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.

1. Introduction

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. The high-gradient-doping technique consists of a thin (10 nm), very-highly-doped ($5 \times 10^{19}$ cm$^{-3}$) surface layer with a lower density doping ($5 \times 10^{17}$ 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. 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 negative-electron-affinity (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 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. 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. While As-oxides and Ga$_2$O-like oxides are liberated at temperatures less than 450°C, the removal of Ga$_2$O$_3$-like oxides requires a higher temperature. Under atomic hydrogen irradiation, Ga$_2$O$_3$-like oxides are converted to more volatile Ga$_2$O-like oxides. On the other hand, it has been well demonstrated that atomic hydrogen can passivate both shallow donor and acceptor impurities. 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.

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.

2. Experiment

Two types of GaAs samples were used. Samples (13 × 13 mm$^2$) cut from Zn-doped (1 × 10$^{19}$ cm$^{-3}$) bulk GaAs (001) wafers were used for optimizing the AHC conditions. Strained GaAs samples 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 NH$_4$OH to remove native oxides on the surface. Since NH$_4$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 NH$_4$OH cleaning to intentionally leave native oxides on the surface.

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 surface temperature during AHC was maintained at 300 - 350°C. The heater
A 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. To study the effect of hydrogen ions generated by the rf dissociator, the GaAs sample could be biased negatively to enhance ion collection. 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).

Activation to an NEA surface, and measurement of QE and polarization were made in the CTS. 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.

AHC was performed on NH$_4$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 88-Volt 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 1 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. Ions are more effective than atomic hydrogen at passivating the dopants.
AHC was also performed on bulk GaAs samples without the NH$_4$OH cleaning. QEs as high as 14% were obtained after 1 hour of AHC (open square in Figure 1). 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. This indicates the AHC time must be optimized depending on the oxide level on the GaAs surface. The NH$_4$OH etching establishes a reproducible level of native oxides.

Figure 1. 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 NH$_4$OH.

Studies at Jefferson Lab indicate that a significant depolarization may occur as a result of long exposures to atomic deuterium. 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. The AHC was performed with the magnet and no bias voltage. Figure 2 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 ∼100 times longer exposure time than the optimum time, of AHC.
3. Conclusions

Atomic hydrogen cleaning can be used to prepare high-QE GaAs photocathodes at the lower heat-cleaning temperature of 450°C. Photocathode quantum efficiencies 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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