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# ANALYTICAL STUDY ON TPD MEASUREMENTS DURING NEA ACTIVATION PROCESS

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## Abstract

We have investigated the desorption of adsorbed Cs-related species on the sample surface by temperature programmed desorption (TPD). After forming the negative electron affinity (NEA) surface by alternating supply of Cs and O<sub>2</sub> onto the clean p-GaAs (100) surface in an ultra-high vacuum condition. It was found that Cs had several forms of adsorption states on the NEA surface from TPD measurements. The quantum efficiency under 826 nm illumination drops to zero over 300°C, while that with 367 nm drops to zero at about 500°C. It is considered that Cs desorbed about 100 to 300°C was deeply involved in the formation of the NEA surface.

## I. Introduction

A negative electron affinity (NEA) surface has the vacuum level lower than the bottom of the conduction band, and electrons can escape into a vacuum from surface by irradiating the light with a higher energy than substrates band gap. The electron beam emitted from the NEA surface has various advantages such as low emittance, ultrashort pulse, large current, and high spin polarization, and it is expected as the innovative next-generation electron sources. The NEA surface is formed by the yo-yo method, in which Cs and O<sub>2</sub> are alternately supplied to a clean p-GaAs surface<sup>1)</sup>. In the yo-yo method, the local maximum value of the quantum efficiency is gradually increased while repeating that the supply of O<sub>2</sub> at increase region of quantum efficiency and supply of Cs at decrease region of quantum efficiency. However, this method is empirical and the detailed surface processes are unknown. Several models for the NEA surfaces have been proposed, but none of them can comprehensively explain the NEA natures. We believe that the deep understanding of these complicated nature is important for practical use of the NEA surface. In this study, we investigated the relationship between the quantum efficiency during the NEA surface formation process and the adsorption state of Cs by TPD at the local maximums of quantum efficiency in the yo-yo method.

## II. Experimental detail

NEA surfaces were formed by the yo-yo method in an ultra-high vacuum chamber of about 10<sup>-8</sup> Pa. The samples used were Zn-doped p-GaAs (100) with ~10<sup>19</sup>cm<sup>-3</sup> of carrier density. The 826 nm excitation light selected from a Hg-Xe lamp with optical spectrometer was introduced through a quartz viewport to the sample surface with 296 μW/cm<sup>2</sup> of light intensity. During the NEA activation, the excitation light always irradiated the surface to emit electrons, and the quantum efficiency defined as the ratio of the number of photons of the excitation light to that of emitted electrons was continuously measured. The experiment system is equipped with a quadrupole mass spectrometer (QMS) for measuring the internal gas, a dispenser for supplying Cs, and a variable leak valve for sending O<sub>2</sub> inside. A bias voltage of -100V was applied to the sample, and a

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heater is attached to the sample to perform heat treatments and TPD measurements. The following are the detailed experimental procedure:

1. The GaAs surface was cleaned by heating at 700°C for 10 min, then the sample temperature was cooled down to room temperature.
2. The NEA activation process was performed at room temperature.
3. After the NEA activation process was done, the sample temperature was elevated for the TPD measurement to detect the desorbed species by QMS. The temperature was raised up to 600°C at a rate of 10°C/min.
4. The sample temperature was kept at 600 °C for an hour to confirm decrease of desorption, and the temperature was again cooled down to a room temperature to enable the NEA activation.
5. Repeating above steps 2-4, TPD measurements were performed after every NEA activation process with the same sample.

In this study, we discussed TPD spectra at each peak during yo-yo process, and TPD spectra at 1<sup>st</sup>, 2<sup>nd</sup>, 4<sup>th</sup>, 7<sup>th</sup>, 10<sup>th</sup>, and 12<sup>th</sup> local maximum peaks were measured in the 95, 94, 88, 93, 90 and 85 times of repetition of NEA activation process, respectively.

### III. Results and discussion

Figure 1 shows the time course of the quantum efficiency during the yo-yo process for the NEA activation. Cs supply started at time zero of the figure. After a few minutes incubating time, the 1<sup>st</sup> peak was seen and the quantum efficiency immediately returned zero. Here, Cs was switched to O<sub>2</sub>, and the quantum efficiency increased again to a higher value than the 1<sup>st</sup> peak. At a local maximum value (2<sup>nd</sup> peak), the quantum efficiency changed to decrease, and eventually reached zero by switching from O<sub>2</sub> to Cs. Switching from Cs to O<sub>2</sub> again, the quantum efficiency increased again to a higher value (3<sup>rd</sup> peak) than 2<sup>nd</sup> peak. Repeating the switching like this, as seen in Fig.1, the highest value in the whole NEA activation was obtained at the 12<sup>th</sup> peak. The NEA nature is extremely sensitive to environmental conditions, therefore the quantum efficiency continued to decrease after the NEA activation in the present vacuum condition.

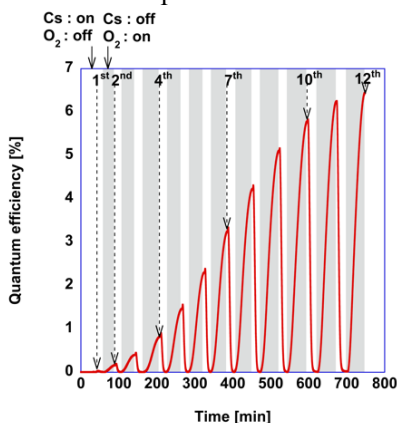


Fig. 1 Time course of quantum efficiency during NEA activation by yo-yo method. The local maximum value gradually increased while the quantum efficiency went up and down.

Figure 2 shows the quantum efficiency change (upper part) and Cs desorption characteristics (lower part) during TPD measurements. The QMS signal was shown in a logarithmic scale, and the detection limit was almost at  $10^{-14}$ . Substrate temperature could not be precisely controlled below  $100^{\circ}\text{C}$ , and the TPD spectra were monitored in the temperature range of  $100 - 600^{\circ}\text{C}$ . As shown in Fig.2, Cs desorption curve showed several peaks, for, at the 12<sup>th</sup> peak, shoulders are seen at around  $250^{\circ}\text{C}$ , and the QMS signal saturated at around  $450^{\circ}\text{C}$  shown with in Fig.2. Sakai *et al.*<sup>2)</sup> have reported that the desorption peaks were formed at  $250^{\circ}\text{C}$  and at  $440^{\circ}\text{C}$ . In this study, desorption peaks of Cs and As were simultaneously observed at  $\sim 440^{\circ}\text{C}$ , which showed the similar tendency to the previous results<sup>2)</sup>.

Focusing on the desorption spectrum at the 7<sup>th</sup> peak, small shoulder was seen at  $\sim 330^{\circ}\text{C}$ . Goldstein<sup>3)</sup> has reported that the Auger electron signals of Cs and  $\text{O}_2$  did not change depending on the stage of NEA formation. Therefore, the plausible surface structures of Cs-related compounds were almost similar from the 2<sup>nd</sup> peak to the 12<sup>th</sup> peak. There are desorption peaks at  $250^{\circ}\text{C}$ ,  $330^{\circ}\text{C}$  and  $440^{\circ}\text{C}$  with any stage of yo-yo process. However, the Cs signal is quite broad, and there may be possibly more desorption peaks. Focusing on differences in quantum efficiency due to changes in temperature, it becomes zero over  $300^{\circ}\text{C}$  of substrate temperature regardless of the stage of yo-yo process and no electrons are emitted.

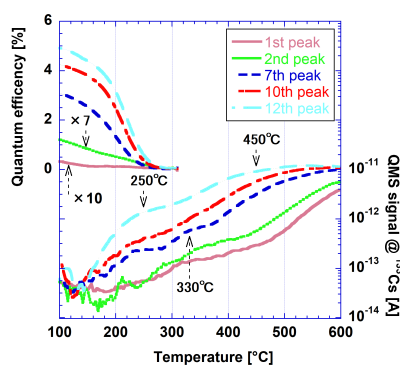


Fig. 2 the quantum efficiency change (upper part) and Cs desorption characteristics (lower part) and quantum efficiency during TPD.

Figure 3 shows a degrading nature of quantum efficiency during TPD measurement with the excitation light  $367\text{ nm}$  of wavelength. Although the quantum efficiency decreased, the electron emission continued to around  $500^{\circ}\text{C}$ . Detailed discussion was not done at present, we are considering the possibility that the wavelength of excitation light does not affect to the NEA activation. Both at  $367\text{ nm}$  and  $826\text{ nm}$  of incident photon wavelength, clean GaAs surfaces before the NEA activation do not emit electrons because the photon energy was not enough to excite electrons to the vacuum level. Since electrons were emitted up to  $500^{\circ}\text{C}$  with the  $367\text{ nm}$  excitation light, it was clarified that the energy required for electron emission is relatively lower than that before activation even about  $300 - 500^{\circ}\text{C}$ . It is suggested that Cs desorbed at a temperature higher than  $300^{\circ}\text{C}$  also plays a role in lowering the work function. However, in the case of  $826\text{ nm}$ , of which energy is approximately same as the bandgap, does not emit electrons at temperatures above  $300^{\circ}\text{C}$ , and so the adsorption state of Cs at  $100 - 300^{\circ}\text{C}$  is

considered to be essential for lowering the vacuum level to the bottom of the conduction band and formed the NEA surface.

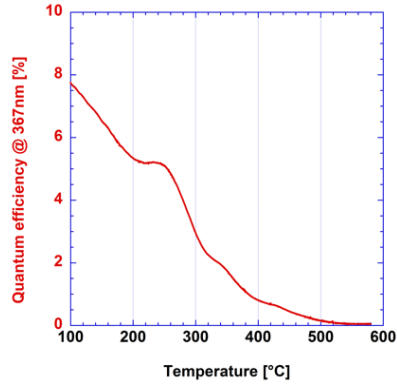


Fig. 3 Relationship between sample temperature and quantum efficiency in TPD measurement with excitation light wavelength of 367 nm.

Figure 4 shows the Arrhenius curve of a TPD spectrum performed on the NEA surface (12<sup>th</sup> peak) under 826 nm light irradiation for the estimation of activation energy. Although the inclination of the Arrhenius plot for each stage of NEA forming process is different, the activation energies calculated by the inclination at around 150°C was estimated about 0.70 to 1.48 eV. It is considered that the energies of Cs that takes this value is physisorption or first-order-chemisorption.

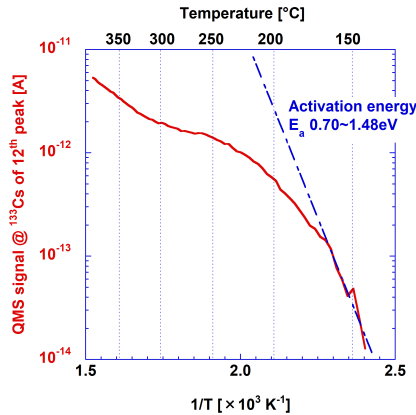


Fig. 4 The Cs peak change as a function of reciprocal temperature during TPD measurement of 12<sup>th</sup> peak. From inclination of the curve at 150°C, the activation energy was estimated.

#### IV. Conclusions

We have discussed the desorption nature of Cs and the quantum efficiency on the NEA-GaAs surfaces. In TPD measurements, Cs desorption was observed in a wide temperature range, even after the quantum efficiency becomes zero. It is considered that there are several adsorption states of Cs on the NEA surface. And it seems that Cs desorbed to 300 °C, where the quantum efficiency becomes zero, is indispensable for the formation of the NEA surface. When the 367 nm excitation light was used instead of the

826 nm, electron emissions continued to a temperature higher than 300°C, and then the quantum efficiency became zero. It is considered that the energy required for electron emission is relatively lower than that before activation about 300-500°C. So, Cs desorbed after 300°C is also involved in the decrease in work function.

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