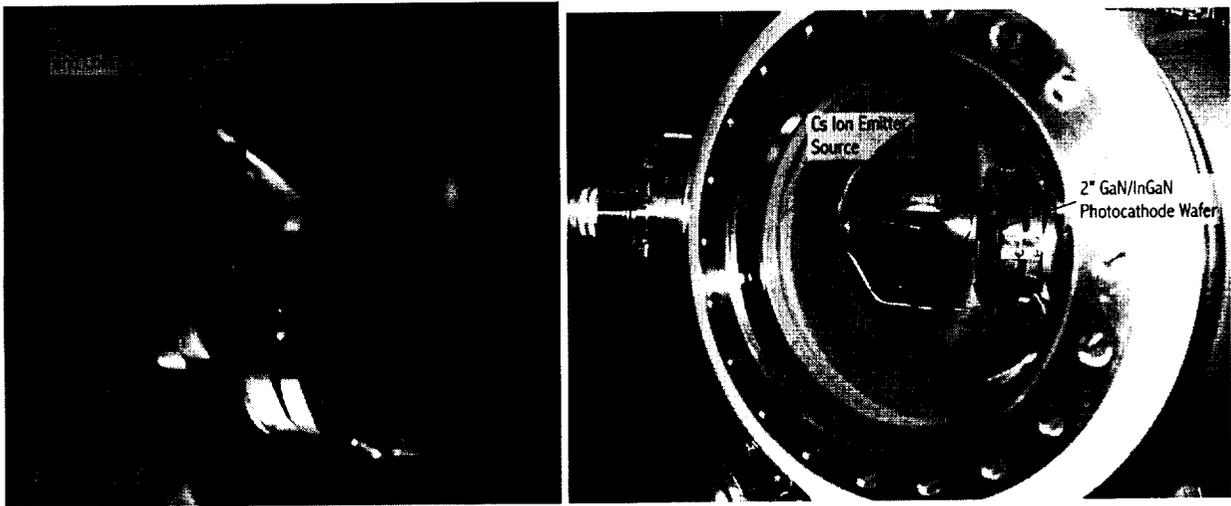


Figure 9. Views inside the vacuum chamber of the quantum efficiency measurement station (left) showing the hybrid phototube housing and photocathode wafer carousel, and the Cesium source for activating photocathode surfaces (right).

The XYZ/angle positioner built into the QE chamber allows the photocathode to be mated to an electron multiplier device in the vacuum chamber (Fig. 9). The photocathode is positioned at the entrance window of a bare hybrid photomultiplier anode structure. A high voltage feedthrough provides a 0-10 kV bias between the photocathode carousel and a segmented array of seven photodiodes. (This device is a windowless version of the DEP P25 HPMT manufactured by Delft Instruments.) Photoelectrons emitted by the cathode are accelerated toward the photodiodes to an energy of 10 keV, liberating ~2000 electrons in the photodiode. In this proximity-focused device, the field is sufficiently large that the electrons travel in a straight line from the photocathode to the corresponding segment of the photodiode array. The arrangement of photodiodes is such that a single central pixel is surrounded by a guard ring of six hexagonal-close-packed detectors. Signals from these photodiodes are read out through another vacuum feedthrough to the external preamplifiers. Hybrid photomultiplier tubes (HPMT) of this variety are ideally suited for efficiency measurements. The gain is linearly dependent on the bias voltage, unlike the dynode chains of photomultiplier tubes. These devices also have the potential

to provide excellent single photoelectron resolution that allows an absolute gain calibration by identifying, e.g., the one, two and three-photoelectron peaks.

The signals from the reference silicon detector and the HPMT detector are read out with AMPTEX 250 low-noise preamplifiers with input JFETs matched to the capacitance of the silicon detectors. These two signals are then fed to shaping amplifiers and analog to digital converters. A LabView application controls the light pulser, scans the monochromator, and simultaneously captures the waveforms from signals in the calibrated reference detector and from the photocathode/HPMT. Capturing the triggered waveforms allows for real-time pedestal subtraction, and provides an evaluation of electronic noise not available in electrometer or lock-in systems. Like a lock-in, the light pulses can be averaged over the appropriate time-window (following the trigger) increasing the signal to noise ratio with acquisition time. The relative measurement corrects for drift or fluctuations in the light pulser. All of these features combine to provide an excellent handle on systematics in the relative measurement. Figure 10 shows single-shot pulses from a GaN/InGaN:Mg photocathode and from the reference detector obtained with our system for very low light levels using a neutral density filter (ND = 2) in the fiber optic beam line.

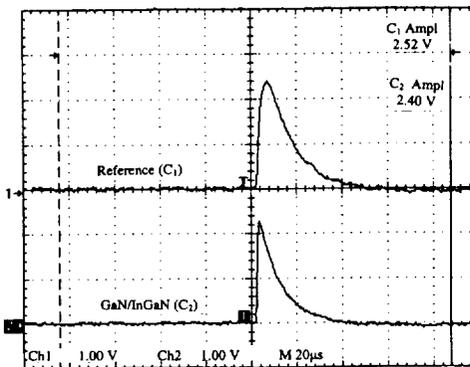


Figure 10: *In-situ* single-shot measurement of photoelectron emission from an MBE-grown GaN/InGaN photocathode compared to a reference detector in response to pulsed UV light excitation at 300 nm.

The system is calibrated for absolute measurements by placing a calibrated photodiode (identical to the reference device) inside the vacuum chamber and performing a cross calibration. This procedure was used to renormalize the measurements in the reference arm to provide an absolute measurement of the number of photons per light pulse hitting the photocathode. Together with the HPMT gain calibration, this provided a complete absolute calibration of the system.

Traditionally quantum-efficiency has been measured by illuminating a cathode in a simple tube-diode structure to determine the photocathode current for an applied light level. Quantum efficiency is defined in terms of such measurements, as the ratio of the number of electrons collected on the anode to the number of incident photons. However, intrinsic gain in devices can give rise to an apparent quantum efficiency in excess of the actual photon detection efficiency. Our system has the potential to distinguish between the single photon detection efficiency and the quantum efficiency.

The Cs stage we have designed for activating photocathode surfaces is also novel. A Cs ion emitter source is used and the photocathode wafer is biased to -300 Volts to attract the Cs ions. By measuring the ion current the overall exposure, and thus, surface coverage can be accurately determined. Repeated exposures can be evaluated by transferring the photocathode into the quantum efficiency chamber under UHV conditions.

The unique features of the measurement system we have developed are described below:

- Photocathode need-not be removed from UHV, eliminating problems with surface treatments to restore the cathode surface.
- The photocathode is integrated with a detector housing (HPMT) to evaluate the total detector performance including the charge collection efficiency, single photoelectron resolution and time structure of the detector signals.
- The measurements determine the probability of a single photon giving rise to a detectible signal as well as the quantum efficiency, allowing us to rigorously determine intrinsic gain in the photocathode structure.
- The photocathode can be moved back and forth between the Cs source and QE chamber to investigate the effect of varying the activation by changing the total exposure of the photocathode to the Cs ion current.
- A triggered, pulsed light source provides a method of measuring the pulse height distribution of the photoelectron peaks, provides a waveform measurement for debugging noise problems and has the advantages of a lock-in amplifier for maximizing the signal to noise ratio.
- Use of an HPMT makes gain calibration straightforward given the linearity, large dynamic range, and excellent single photoelectron resolution of these detectors.
- The QE chamber and positioners serve as a model for a system that will eventually be used to integrate and bond photocathodes with anode structures in the vacuum chamber to fabricate complete self-contained devices.

This entire system has been successfully used to determine the spectral response and absolute quantum efficiency of GaN/InGaN:Mg photocathodes before and after Cesium activation. An example of the quantum efficiency and spectral response measured on two MBE-grown GaN/GaInN:Mg photocathode 2" diameter wafers is shown in Fig. 11. The InGaN layers were graded to extend wavelength coverage into the blue as well as to provide an external field to drive photoelectrons toward the emitting surface. The photocathode with higher p-type doping (near 10^{18} cm^{-3}) has a quantum efficiency near 30 % at 250 nm. The sample with lower doping (low 10^{17} cm^{-3}) exhibits a significantly smaller quantum efficiency.

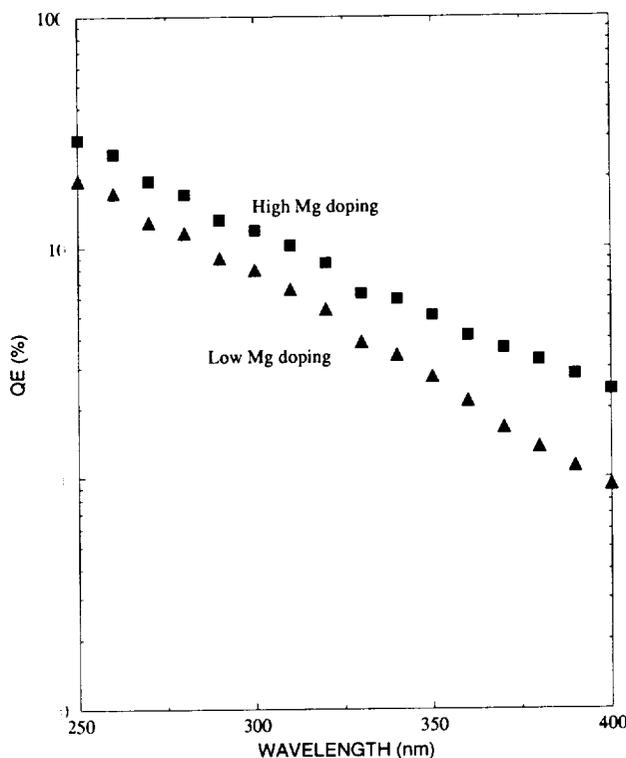


Figure 11. Quantum efficiency measured on two-inch diameter GaN/InGaN wafers after Cs surface activation.

We believe there is considerable room for further improvement in quantum efficiency through atomically tailored MBE-grown heterostructures by varying some other design parameters, as was shown in Fig. 3. We have plans to continue this photocathode research and development by growing additional epitaxial films of GaAlN/GaInN on sapphire and possibly other substrates in order to further optimize photocathodes. We are also interested in optimizing the epitaxial layers for the shorter wavebands used in UV and UV/visible imaging. This can be accomplished by incorporating Al in the GaAlN/GaInN active layers to enhance the short wavelength response. The spectral response and quantum efficiency of these shorter wavelength devices can also be evaluated in ultra-high vacuum with our *in-situ* hybrid phototube system. Other issues such as wafer uniformity should be evaluated as it pertains to large-area imaging devices. Also, run-to-run repeatability needs to be examined to address uniformity issues for use in experiments with large numbers of photocathodes. In the future we intend to explore the possibilities for eliminating the need to activate the photocathode surface with cesium by use of an AlGaIn surface layer doped n-type with silicon as was illustrated in Fig. 3. Also, other substrates such as AlN might be used with these photocathode layers in an attempt to reduce the defect density and perhaps improve the quantum efficiency. Finally, we intend to send a few photocathodes to Burle Industries for packaging and further measurements of quantum efficiency. Astrophysics experiments involving UV imaging as well as Chrenkov and scintillation light detection should benefit from these continued studies.

References

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