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# Atomic Hydrogen Cleaning of Polarized GaAs Photocathodes

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## Abstract

Atomic hydrogen cleaning followed by heat cleaning at 450°C was used to prepare negative-electron-affinity GaAs photocathodes. When hydrogen ions were eliminated, quantum efficiencies of 15% were obtained for bulk GaAs cathodes, higher than the results obtained using conventional 600°C heat cleaning. The low-temperature cleaning technique was successfully applied to thin, strained GaAs cathodes used for producing highly polarized electrons. No depolarization was observed even when the optimum cleaning time of about 30 seconds was extended by a factor of 100.

Polarized electron sources based on photoemission from negative-electron-affinity (NEA) III-V semiconductor photocathodes [1] are in widespread use with electron linear accelerators. [2] Recently the high-gradient-doping technique has been applied to photocathode structures to successfully overcome the surface charge limit effect while maintaining high spin polarization. [3] [4] The high-gradient-doping technique described here consists of a thin (10 nm), very-highly-doped ( $5 \times 10^{19} \text{ cm}^{-3}$ ) surface layer with a lower density doping ( $5 \times 10^{17} \text{ cm}^{-3}$ ) in the remaining active layer. High dopant density promotes recombination of the minority carriers trapped at the surface. Trapped carriers increase the surface barrier in proportion to the arrival rate of photoexcited conduction band (CB) electrons. [5] Because CB electrons depolarize as they diffuse to the surface of heavily doped materials, the highly doped layer must be very thin, typically no more than a few nanometers. However, to achieve high quantum efficiencies, an NEA surface is required, which in turn must be prepared on an atomically clean surface. The conventional way to achieve a surface free of all surface oxides and carbon-related contaminants is to heat the crystal to  $600^\circ\text{C}$  for about 1 hour. After only about 2 hours at this temperature, diffusion of the dopant in the thin, highly-doped layer results in the re-appearance of the surface charge limit effect. [6] Therefore, high temperature heat cleaning should be avoided.

Atomic hydrogen cleaning (AHC) is a well known technique for removing oxides and carbon-related contaminants at relatively low temperatures. The ability of AHC to preserve stoichiometry and sharp doping profiles is fully utilized in molecular beam epitaxy. The chemical reactions underlying oxide removal have been investigated using X-ray photoelectron spectroscopy (XPS) and reflection high-energy electron diffraction (RHEED). [7], [8], [9] While As-oxides and  $\text{Ga}_2\text{O}$ -like oxides are liberated at temperatures less than  $450^\circ\text{C}$ , the removal of  $\text{Ga}_3\text{O}$ -like oxides requires a higher temperature. Under atomic hydrogen irradiation,  $\text{Ga}_3\text{O}$ -like oxides are converted to more volatile  $\text{Ga}_2\text{O}$ -like oxides. On the other hand, it has been well demonstrated that atomic hydrogen can passivate both shallow donor and acceptor impurities. [10] [11] The passivation rate increases rapidly with the doping concentration. Since the band-bending in the photocathode is controlled by the  $p$ -type doping,

the dopant passivation may have an adverse effect on QE.

AHC has been employed previously for surface preparation of NEA photocathodes. [12] [13] QEs as high as 11 - 14% at 632.8 nm were achieved for bulk GaAs. Recently a significant spin depolarization was reported for a strained photocathode after long exposure to deuterium. [14] In the present paper, a systematic study of AHC in a vacuum-loading system is reported. The AHC system and the associated analysis system remain under UHV, while the sample is introduced in the UHV system through a loading chamber, and transferred between the AHC and analysis systems under vacuum. The SLAC vacuum-loading system provides a rapid and reliable way to exchange photocathodes without venting to atmospheric pressure followed by subsequent vacuum bake. More than 30 photocathodes were studied in the present experiment.

Two types of GaAs samples were used. Samples ( $13 \times 13 \text{ mm}^2$ ) cut from Zn-doped ( $1 \times 10^{19} \text{ cm}^{-3}$ ) bulk GaAs (001) wafers were used for optimizing the AHC conditions. Strained GaAs samples [15] with the active 100-nm GaAs layer Zn-doped at  $5 \times 10^{18} \text{ cm}^{-3}$  were used for studying the AHC effect on polarization. Prior to installation in the loading chamber, a sample was degreased in a boiling solution of trichloroethylene and chemically cleaned in  $\text{NH}_4\text{OH}$  to remove native oxides on the surface. Since  $\text{NH}_4\text{OH}$  etches only oxides without disturbing the stoichiometry of GaAs, it was used for the epitaxial photocathodes as well. Some samples were installed without the  $\text{NH}_4\text{OH}$  cleaning to intentionally leave native oxides on the surface. Previous XPS analyses showed that GaAs surface cleaned in  $\text{NH}_4\text{OH}$  had 0.3 nm [16] to 0.6 nm [7] of oxides while native oxide thickness varied from 2.4 nm [17] to 5.0 nm [18].

The experiments were carried out in a three-chamber UHV system consisting of a loading chamber, an AHC system and an analysis system called Cathode Test System (CTS). The AHC system was equipped with an rf plasma discharge source, a heater tower, and a linear translator. The GaAs sample sat on a molybdenum platter, which in turn sat on the heater tower. The heating was provided by a tungsten filament, and the GaAs surface temperature was measured by an infrared pyrometer. The surface temperature during AHC

was maintained at 300 - 350°C. The heater tower was electrically isolated from the AHC system so that a bias voltage could be applied to the GaAs sample during AHC. Atomic hydrogen was produced by dissociating molecular hydrogen in a 2.5 cm diameter Pyrex glassware surrounded by a helical rf resonator following the design used at Jefferson Lab. [12] Hydrogen atoms passed through a 1-mm diameter hole in the dissociator and traveled 25 cm to the GaAs sample. To study the effect of hydrogen ions generated by the rf dissociator, the GaAs sample could be biased negatively to enhance ion collection. The ion current reaching the GaAs sample was typically 8  $\mu$ A when the bias voltage was -88 V. To reduce the ion current, a transverse magnetic field was applied at the exit of the dissociator using a permanent magnet. With the magnet in place, the ion current was negligible ( $< 1$  nA). The dissociation was performed with a hydrogen pressure of 18 mTorr. Typically 50 Watts of rf power was applied, and the rf frequency was varied between 100 and 110 MHz to find the resonance frequency yielding the maximum rf absorption. The absorbed rf power was 35 - 45 Watts. During AHC the hydrogen pressure in the AHC chamber was  $3 \times 10^{-5}$  Torr pumped by a combination of a non-evaporable getter (NEG) pump, an ion pump, and a turbo-molecular pump. The base pressure of the AHC system was  $2 \times 10^{-10}$  Torr.

Activation to an NEA surface, and measurement of QE and polarization were made in the CTS. The CTS is a UHV system pumped by a combination of ion and NEG pumps. Polarization measurements were made using an electron transport column, an electrostatic 90° spin-rotator and a 20 keV Mott polarimeter. After AHC, the sample was transferred to the CTS under vacuum when the AHC system pressure dropped to a few  $10^{-8}$  Torr, typically within 30 minutes after AHC. The cathode activation method used to obtain an NEA surface consisted of heat cleaning for 1 hour, cool-down for an hour, followed by application of cesium until the photo-yield peaked, and then cesium and nitrogen-trifluoride co-deposition until the photo-yield was again maximized. The heat-cleaning temperature was monitored via an infrared pyrometer. The cathode was activated while monitoring the photo-yield with a white light and a 670 nm diode laser. Once a red response was observed from the diode laser, the white light was turned off and the diode laser was used to complete

the activation. The absolute QE was measured using the diode laser at a photon wavelength of 670 nm. A tungsten lamp and a monochromator were used to measure the relative QE as a function of photon wavelength, and these measurements were then normalized to the diode laser measurement at 670 nm.

To study the effect of the heat-cleaning temperature on the QE, a  $\text{NH}_4\text{OH}$ -cleaned bulk GaAs sample was first heat-cleaned at four different temperatures - 450, 500, 550, and 600°C - without AHC. Figure 1 shows the resulting QE spectra. The QE at 670 nm increased with the heat-cleaning temperature from 6.1% (450°C), to 9.7% (500°C), 11.9% (550°C), and 12.5% (600°C). The heat-cleaning temperature dependence was reproducible. The QE obtained for 450°C was typically a factor of two smaller than the QE for 600°C. The goal of atomic hydrogen cleaning is, therefore, to be able to achieve 12% QE using 450°C heat-cleaning temperature.

AHC was performed on  $\text{NH}_4\text{OH}$ -cleaned bulk GaAs samples under three different conditions that control the ion current: 1) with no bias and no magnet, 2) with a negative bias and no magnet to enhance the ion effect, and 3) with magnet and no bias to eliminate the ion effect. For each AHC, a fresh cathode sample was used and only the AHC time was varied while all other conditions were fixed. After AHC, the sample was transferred to the CTS under vacuum, heat-cleaned at 450°C, activated, and the QE measured. Figure 2 shows the QE at 670 nm as a function of the AHC time. QEs as high as 16% were obtained with only 15 - 30 seconds of AHC. The QE decreased with prolonged cleaning, yielding only 1.8% after 40 minutes of AHC. The QE was higher when the ion current was eliminated using the magnet, and lower when the ion current was enhanced using the negative bias. The data indicate that the excessive absorption of atomic hydrogen in GaAs is detrimental for the QE. Under atomic hydrogen irradiation, the native oxides on the surface are converted to more volatile oxides and get liberated. If the irradiation continues, atomic hydrogen is absorbed in the GaAs, passivating the *p*-type dopants in the band bending region. Since the doping concentration at the surface controls the band bending, dopant passivation raises the vacuum level, resulting in a lower QE. Acceptor passivation by hydrogen proceeds through

ion pair formation of negatively charged acceptors and positively charged hydrogen ions. [19] Ions are more effective than atomic hydrogen at passivating the dopants. The absorbed atomic hydrogens did not seem to be completely liberated from the GaAs even after 1 hour of heat-cleaning at 450°C. Using the sample cleaned for 40 minutes, the heat-cleaning temperature was raised to 500°C for 2 hours to see if the QE could be recovered. The QE increased to 2.6%, but the recovery was negligible, indicating that the dopant reactivation requires a higher temperature or a longer cleaning time, which defeats the purpose of AHC.

AHC was also performed on bulk GaAs samples without the  $\text{NH}_4\text{OH}$  cleaning. QEs as high as 14% were obtained after 1 hour of AHC (open square in Figure 2). The sample with native oxides produced a high QE after prolonged AHC, indicating the oxide layer was protecting the GaAs surface from impinging atomic hydrogen. [9] This indicates the AHC time must be optimized depending on the oxide level on the GaAs surface. The  $\text{NH}_4\text{OH}$  etching establishes a reproducible level of native oxides.

Studies at Jefferson Lab [14] indicate that a significant depolarization may occur as a result of long exposures to atomic deuterium followed by venting to atmospheric pressure and vacuum bake. The electron polarization was measured in the present experiment as a function of the AHC time using thin strained photocathodes. The sample was heat-cleaned at 570°C without AHC and the polarization was measured. Then, a sequence consisting of 15 minutes of AHC followed by polarization measurements was repeated four times for the same sample without breaking vacuum. The AHC was performed with the magnet and no bias voltage. Figure 3 shows the polarization spectrum for 1) no AHC, 2) 30 minutes AHC, and 3) 60 minutes AHC. All three data sets are consistent within the statistical errors. No depolarization was observed after 60 minutes, which is  $\sim 100$  times longer exposure time than the optimum time, of AHC in the vacuum-loading system. Using a different sample, the measurements were repeated without using the magnet. Again no depolarization was observed after 60 minutes of AHC.

In conclusion, atomic hydrogen cleaning can be used to prepare high-QE GaAs photocathodes at the lower heat-cleaning temperature of 450°C. Photocathode quantum efficien-

cies as high as 15% were obtained when hydrogen ions were eliminated. Extended exposure to atomic hydrogen was found to have no effect on the electron polarization.

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## LIST OF FIGURES

Figure 1 QE as a function of the excitation wavelength for 450°C (dash), 500°C (dots), 550°C (dot-dash), and 600°C (solid) heat-cleaning temperature.

Figure 2 QE at 670 nm as a function of the AHC time. Three different conditions are used to control ions: solid circles are no bias and with magnet, squares are no bias and without magnet, and triangles are with -88 V negative bias without magnet. One sample (open square) was not cleaned in  $\text{NH}_4\text{OH}$ .

Figure 3 Polarization and QE as a function of wavelength. Solid circles are measurements without AHC, triangles are measurements after 30 minutes of AHC, and squares are measurements after 60 minutes of AHC.

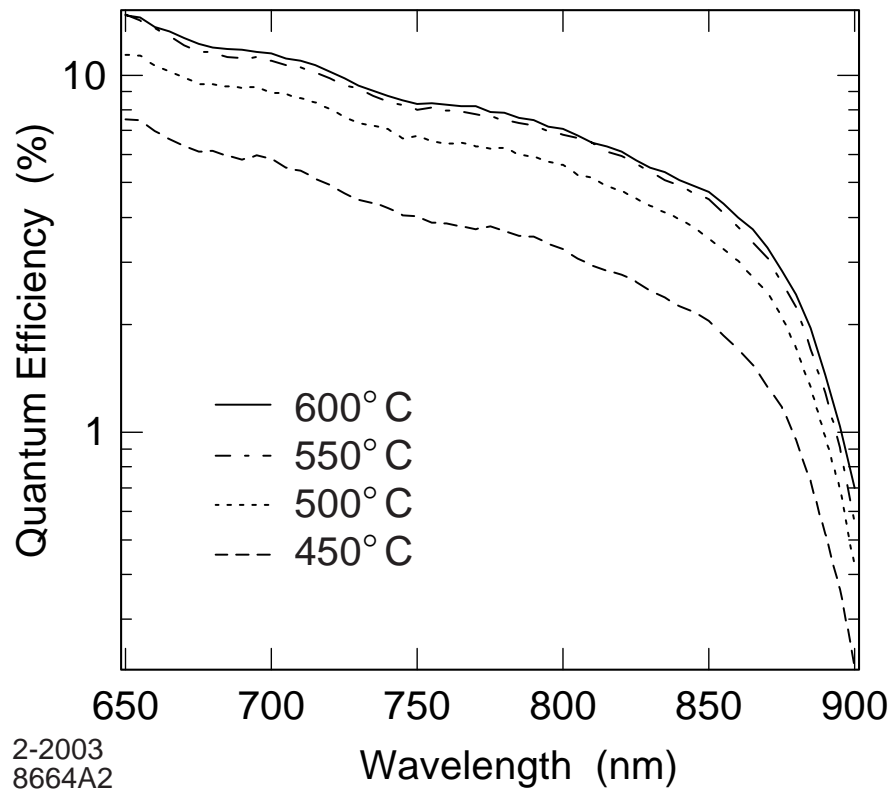
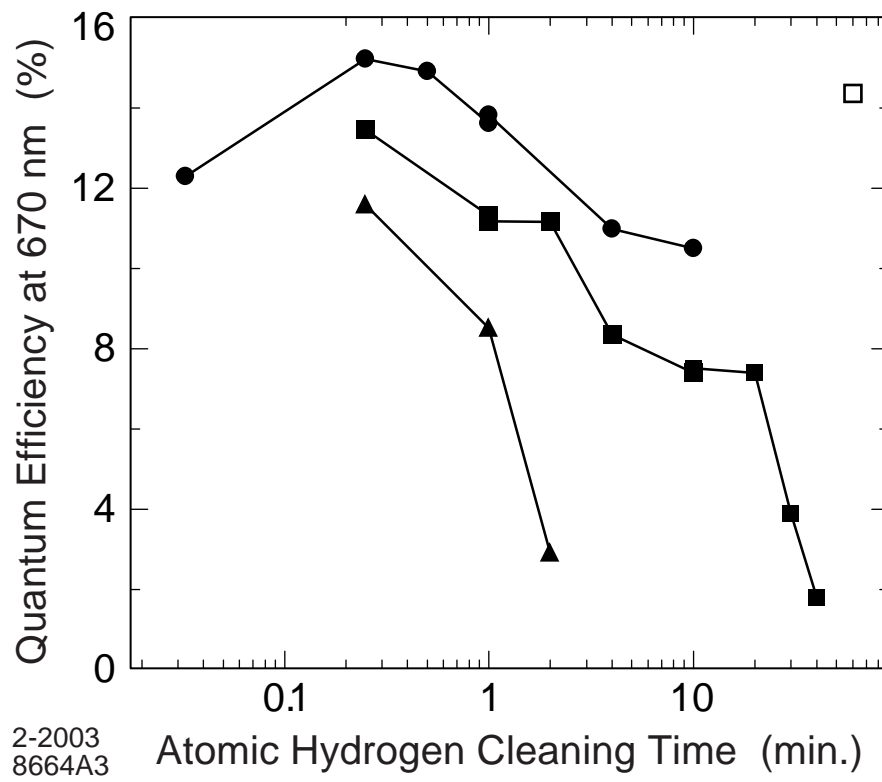
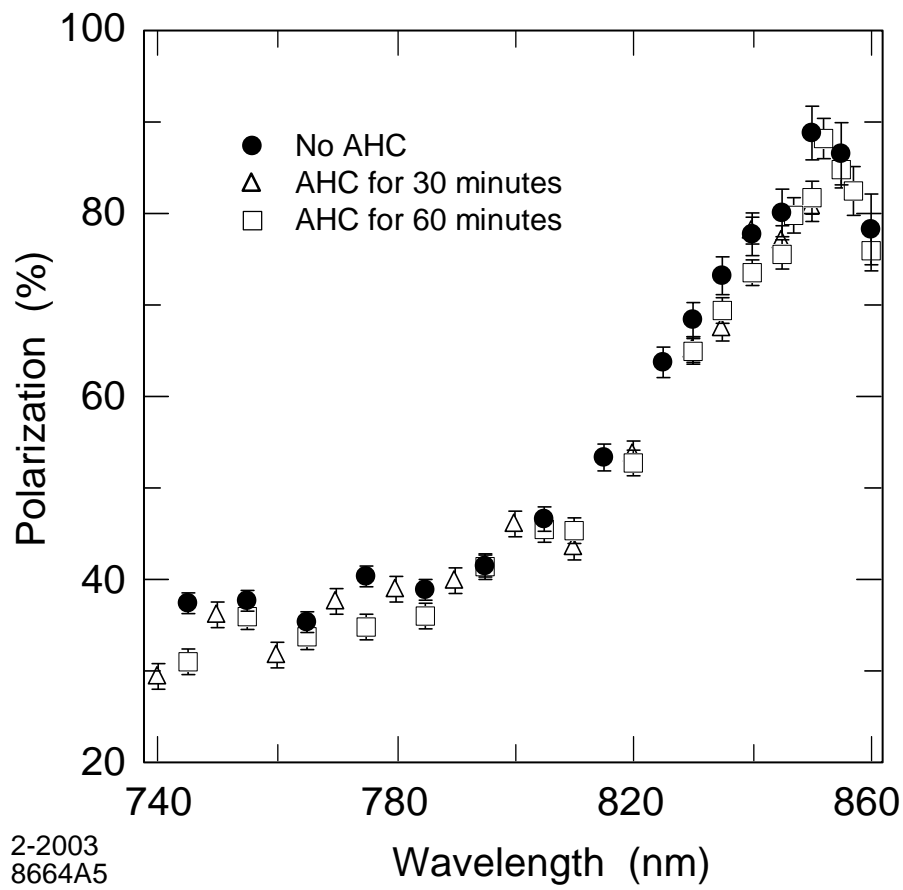


Figure 1



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Figure 2



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Figure 3