Analysis of Cs/GaAs NEA surface by XAFS

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Abstract. By exposing a GaAs surface to Cs and O₂, a surface which is called negative electron affinity (NEA) surface can be obtained where the vacuum level is lower than the bottom of GaAs conduction band. The Cs/GaAs NEA surface has been attracting great attention in recent years, because of its availability for a highly functional electron source which can be controlled by excitation light. In this work, XAFS and X-ray fluorescence measurements were conducted for Cs/GaAs NEA surface prepared on GaAs (001) and (110) substrates. As the result, As and O were considered as near neighbor atoms of center Cs for both of the samples. Most of Cs formed some kind of Cs-oxide and the Cs atoms at interface between Cs-oxide and GaAs were observed as forming Cs-As bond. Taking account of the ratios of coordination numbers and the fluorescence X-ray yield, the Cs-oxide on GaAs (001) surface forms island like structure in which the body/interface ratio is large, and the Cs-oxide on GaAs (110) surface forms layer like structure in which the body/interface ratio is small.

1. Introduction

Cs adsorbed GaAs surface shows negative electron affinity (NEA) when the surface is properly prepared with O₂. [1,2] At the NEA surface, the vacuum level is lower than the bottom of the conduction band of the base semiconductor, GaAs. Therefore when electron-hole pairs are excited in GaAs by irradiating light, the electrons in the conduction band are easily emitted from the surface. The surface is utilized for highly functional electron source that can be controlled by light, which is so called photo-cathode. The distributions of energy and momentum of electrons emitted from the surface directly reflect the distributions of them in the base semiconductor, which can be controlled by changing the energy of the excitation light. When the energy of the light is tuned in very near to the band gap energy of the base semiconductor, the distributions of energy and momentum emitted from the surface can be so small as those defined by environmental temperature. For example it was reported 8 meV at 90K.[3] Because of such availability for a highly functional electron source, the Cs/GaAs NEA surface has been attracting great attention in recent years. However, the Cs/GaAs surface has been performed only in an ultra high vacuum environment and the life-time of the surface is reported to be sensitively affected by the background pressure.[4] For the practical use of the Cs/GaAs NEA surface, it is necessary to realize highly durable and long life-time NEA surface by understanding the structure of the NEA surface formed with Cs.

In this work, the Cs/GaAs NEA surface was formed on GaAs (110) substrate to investigate the characteristics of the surface by comparing them with those on GaAs (001) substrate. The local structures around Cs on GaAs (110) and (001) substrates were investigated by using X-ray absorption
fine structure (XAFS) measurement at Cs-L_{III} edge, while total amount of Cs on the surface was monitored by fluorescence X-ray yield measurement.

2. Preparation of the NEA surface

An NEA activation chamber specially designed to set on the XAFS measurement line was prepared. The chamber was equipped with ion-pump and NEG (non-evaporative getter) pump to realize ultra-high vacuum (UHV) background up to $10^{-9}$ Pa order and had 3 Be-windows to introduce X-rays into the UHV environment and to detect fluorescence X-ray emitted from the samples. After the GaAs (110) or (001) substrate was set on the sample holder in the chamber, the chamber was pumped and baked out to realize the UHV environment. When the UHV environment was realized, the substrate was heated up to more than 580°C and kept at the temperature for more than 1 hour to obtain a clean surface. Then, the sample was cooled down to R.T. before starting the process to obtain NEA surface. The process, which is so called “Yo-Yo” process [2], was started by the supply of Cs while the sample was biased at -100 V and irradiated by X-ray of 5100 eV to monitor photo-emitting electron current and measure the yield of Cs-L_{α} fluorescence X-ray. When Cs was supplied, the typical vacuum level was about $5.0 \times 10^{-7}$ Pa. Figure 1 schematically shows the change of the photo-current during the Yo-Yo process.

![Figure 1](image.jpg)

Figure 1. Schematicall drawn photo-current change during the Yo-Yo process.

Several minutes after starting Cs supply, a weak photo-current was detected as shown in Figure 1. With the proceeding Cs supply, the photo-current reached to the first small peak and then decreased. When the photo-current became very small to observe, the Cs supply was stopped and O_{2} supply was started alternatively. Typically, the timing was 10 to several 10min after the start of Cs supply. When O_{2} was supplied, the vacuum level was about $2.0 \times 10^{-6}$ Pa. On the O_{2} supply, the photo-current rapidly increased and reached to the second peak which was usually much higher than the first one. Then the O_{2} supply was switched to the Cs supply and the photo-current decreased again. When it was observed that the photo-current reached to a valley, the Cs supply was again switched to O_{2} supply. After that, O_{2} and Cs were alternatively supplied by switching them at the peak and valley of the photo-current. The photo-current peak heights gradually increased with the sequence as shown in Figure 1. Finally, when the increase of the photo-current peaks was saturated, the full process was finished. Since the NEA surface must be prepared with such an artful process, Cs is expected to form some special structure on the surface with oxygen. However the fragility of the surface has prevented us from investigating the structure.

3. In-situ X-ray fluorescence and XAFS measurements

In this work X-ray fluorescence and XAFS measurements were conducted by setting the NEA activation chamber on the XAFS measurement beam line 9A at Photo Factory in KEK in Tsukuba, Japan. By introducing the synchrotron radiation X-ray into the chamber through a Be window, the fluorescence X-ray from the sample was observed through another Be window. The Yo-Yo process
was conducted on line and the amount of Cs on top of the surface was monitored in-situ by measuring the yield of the Cs-L$_{\alpha}$ fluorescence X-ray.

The XAFS measurements were conducted in fluorescence X-ray detection mode with X-rays polarized normal to the surface for the finally obtained NEA surfaces on GaAs (110) and (001) surfaces. The fluorescence yield measurements were conducted also for the finally obtained NEA surfaces on GaAs (110) and (001) surfaces. During the XAFS measurement, the sample temperature was kept at about -90°C and the measurements spent 16 hours for each sample.

4. Results

Figure 2 shows (a) measured Cs-L$_{\alpha}$ fluorescence yield and (b) normalized $k^3\chi(k)$ spectra.

![Figure 2](image)

**Figure 2.** (a) Measured fluorescence X-ray yield and (b) normalized $k^3\chi(k)$ spectra.

First of all, no change was observed in XANES region in the spectra, which means the chemical status of Cs on GaAs (001) and (110) surface were almost the same. Then we should concentrate on the EXAFS spectra.

As shown in Figure 2, the EXAFS oscillations were observed very weak although the fluorescence yield was not so small. As a result, the S/N rations of the obtained $k^3\chi(k)$ spectra were small. Reported Debye-Waller factors of Cs-related compounds were often very large. [5] It might be the reason that the oscillations were so weak and we need to spend so long time to measure the XAFS spectra.

Figure 3 shows the radial-distribution functions obtained by Fourier transformation of the normalized XAFS spectra.

![Figure 3](image)

**Figure 3.** Radial distributions

As shown in Fig. 3, main peaks were observed at around 2.5 Å, and the peaks shifted between the samples on GaAs (110) and (001) surfaces. Curve fittings for the Fourier filtered XAFS spectra for the main peaks were conducted assuming Cs, As and O as near neighbor atoms around center Cs. The best fit curves were obtained when As and O were assumed to be the neighbor atoms for both of the spectra. Obtained best fit parameters were listed in Table I and the best fit curves were shown in
Fig. 4. The error ranges are shown with each parameter in parenthesis in Table I, which were estimated as the ranges where the R-factor increased up to twice of the minimum.

| Table I Fitting parameter | GaAs(001) | GaAs(110) |
|---------------------------|-----------|-----------|
| Assumed atom              | Distance  | Coordination number | Distance  | Coordination number |
| As                        | 2.83Å     | (±0.01)    | 3.12Å     | (±0.02, -0.01)      |
| O                         | 2.93Å     | (±0.005)   | 2.92Å     | (±0.01)             |

The Cs-As distances were changed between the samples and the change was agreed with the observed peak shift in Fig. 3. The difference in coordination number of As was large while that of O was rather small, although the coordination numbers were not so reliable since the S/N ratio was not so good. Figure 5 shows the intensity of the Cs-Lα fluorescence X-ray from the Cs/GaAs NEA surface that were measured after the full Yo-Yo process on GaAs (001) and (110).

![Image of Figure 4](image-url)

**Figure 4.** Fourier filtered $k^2 \chi(k)$ spectra and fitted curves for the spectra of the samples on (a) GaAs (110) and (b) GaAs(001) substrates.

The Cs-As distances were changed between the samples and the change was agreed with the observed peak shift in Fig. 3. The difference in coordination number of As was large while that of O was rather small, although the coordination numbers were not so reliable since the S/N ratio was not so good. Figure 5 shows the intensity of the Cs-Lα fluorescence X-ray from the Cs/GaAs NEA surface that were measured after the full Yo-Yo process on GaAs (001) and (110).

![Image of Figure 5](image-url)

**Figure 5.** Intensity of the Cs-Lα fluorescence X-ray yield from Cs/GaAs surfaces.

As shown Fig. 5, the peak heights were almost the same, in other words, the amount of Cs on top of the GaAs (001) and (110) surfaces were almost the same.
5. Discussions
The result that the coordination number of O, \(N_\text{O}\), is larger than that of As, \(N_\text{As}\), for both of the samples indicated that most of the Cs atoms on NEA surface bond with O. In other words, most of Cs formed some kind of Cs-oxide. As described before, we had to assume As with also O as neighbours, although the deduced amount of As was small. Since the NEA surface was formed on GaAs substrate, it is naturally speculated that the Cs-oxide was adsorbing on GaAs surface by the Cs-As bonds at the interface.

The difference of the ratios of coordination numbers, \(N_\text{As}/N_\text{O}\), reflects the difference of the ratios of Cs atoms located at the Cs-oxide/GaAs interface and in Cs-oxide body. The ratios \(N_\text{As}/N_\text{O}\) were about 0.05 and 0.26 for the samples on GaAs (001) and (110) substrate, respectively. The difference indicated that the ratio (interface area)/(Cs-oxide volume) was smaller for the sample on GaAs (001). On the other hand, the amount of Cs should be almost the same since the Cs-L\(\alpha\) fluorescence X-ray intensity was almost the same for both of the samples. These two results that \(N_\text{As}/N_\text{O}\) ratio was different while the amount of Cs was constant might be explained by assuming that the Cs-oxides on GaAs (001) surface forms island like structure in which the interface/body ratio is small and the Cs-oxide on GaAs (110) surface forms layer like structure in which the interface/body ratio is large. These differences of the structure on NEA-Cs/GaAs surface may affect the performance of the NEA surface such as the life-time or the behaviour of photocurrent during Yo-Yo process.

6. Conclusions
XAFS and X-ray fluorescence measurements were conducted for Cs/GaAs NEA surface prepared on GaAs (001) and (110) substrates. As the result, As and O were considered as near neighbor atoms of center Cs for both of the samples. Most of Cs formed some kind of Cs-oxide and the Cs atoms at interface between Cs-oxide and GaAs were observed as forming Cs-As bond. Taking account of the ratios of coordination numbers and the fluorescence X-ray yield, the Cs atoms on GaAs (001) surface forms island like Cs-oxide structure in which the body/interface ratio is small, and the Cs atoms on GaAs (110) surface forms layer like structure in which the body/interface ratio is large.

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