ATOMIC HYDROGEN CLEANING OF SEMICONDUCTOR PHOTOCATHODES

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Abstract
Negative Electron Affinity (NEA) semiconductor photocathodes are widely used for the production of polarized electron beams, and are also useful for the production of high brightness electron beams which can be modulated at very high frequencies. Preparation of an atomically clean semiconductor surface is an essential step in the fabrication of a NEA photocathode. This cleaning step is difficult for certain semiconductors, such as the very thin materials which produce the highest beam polarization, and those which have tightly bound oxides and carbides. Using a small RF dissociation atomic hydrogen source, we have reproducibly cleaned GaAs wafers which have been only degreased prior to installation in vacuum. We have consistently prepared very high quantum efficiency photocathodes following atomic hydrogen cleaning. Details of our apparatus and most recent results are presented.

1 INTRODUCTION

NEA photocathodes have two broad areas of application as electron sources for accelerators. They are at the heart of essentially all polarized electron sources in use at the present, and they provide a high quantum efficiency photocathode for the generation of high brightness beams which may be modulated at very high frequencies [1]. These cathodes are formed on atomically clean surfaces of direct bandgap semiconductors by the addition of cesium and an oxidant, typically oxygen or nitrogen trifluoride. The preparation of an atomically clean surface on the semiconductor is an essential step in this process, and the quantum yield of the resulting photocathode depends strongly on the quality of the result achieved in the cleaning step [2]. Most cleaning techniques used to date have employed some type of wet chemical processing prior to the introduction of the semiconductor material into the gun vacuum system, followed by heating the cathode to high temperatures in the gun after a suitable ultrahigh vacuum environment has been established. More recently, with the use of epitaxially grown semiconductors, it has been possible in some cases to grow a protective cap layer on the semiconductor surface which can later be removed by heating in vacuum.

Each of the above cleaning methods has its drawbacks. Wet chemical processes typically remove a significant amount of material - more than is present in the case of the thin layers which produce the highest beam polarization, for example. Heating in vacuum cannot remove certain oxides and carbides from many semiconductors. Heating in vacuum may also crack residual gases and thereby create contamination on the semiconductor surface. Heating may damage some of the specialized semiconductor structures developed to provide either high polarization or high quantum yield. Finally, growth of protective cap layers has a record of mixed success to date, and cannot be done with all methods of epitaxial growth.

It is highly desirable to have a cleaning process which can be employed in ultrahigh vacuum; which will remove all oxides, carbides, and other contamination without removing a significant amount of the base semiconductor material; and which will minimize the maximum temperature and the temperature-time product of any heating cycles involved. Cleaning by exposure to atomic hydrogen meets all of these criteria.

It is well established that the exposure of many III-V, II-VI, and elemental semiconductors to atomic hydrogen, typically at modestly elevated temperatures, produces a semiconductor surface entirely free of contamination [3]. In particular, atomic hydrogen exposure is capable of removing such difficult contaminants as oxygen on silicon, and carbon on GaAs. This cleaning process, possibly followed by a heating cycle, leaves surfaces which show sharp LEED patterns, indicating good stoichiometry and surface order. The process is readily adaptable to *in situ* use in ultrahigh vacuum.

2 CLEANING PROCEDURE DEVELOPMENT

Our initial experiments were done by placing the sample to be cleaned in DC hydrogen glow discharges in various geometries. These experiments demonstrated clear evidence for surface cleaning in some cases, both by Auger measurements on the cleaned surface, and by the photoresponse of the cleaned surface to cesium. However, we also saw evidence of transport of contamination from the chamber walls to the semiconductor surface. In addition, it was difficult to imagine adapting this scheme for use in an ultrahigh vacuum electron gun. Accordingly, we decided to develop an RF dissociation atomic hydrogen source.

Our atomic hydrogen source is a modification of one developed for use in a polarized atomic hydrogen target [4]. It employs a helical resonator surrounding a 2.5 cm diameter Pyrex tube containing the hydrogen. Ultrapure hydrogen is admitted to this chamber through an ultrahigh vacuum leak valve. Atomic hydrogen exits the discharge

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region through a small aperture (typically 1 mm or smaller), and is conducted to the sample to be cleaned by an aluminum tube. Aluminum is chosen as it has a low atomic hydrogen recombination coefficient. The resonator is made of stainless steel, as it is within the region subject to ultrahigh vacuum bakeout. The source is mounted on a multiport stainless steel vacuum chamber which contains the sample, ultrahigh vacuum pumping, and apparatus to permit the illumination and fabrication of a NEA photocathode on the clean sample. The sample itself is mounted on a stalk which may be heated, and which is identical to those used in our photoemission electron guns. The complete apparatus, including the atomic hydrogen source, is bakeable to 250 C, and is shown schematically in Figure 1.

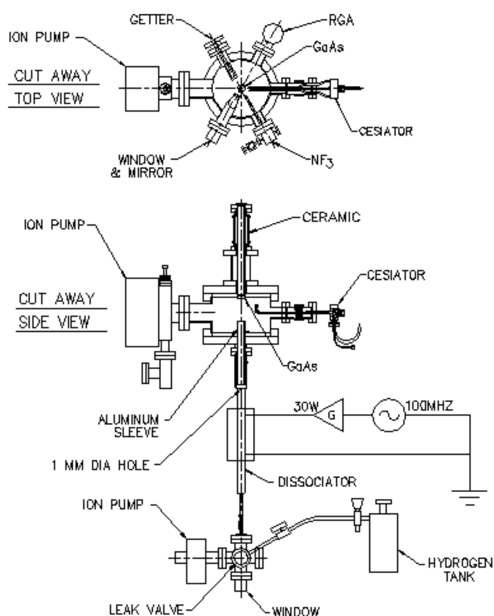

Figure 1. Schematic view of the experimental apparatus.

Following an initial vacuum bakeout, the chamber pressure typically fell below 10^{-8} mbar within a few hours after careful dry nitrogen backfilling and the introduction of a new sample. At these low pressures, it is feasible to conduct atomic hydrogen cleaning and cesium photoresponse measurements without the need for a time consuming bakeout. This allowed us to make a large number of photoresponse measurements relatively easily, to establish suitable parameters for the atomic hydrogen cleaning process. We determined the proper RF frequency, power and hydrogen pressure to achieve a high degree of hydrogen dissociation and a good atomic hydrogen flux on the sample, as well as the cleaning time and sample temperature which resulted in the best photoresponse to cesium. While hydrogen dissociation occurs over a broad range of hydrogen pressure and RF frequency, it is necessary to consider recombination as well as dissociation to obtain the optimum cleaning conditions. With our resonator, we typically operate with 40 W of RF power at 90-110 MHz, and a hydrogen pressure of 24-30 mbar. We estimate the atomic hydrogen flux at the sample is of order 10^{16}/cm^2/sec.

Much hydrogen, both molecular and atomic, enters the vacuum chamber during the cleaning, requiring a high hydrogen pumping speed. In the test chamber, this was provided by a 30 l/s DI pump and a 220 l/s non-evaporable getter. The non-evaporable getter pumps hydrogen reversibly, and can be used for a large number of cleaning cycles. Under our conditions, the pressure in the main chamber during the cleaning cycle is below 10^{-5} mbar. Once the cleaning cycle is complete and the hydrogen flow stopped, the chamber pressure rapidly recovers to the ultrahigh vacuum range.

3 RESULTS

Once we established a reasonable set of parameters for the atomic hydrogen cleaning process in the unbaked chamber, we installed a wafer of relatively low dopant density (*ca* 2-3 x 10^{18}/cm^3 Zn) bulk GaAs which had been only degreased. The entire apparatus was vacuum baked at 250 C for about 30 hours, and reached a base pressure below 10^{-10} mbar following cooldown. Atomic hydrogen cleaning of the sample was done at a sample temperature of ~ 300 C for 45 minutes. Following the cleaning cycle, the sample was heated to ~ 450 C to remove bound and sorbed hydrogen [3]. After cooling to room temperature, the sample was activated to NEA by the application of cesium and either nitrogen trifluoride or nitrous oxide.

A typical measurement of quantum efficiency as a function of wavelength is shown in figure 2. These results have been repeated in this apparatus on several similar GaAs samples. It is interesting to note that these very good quantum yields are obtained on samples with low dopant density. It is believed that higher dopant density is detrimental to producing the highest beam polarizations, but necessary for obtaining the highest quantum yields. It will be interesting to explore this tradeoff using the atomic hydrogen cleaning process.

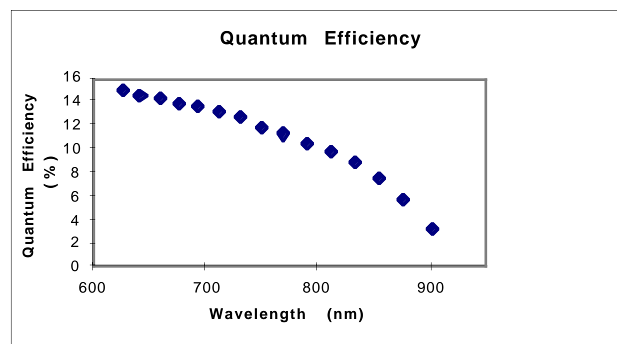

Figure 2. Quantum Efficiency versus wavelength for an NEA GaAs photocathode prepared after atomic hydrogen cleaning.

Following the excellent results above, we transferred this process to the polarized source group of the MAMI accelerator at Mainz. This group has obtained similarly good quantum efficiency on bulk GaAs, and has activated samples of thin strained GaAs with good results as well. The Mainz group has measured the beam polarization from atomic hydrogen cleaned bulk GaAs and found it to be normal [5].

Okada and Harris [3] have pointed out that the atomic hydrogen cleaning process leaves a fully passivated GaAs surface. It should thus be possible to transfer an atomic hydrogen cleaned GaAs sample through air without detrimental effects. Accordingly, we constructed a small "roll-around" atomic hydrogen cleaning station. Using this, we cleaned GaAs wafers, and, after venting the cleaning station to dry nitrogen, transported the cleaned wafers through room air and installed them in our photoemission guns. We have successfully prepared high quantum yield cathodes on wafers transported through air after atomic hydrogen cleaning.

We plan to incorporate the atomic hydrogen cleaning process directly into our photoemission guns. To do this, we have constructed a modified version of the atomic hydrogen source. In this design, the volume containing the hydrogen glow extends into the primary vacuum chamber of the electron gun. The atomic hydrogen exits through a small aperture directly below the cathode wafer. The RF resonator is outside the vacuum chamber. We have demonstrated that the glow in this arrangement extends fully into the vacuum, even though the RF excitation is entirely outside the vacuum. This source is mounted on a bellows, allowing us to position the exit aperture under the cathode for cleaning, and to remove it for electron beam operation. Tests will be conducted in a complete photoemission electron gun shortly.

4 ACKNOWLEDGMENTS

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REFERENCES

[1] D. Engwall *et al.*, "*A High-DC-Voltage GaAs Photoemission Gun: Transverse Emittance and Momentum Spread Measurements*", these proceedings.

[2] J. J. Uebbing, J. Appl. Phys. **41**, 802 (1970); J. S. Escher in *Semiconductors and Semimetals*, v. 15, Academic Press, N.Y., 1981, p. 195.

[3] There is a very extensive literature on this topic, primarily directed to device applications. Recent examples include: Y. Luo *et al*., Appl. Phys. Lett. **67**, 55 (1995); Y. Okada and J. S. Harris, J. Vac. Sci. Technol. **B14**, 1725 (1996); Z. Yu *et al*., Appl. Phys. Lett. **69**, 82 (1996).

[4] M. Poelker *et al*., Nucl. Instr. Meth. **A364**, 58 (1995).

[5] Peter Hartmann, Johannes Gutenberg Universität, Mainz, private communication.