Atomic hydrogen cleaning of polarized GaAs photocathodes

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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 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 s was extended by a factor of 100. © 2003 American Institute of Physics. [DOI: 10.1063/1.1581981]

Polarized electron sources based on photoemission from negative-electron-affinity (NEA) III-V semiconductor photocathodes¹ are in widespread use with electron linear accelerators.² Recently, the high-gradient-doping technique has been applied to photocathode structures to 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 °C for about 1 h. After only about 2 h at this temperature, diffusion of the dopant in the thin highly-doped layer results in the reappearance 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.⁷⁻⁹ While As oxides and Ga₂O-like oxides are liberated at temperatures less than 450 °C, the removal of Ga₃O-like oxides requires a higher temperature. Under atomic hydrogen irradiation, Ga₃O-like oxides are converted to more volatile Ga₂O-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 the quantum efficiency (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 a long exposure to deuterium.¹⁴ In the present letter, a systematic study of AHC in a vacuum-loading system is reported. The AHC system and the associated analysis system remain under vacuum, 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 a subsequent vacuum bake. More than 30 photocathodes were studied in the present experiment.

Two types of GaAs samples were used. Samples (13×13) mm²) cut from Zn-doped (1×10^{19} cm⁻³) bulk GaAs (001) wafers were used for optimizing the AHC conditions. Strained GaAs samples¹⁵ with the active 100 nm GaAs layer Zn doped at 5×10^{18} 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 NH4OH to remove native oxides on the surface. Since NH₄OH etches only oxides without disturbing the stoichiometry of GaAs, it was used for the epitaxial photocathodes as well. Some samples were installed without the NH₄OH cleaning to intentionally leave native oxides on the surface. Previous XPS analyses showed that GaAs surface cleaned in NH₄OH had 0.3 nm (Ref. 16) to 0.6 nm (Ref. 7) of oxides while the native oxide thickness varied from 2.4 nm (Ref. 17) to 5.0 nm.¹⁸

4184

The experiments were carried out in a three-chamber UHV system consisting of a loading chamber, an AHC sys-

tem, 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 travelled 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 μ 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 W 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 W. During AHC, the hydrogen pressure in the AHC chamber was 3×10^{-5} Torr pumped by a combination of a nonevaporable getter (NEG) pump, an ion pump, and a turbomolecular pump. The base pressure of the AHC system was 2×10^{-10} Torr.

Activation to an NEA surface, and measurement of the 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 min after AHC. The cathode activation method used to obtain an NEA surface consisted of heat cleaning for 1 h, cool-down for 1 h, followed by application of cesium until the photoyield peaked, and then cesium and nitrogen-trifluoride codeposition until the photoyield was again maximized. The heat-cleaning temperature was monitored via an infrared pyrometer. The cathode was activated while monitoring the photoyield 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 NH₄OH-cleaned bulk GaAs sample was first heat cleaned at four different temperature—450, 500, 550, and $600 \,^{\circ}\text{C}$ —without AHC. Figure 1 shows the resulting QE spectra. The QE at 670 nm increased with the heat-cleaning



FIG. 1. QE as a function of the excitation wavelength for 450 °C (dashed), 500 °C (dotted), 550 °C (dotted–dashed), and 600 °C (solid) heat-cleaning temperature.

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 NH₄OH-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 a 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 s of AHC. The QE decreased with prolonged cleaning, yielding only 1.8% after 40 min of AHC. The QE was higher when the ion current was eliminated using the magnet, and lower



FIG. 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 NH₄OH.

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

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 h of heat cleaning at 450 °C. Using the sample cleaned for 40 min, the heat-cleaning temperature was raised to 500 °C for 2 h 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 NH₄OH cleaning. QEs as high as 14% were obtained after 1 h of AHC (open square in Fig. 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 NH₄OH etching establishes a reproducible level of native oxides.

Studies at Jefferson Lab¹⁴ indicate that a significant depolarization may occur as a result of long exposures to atomic deuterium followed by venting to atmospheric pressure and a 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 min of AHC followed by polarization measurements was repeated four times for the same sample without breaking the vacuum. The AHC was performed with the magnet and no bias voltage. Figure 3 shows the polarization spectrum for (1) no AHC, (2) 30 min AHC, and (3) 60 min AHC. All three data sets are consistent within the statistical errors. No depolarization was observed after 60 min, which is ~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 min of AHC.

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