OXIDE EFFECTS ON PHOTOEMISSION FROM
HIGH CURRENT GaAs PHOTOCATHODES*

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ABSTRACT

During four years of on line operation of the SLAC polarized electron gun (PEGGY) and polarized LEED (PLEED) system, we have observed and characterized the failure modes of the GaAs (100) photocathodes (PC's) used in these systems. Several modes are observed. Gradual decreases in electron polarization and intensity are attributed to the physisorption of CO on the PC's during running at 1N₂ temperatures. Such PC's can be rejuvenated by warming to 90K, i.e., above the CO₂ desorption temperature. These PC's recover 90% of their original intensity. A second well-characterized failure mode results from overheating the PC during in-situ heat cleaning prior to activation. In this mode, As is preferentially evaporated from the GaAs, leaving a Ga₂O₃ layer on the surface. This effect has been studied by AES sputter profiling which indicates that the substantial thickness of the oxide layer blocks photoemission. These PC's may

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only be recovered by chemically removing the oxide layer. A third mode which is not as well characterized appears for thin Ga oxide layers. Properties of these PC's include reduced emission and the presence of a cutoff bias level. Such PC's are also not recoverable in-situ.

INTRODUCTION

Negative-electron-affinity (NEA) Cs oxide-coated GaAs was proposed by Garwin et al.¹ in 1974 as a high-intensity photoemission source of polarized electrons. A polarized electron gun (PEGGY) source was subsequently developed by SLAC for use, beginning in 1977, on the linear accelerator in an experiment to measure parity non-conservation in the inelastic scattering of polarized electrons from deuterium². This source has also been adapted for use at very low energies in the SLAC polarized LEED (PLEED) system³. The source possesses high brightness and current, in addition to which the polarization of the photoemitted electrons may be reversed by reversal of the optical polarization of the photo exciting laser light. These properties (especially high current) also make the source desirable for use on the proposed SLAC Linear Collider⁴.

Beginning with our early developmental work on the source, we have used some tens of GaAs photocathodes (PC's). Operating characteristics have been noted and cathode failures and anomalies, where they have occurred, have been studied both in-situ and in a separate Auger electron spectroscopy (AES) system. A number of distinct cathode operational modes have been observed. The increasing popularity of the source⁵ motivates dissemination of the results of these studies.

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CATHODE PREPARATION

Briefly, cathodes are prepared by the following steps: 1) chemical etching, 2) insertion into vacuum and bake-out, 3) heat cleaning to 580-660 °C, 4) quenching to 20° C, followed by activation with Cs and O₂ and, 5) cooling to an operational temperature of ~80K.

Sources were usually made on 6×10^{18} to 4×10^{19} Zn-doped p-GaAs (100) wafers, although some experiments were done of p-GaAs (111). Results appear similar for both types. Crucial to the production of a good high quantum efficiency (QE) PC in-situ was the etching procedure used prior to introduction into vacuum. The PC's cannot be effectively cleaned of C contamination or thick oxide layers by in-situ heat treatment. The etching process must leave only a few per cent or less of C or oxide on the surface before insertion into UHV. Deposition of Cs onto the GaAs prior to bake-out prevents oxidation of the GaAs surface during the bake and is useful in removing the remaining few per cent of C during the first heat cleaning. Our etching procedure is developed from the work of Shiota et al.⁶ and may be found reproduced exactly in Pierce et al.⁷ where further details of the SLAC source are included. Our AES studies show that very clean GaAs surfaces and high QE (for the bulk material used here) PC's are produced using this etch procedure. Thin oxide layers can be removed by in-situ heat treatment to 580° C, although much of our work used a 660° C treatment temperature.

PC activation is done by simultaneous exposure to Cs vapor and O₂ gas. The photo-emitted current generated by white (tungsten lamp) or red band gap light (obtained by inserting a filter possessing long wavelength pass and a 50% cutoff at 710 nm) is monitored while the Cs and O₂ rates are adjusted for maximum QE. Long (~ 1 hour) additional exposures of low O₂ pressures led to the

most stable cathodes. Typical QE's for good PC's were 4% (maximum 20%) with white to red light (W/R ratio) photocurrents of 3/1 or less. Poor PC's had a QE of less than 2% and W/R greater than 4. Undamaged cathodes could be heat-cleaned of Cs oxide and re-activated in-situ, if desired. The operational characteristics of the PEGGY and PLEED system sources are given in Table 1. It was possible to generate larger electron current pulses (> 1 A peak, 1.0 μ sec pulses) than the linear accelerator could accept at the injection energy of 65 keV.

AES SYSTEM

The AES system is of standard UHV design, incorporating a CMA with axial electron gun and Ar sputter ion gun. Beam incidence angles to the surface normal for the electron and ion beams were 30° and 41° , respectively. The sputter etch rate for Ga_2O_3 at this angle and 1 keV energy was measured on thermally grown thick oxides on GaAs as $1.92 \text{ (Å/min)}/\mu \text{ A/cm}^2$. The oxide stoichiometry was verified by X-ray analysis. This rate is similar to that for GaAs and is used in the depth profiles presented here.

Auger sensitivities were determined for our system using sputter-cleaned bulk material or thick films. Depth profiles are presented as Auger peak-to-peak heights divided by their appropriate sensitivities. Peaks and sensitivities used were for elemental As (34 eV), elemental Ga (55 eV), graphitic C (~ 270 eV), O from Ga_2O_3 (~ 515 eV) and Cs (~ 567 eV). Cs also has a major peak at 46 eV, so it was not possible to monitor the oxidized Ga peak on cesiated samples. The presence of oxidized Ga was inferred from shifts in energy and change of shape in the Ga 55 eV peak⁶. Other evidence for the presence of Ga oxidation will be presented in the discussion on non-recoverable PC's.

The PC's were removed from the PEGGY or PLEED systems by ceasing and then exposing the PC to several hundred torr of pure O_2 just prior to opening. This step saturates the Cs layer and prevents water vapor reaction with its consequent bubble formation. Thus, the actual Cs layer observed in the AES system may be (and probably is) different than that present in actual PC operation. Nevertheless, the studies presented here are useful because they compare profiles of "good" PC's with those that have failed in operation, noting that both types are treated identically during removal.

CATHODE CHARACTERISTICS

All GaAs cathodes used at SLAC sooner or later show a decline in QE with usage. Some were recoverable for many cycles in-situ; the rest were not. One of the PC's examined was used for nine months in PEGGY on the parity violation experiment. It was removed at the termination of the experiment for examination. Typical on-line use of this PC was 24 hours/day, 100 to 150 μA (10^{12} to 1.5×10^{12} electrons) pulses, 1 μ sec long at 120 pulses/sec.

Recoverable Cathodes:

Recoverable PC's suffered from one or more of the following: 1) CO_2 adsorption, 2) Cs loss by surface diffusion, and 3) excess O_2 adsorption caused by electron-induced gas desorption from the electron optics.

PC's have higher electron polarization at low temperatures, so cathodes were generally LN_2 cooled. This inevitably led over long time periods to physisorption of CO_2 with consequent decay in PC current and polarization. These PC's are nearly totally recoverable by warming the PC to above the thermal

desorption temperature of CO_2 , i.e., above 90K (generally we went to 200K) and then recooling to LN_2 temperature.

Cs loss (presumably by surface diffusion) was caused by running PC's at higher ($\sim 20^\circ\text{C}$) temperatures. Such PC's could be rejuvenated by addition of more Cs and O_2 at 20°C . Activation in any case is most efficient at this temperature because the Cs and O_2 are mobile enough to form the dipole layer needed for NEA without the rapid loss of Cs from the PC that would occur at still higher temperatures.

PC's which picked up too much O_2 , either by EID or improper NEA activation could be recleaned by heat treatment to $580\text{--}650^\circ\text{C}$ and subsequent reactivation, provided that a thick oxide layer had not formed on the GaAs itself. Thermal desorption of gases, such as CO_2 , from the electron optics structure "seen" by the PC was recognized early in the developmental program as a cause of fast QE decay. This effect was minimized by cooling these parts with LN_2 .

Non-recoverable Cathodes:

In-situ non-recoverable PC's fall into several distinct types: 1) C-contaminated surfaces, 2) Ga-rich surface layers oxidized in-situ or upon O_2 exposure during removal and, 3) thinner oxide layers formed between the Cs oxide overlayer and the GaAs substrate.

C-contaminated PC's were rare due to the cleanliness of both the PLEED and PEGGY systems. The source of the C was unknown but may be present on the cathode holder prior to insertion and then migrates to the PC surface during operation. This effect was best characterized at PEGGY. In-situ experiments, involving steering the laser spot across the PC surface, indicated that PC emission was occurring from patches on the surface. Typical performance was a

PC displaying a low W/R ratio (indicative of good NEA) but also low beam current. Subsequent depth profile examination (Figure 1) shows a high C concentration at the surface.

The second type of failure occurred when a PC was inadvertently overheated ($> 660^{\circ}\text{C}$) during a cleaning cycle prior to activation. By exceeding the congruent evaporation temperature of GaAs ($T_c = 663^{\circ}\text{C}$), As is preferentially evaporated, leaving behind a thick Ga_2O_3 layer. Generally the damage was visible by optical inspection as an alteration in the mirror surface of the PC. The depth profile showed that the O concentration extended well into the bulk of the GaAs. These PC's could no longer be activated in-situ and were removed for chemical etching of the damaged layer. Figure 2 shows the clear similarities between the Auger spectra of these PC's and thermally grown Ga_2O_3 layers.

The most common type of in-situ PC failure occurred when too much O_2 was introduced into the Cs oxide layer during activation. The PC's showed low QE and poor W/R ratios. In addition, the photoemission increased with increased cathode extraction bias, although patch emission was not detected, as in the C-contamination case. Heat cleaning and re-activation did not improve, and generally caused further degradation in the PC quality. This indicates that a permanent change had occurred on the native GaAs surface. Comparison of depth profiles for normal PC's and these (Figures 3, 4) shows that a high O concentration extends beyond the Cs layer and into the GaAs. The time evolution of the cathode bias effect observed is shown in Figure 5. In the presence of illumination and applied bias, the onset of photoemission took place at lower and lower applied bias as time progressed. If either illumination or bias were removed, the point at which the next onset would occur shifted to higher bias.

We ascribe, therefore, this last type of PC failure to space-charge-limited photoemission through an oxide layer present between the Cs oxide and the GaAs bulk. These PC's were fully recoverable only by chemical etching.

CONCLUSION

We find that the primary causes of permanent cathode degradation are overheating during the cleaning cycle and over-oxidation during Cs oxide activation. Both of these may be avoided with proper care.

Our experience at SLAC shows that NEA GaAs is a dependable long-lived high current electron source. Typical electron polarization from this source is $40 \pm 5\%$, close to the predicted theoretical value¹ of 50%. We are presently engaged in a polarization improvement program. This involves producing source types with GaAs⁺ present high current but with improved polarization. These include stressed-GaAs, MBE multilayer structures, and chalcopyrite emitters. All promise or have already shown higher polarization than NEA-GaAs; that one which will also show operational convenience will be the polarized-electron cathode of the future.

REFERENCES

1. E. L. Garwin, D. T. Pierce and H. C. Siegmann, *Helv. Phys. Acta*, 47, 1974, 393.
2. C. Prescott, W. B. Atwood, R. L. Cottrell, H. C. DeStaebler, E. L. Garwin, A. Gould, R. H. Miller, L. S. Rochester, T. Sato, D. Sherden, C. K. Sinclair, S. Stein, R. E. Taylor, J. E. Clendenin, V. W. Hughes, N. Sasao, K. P. Ehuler, M. Borghini, K. Lubelsmeyer and W. Jentschke, *Phys. Rev. Lett.*, 77B, 1976, 347.
3. E. L. Garwin and R. E. Kirby, *Proc. 7th Int. Vac. Cong. and 3rd Int. Conf. Solid Surfaces*, Vienna, Austria, 12-16 Sept. 1977, p. 2399.
4. B. Richter, R. Bell, K. L. Brown, A. W. Chao, J. E. Clendenin, K. F. Crook, W. A. Davies-White, H. C. DeStaebler, S. D. Ecklund, G. E. Fischer, R. A. Gould, R. J. Hollebeck, M. J. Lee, A. V. Lissin, G. A. Loew, R. Melen, R. H. Miller, D. Ritson, D. Sherden, C. K. Sinclair, J. Spencer, R. Stiening, P. B. Wilson and C. Y. Yao, *Proc. XIth Int. Conf. on High Energy Accelerators*, CERN, Geneva, Switzerland, 7-11 July 1960.
5. B. Reihl and B. I. Dunlap, *Appl. Phys. Lett.*, 37, 1960, 941.
6. I. Shiota, K. Motoya, T. Gami, N. Miyamoto and J. Nishizawa, *J. Electrochem. Soc.*, 124, 1977, 155.
7. D. T. Pierce, R. J. Celotta, G. C. Wang, W. N. Unertl, A. Galejs, C. E. Kuyatt and S. R. Mielczarek, *Rev. Sci. Instr.*, 51, 1980, 478.
8. W. Ranke and K. Jarosh, *Surf. Science*, 47, 1975, 525.

FIGURE CAPTIONS

1. Depth profile for C-contaminated cathode. Apparently over thick layer of Cs and O due to ion-knock effects and greater Auger electron escape depth than that for As and Ga.
2. AES spectra for a) clean GaAs, b) thermally grown thick layer of Ga_2O_3 and c) overheated PC. Energy shifts and shape changes in c) are consistent with oxidized GaAs⁸.
3. Typical depth profile for undamaged PC's. Ion knock-on and escape depth effects are apparent in Cs and O line shapes.
4. Depth profile for "thin oxide" interface layer. Compare to Figure 3. Source of the maxima in the Cs and O lines is unknown.
5. Change in cathode extraction bias potential as a function of elapsed illumination time for "thin oxide" layers.

TABLE 1. PC Operational Systems

	<u>PEGGY</u>	<u>PLEED</u>
Final Electron Energy	22 GeV	10-200 eV
Beam Current	> 1000 mA, peak	1-3 μ A
Cathode Field	13 kV/cm	25 V/cm
Laser wavelength	710 nm	674.6 nm
Laser Power Density	10 kW/cm ²	30 W/cm ²
Repetition Rate	1.6 μ sec pulse, 120 Hz	DC
Spot Size	.6 cm	.05 cm

Fig. 1

Fig. 2

Fig. 3

Fig 4

Fig. 5