

# SURFACE ANALYSIS OF A DEGRADED NEA-GaAs PHOTOCATHODE BY TEMPERATURE PROGRAMMED DESORPTION TECHNIQUE\*

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## Abstract

An analysis of a degraded GaAs surface activated to negative electron affinity (NEA) was investigated by means of temperature programmed desorption (TPD). The NEA-GaAs photocathode is an important device for not only high-average-current electron accelerators such as a next-generation light source based on an energy recovery linac, but also dynamic transmission electron microscopes. The quantum efficiency of the NEA-GaAs photocathode is decaying with time elapsing, even if the electron beam is not extracted. The degradation is mainly caused by adsorption of residual gases in a vacuum chamber. In order to analyze such surface states, we have measured TPD spectra from the degraded NEA-GaAs photocathode with a quadrupole mass spectrometer. The desorption peaks of hydrogen, carbon oxide and carbon dioxide from the degraded NEA surface were observed.

## INTRODUCTION

A GaAs photocathode activated the surface to negative electron affinity (NEA) is an important device for not only high-average-current electron accelerators, such as a next-generation light source based on an energy recovery linac, but also dynamic transmission electron microscopes. The NEA surface is normally formed by a yo-yo technique in which cesium (Cs) and oxygen (O<sub>2</sub>) are applied onto the clean surface of GaAs alternately in ultra-high vacuum. Although the quantum efficiency (QE) of the NEA-GaAs cathode is relatively larger than that of another cathode, the lifetime is shorter than that of another cathode. The QE degradation is caused by adsorption of residual gases in the vacuum chamber, ion back-bombardment and thermal desorption of Cs/O [1,2].

In previous studies, effects of the residual gases for the cathode lifetime were reported. T. Wada et al. reported that carbon dioxide degraded the QE of the cathode, but carbon monoxide almost never degraded the QE [3]. D. Durek et al. demonstrated that the lifetime was proportional to the reciprocal of partial pressure of water vapour [4]. We studied the effect of the total vacuum pressure for the lifetime with the vacuum range of  $5 \times 10^{-9} \sim 5 \times 10^{-8}$  Pa. The result indicated that the lifetime longer than 1000 hours could be achieved for the vacuum pressure of  $1 \times 10^{-9}$  Pa. However, there is a few of investigations for the surface states of the degraded cathode.

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In this work, a surface analysis of the NEA-GaAs cathode whose quantum efficiency was degraded due to the adsorption of residual gases in a vacuum chamber was performed by means of temperature programmed desorption (TPD) technique with combination of a quadrupole mass spectrometer (QMS). The result was evaluated to compare with the TPD spectrum from an non-activated surface.

## EXPERIMENTAL PROCEDURE

The experiment was performed at Hiroshima University [5,6] by using of a simple system consisting of stainless steel chambers equipped with a 160 l/s ion pump and a 310 l/s non-evaporable getter pump. The QMS (M101QA-TDM-W, ANELVA), which is able to measure the mass-to-charge ratio ( $m/z$ ) up to 100, is placed to detect desorption signals efficiently as shown in Fig. 1.

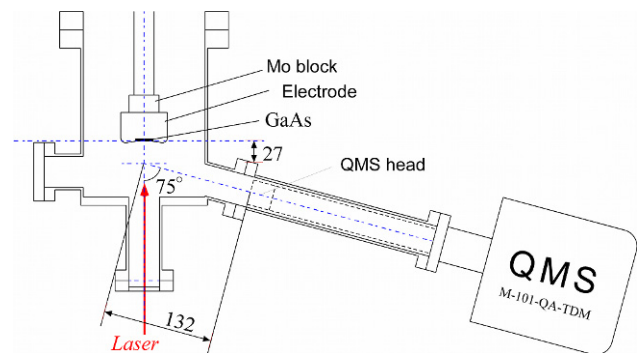


Figure 1: A cross-sectional view of the QMS-TPD system.

The p-type, Zn-doped bulk GaAs(100) was used as a cathode sample. Usually, a HCl-isopropanol treated GaAs substrate is used to avoid the surface contamination [7]. In our case, the sample surface was not treated in the HCl-isopropanol before installing into the vacuum chamber. However the QE of 10 % for the wavelength of 633nm was obtained. The GaAs sample was soldered by indium onto a molybdenum block in which a cartridge heater for a heat-cleaning of the sample surface and a chromel-alumel thermocouple to monitor the surface temperature were inserted. The surface temperature heated by the cartridge heater was confirmed with a melting point of indium and desorption peak temperatures of As. Figwtg 2 shows the TPD spectrum of the  $m/z=75$  at the programming rate of 16 K/min. The each point indicates an average of 4 measurements, and the error bar corresponds to the standard deviation. The desorption

peaks at 165 and 360 °C are almost equal to the desorption temperatures reported previously [8].

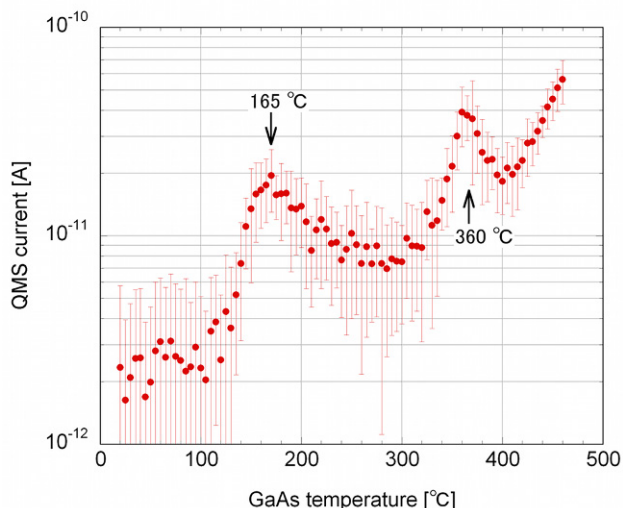


Figure 2: A TPD spectrum for the  $m/z=75$  (As). The desorption peaks at 165 and 360 °C is consistent with the previous measurement [8].

The GaAs sample installed into the chamber was annealed at ~500 °C for tens minutes. After the cooling down to room temperature for a day, the GaAs surface was activated by applying Cs and O<sub>2</sub> alternately (yo-yo technique). The activated sample with the initial QE of ~10 % was kept in the chamber at the vacuum range of  $5 \times 10^{-9} \sim 1 \times 10^{-8}$  Pa. The residual gases measured by the QMS at the base pressure before the TPD measurements were mainly H<sub>2</sub>, H<sub>2</sub>O, CO, Ar and CO<sub>2</sub>. The QE was repeatedly measured by He-Ne laser ( $\lambda=633\text{nm}$ ) for 2 sec every 5 min until the QE was degraded to less than 1 %. During the QE decaying, the QMS was not operated. After the QE was degraded, the QMS-TPD measurement was performed with the programming rate of 16 K/min. The result was compared with the non-activated sample which was maintained in the vacuum chamber after the annealing immediately.

### RESULTS

Figure 3 shows TPD spectra in which the  $m/z$  of 2 (red), 12 (blue), 28 (green) and 44 (orange) are plotted for the degraded cathode (a) and the non-activated cathode (b). The time required to decrease to be 0.9 % of the QE was 12 days after the activation process. During the decay process, the average vacuum pressure in the chamber was  $6 \times 10^{-9}$  Pa. On the contrary, the non-activated sample was kept for 10 days in vacuum evacuated to be  $6 \times 10^{-9}$  Pa. The QMS current at the temperature higher than 300 °C was caused by the desorption from other parts.

As shown in Fig. 3, there is a clear difference in the TPD spectra: The desorption peaks are only observed for the activated sample, but not observed for the non-activated sample. The result reveals that the residual gases adsorb to Cs and O, but not to Ga and As.

The desorption peaks for the  $m/z$  of 2, 12, 28 and 44 were clearly observed from the degraded surface. The fragments for Ga<sup>69</sup> and As<sup>75</sup> were slightly observed from both of activated and non-activated sample. The  $m/z$  between 51 and 100 were not observed, except for  $m/z$  of 69 and 75. Hence, the  $m/z=44$  was dominantly caused by the fragmentation ion of CO<sub>2</sub>. The  $m/z=28$  was caused by the fragment of CO and CO<sub>2</sub>, because the desorption peak of  $m/z=14$  for the fragment of nitrogen did not appear in this measurement. The TPD spectrum corresponding to the  $m/z=12$  was consistent with the cracking pattern of CO and CO<sub>2</sub>. As a result, we concluded that the adsorbate bound to Cs/O layer on the degraded NEA-GaAs cathode were dominantly H<sub>2</sub>, CO and CO<sub>2</sub>.

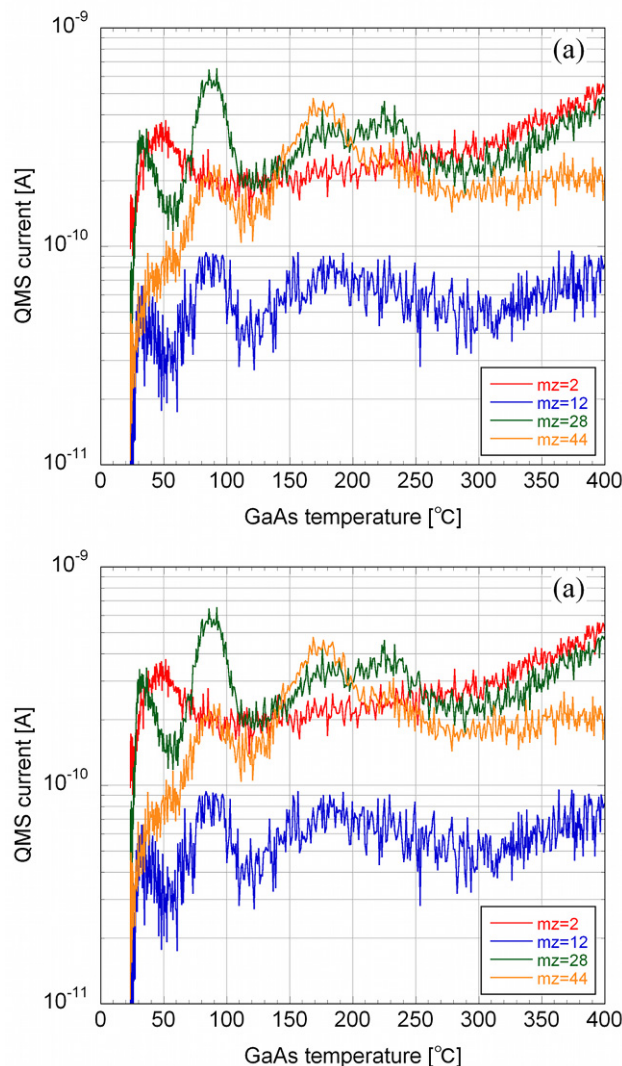


Figure 3: TPD spectra from the degraded NEA-GaAs (a) and the non-activated GaAs (b).

### DISCUSSION

Figure 4 represents the TPD spectra for H<sub>2</sub>, CO and CO<sub>2</sub> in which the background data (Fig. 3. (b)) was subtracted from the measured data (Fig. 3. (a)) and the desorption

rate was estimated by considering the cracking pattern for CO and CO<sub>2</sub>.

The desorption peak of H<sub>2</sub> is smaller than that of CO and CO<sub>2</sub> as shown in Fig. 4. The multiple peaks appear for CO and CO<sub>2</sub>, while the single peak of H<sub>2</sub> is only observed at low temperature. This result suggests that few bonding states on the NEA surface exist for the CO and CO<sub>2</sub> adsorbing onto the Cs/O layer. The simultaneous desorption peaks of CO and CO<sub>2</sub> at the temperature of 84 and 223 °C possibly indicate the fragment of the mass-to-charge ratios larger than 100, such as a cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>).

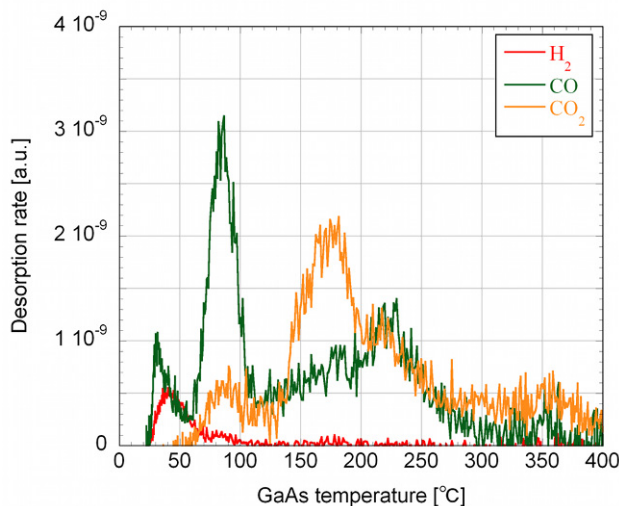


Figure 4: TPD spectra of H<sub>2</sub> (red), CO (green) and CO<sub>2</sub> (orange), estimated by considering the cracking pattern of them. The vertical axis indicates the relative desorption rate in arbitrary unit.

The activation energy  $E_a$  for the desorption peak temperature  $T_p$  as shown in Fig. 4 was calculated by Redhead's equation [9] given as

$$\frac{E_a}{RT_p} = \ln \frac{\nu T_p}{\beta} - 3.64$$

where  $R$  is the gas constant,  $\nu$  is the frequency factor and  $\beta$  is the programming rate. The order of reaction is assumed to be 1 in the equation. The frequency factor is assumed to be  $10^{13}$  /sec, and the programming rate is 0.267 K/sec (16 K/min). The calculated results are summarized in Tabrg 1. The desorption of H<sub>2</sub> and CO at the temperature lower than 41 °C may be physically bound onto the Cs/O layer. On the other hand, the temperature higher than 175 °C were chemically bound onto the Cs/O layer.

We note here that the desorption peaks for the fragment of H<sub>2</sub>O and O<sub>2</sub> were not observed at the temperature up to 500 °C, in spite of the presence of H<sub>2</sub>O and O<sub>2</sub> in the vacuum chamber. Considering the previous report [4] that the cathode lifetime was affected by the

water vapor, we suggest the possibility that the following reactions have occurred on the surface. At first, the Cs and O<sub>2</sub> form cesium oxide (Cs<sub>2</sub>O) on the GaAs surface. The H<sub>2</sub>O is bound to the Cs<sub>2</sub>O and forms a cesium hydroxide (Cs<sub>2</sub>O+H<sub>2</sub>O → 2CsOH). Finally, the CO<sub>2</sub> adsorbs to the cesium hydroxide and forms a cesium carbonate (2CsOH+CO<sub>2</sub> → Cs<sub>2</sub>CO<sub>3</sub>+H<sub>2</sub>O). In this process, the H<sub>2</sub>O contributes the QE degradation, but the desorption peak for the fragment of H<sub>2</sub>O does not appear in the TPD spectrum. Unfortunately, our system cannot measure desorption peaks for the fragment from Cs combination because of its high mass-to-charge ratio. The measurement of the high mass-to-charge ratio including Cs species will give us detailed information about the surface state.

Table 1: The activation energy for the desorption peak calculated by Redhead's equation.

$T_p$ [°C]	31	41	84	175	223
Desorption	CO	H <sub>2</sub>	CO,CO <sub>2</sub>	CO <sub>2</sub>	CO,CO <sub>2</sub>
$E_a$ [eV]	0.87	0.90	1.0	1.3	1.4

## SUMMARY

A surface state of an NEA-GaAs cathode that was degraded due to adsorption of residual gases was investigated by means of temperature programming desorption technique with combination of a quadrupole mass spectrometer. The thermal desorption peak only appeared from the activated sample. The hydrogen, carbon monoxide and carbon dioxide bound to Cs/O layer forming the NEA surface were desorbed, while the water and oxygen were not observed. The multiple desorption peaks in the TPD spectrum suggest the existence of several bonding states of CO and CO<sub>2</sub> to the Cs/O layer.

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