A study on XAFS analysis of Cs/GaAs NEA surface

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Abstract. Although NEA (negative electron affinity) surface has been attracting great interest, atomic level structure of the NEA surface has not been elucidated. In this work, Cs/GaAs NEA surfaces were analyzed by fluorescence XAFS (x-ray adsorption fine structure) method. Cs-L\textsubscript{III} XAFS measurement was conducted on the Cs/GaAs surfaces obtained by Yo-Yo method. By analyzing the local structure around Cs from the XAFS spectra, it was shown that Cs-O-As (or Ga) or O-Cs-As (or Ga) structure might be formed on Cs/GaAs surface. The results suggested that single atomic layer of Cs was adsorbed on GaAs surface intermediated by O on the Cs/GaAs NEA surface.

1. Introduction

NEA (negative electron affinity) surface has been attracting great attention in recent years, because of its availability for a highly functional electron sources. A GaAs surface covered by Cs (Cs/GaAs) is one of the basic structures of the NEA surface. In the Cs/GaAs NEA system, when an electron is excited in GaAs by irradiation of light, the excited electron is easily emitted from the surface. Therefore electron emission can be controlled by irradiation of light and of which energy distribution can be controlled by the energy of the irradiating light. Here, the NEA-photocathode can be a very low-emittance electron source, and can be operated as very short pulse or high repetition rate electron source by controlling the pulse width and repetition rate of the excitation light. The NEA-photocathode is expected to be utilized in the next generation accelerators and in the highly functional electron microscopes, e.g., time resolved electron microscope.

In order to utilize the NEA surface as a production level photo-cathode, the life time should be longer and the quantum efficiency (QE) should be higher. To achieve the longer life time and the higher QE, how the NEA is realized at the surface must be well understood, and for that, the structure of the surface formed by Cs adsorption on GaAs must be well recognized. Several experimental studies using low-energy electron diffraction, scanning tunneling microscopy and photoemission experiment have been performed to investigate the NEA surface [1-4]. Nevertheless, the state of the NEA surface is not still understood well. A few structure models are proposed [5, 6]. However, the actual NEA surface structure is still not clarified.

In this study, we investigated the NEA surface by using X-ray absorption fine structure (XAFS) analysis. The XAFS measurement is a kind of photo-absorption measurement in the X-ray level energy range. When the X-ray absorption measurement is conducted in a wide energy range, jumps are observed on the absorption coefficient spectrum that is caused by excitation of core-level electrons of atoms in target material. When we measure the spectrum precisely after a jump edge, fine structure
is observed, which is the XAFS spectrum. The fine structure reflects information on the atomic level local structure around the X-ray-absorbing atom that causes the jump on the spectrum. Therefore, by measuring and analyzing the XAFS spectra above the jump edge caused by Cs, we can discuss on the local structure formed with Cs on the GaAs surface.

2. Experiments

Be-doped p-type GaAs layers were grown on a GaAs substrate by molecular beam epitaxy (MBE) method, and the surface was capped by amorphous As in the same ultra-high vacuum MBE chamber. Then, the sample was transferred from the MBE chamber to an NEA activation chamber through the air. The amorphous As layer prevents the GaAs surface from pollutions during the transfer through the air. The amorphous As layer was removed by heating the sample in the NEA activation chamber. Then, the activated NEA surface was prepared by supplying Cs and oxygen alternatively monitoring the photo-current. The bias voltage to monitor the photo-current was -100V. The alternative supplying process to obtain the NEA surface is so called Yo-Yo method [7]. The Cs and oxygen on the NEA activated surface is easily removed by heat cleaning at a controlled temperature. After the heat cleaning, the surface is considered to be equivalent to the fresh GaAs surface before the activation process. In this work, the activation process and the heat cleaning were repeated several times.

The NEA activation chamber was specially designed for the in-situ XAFS measurement. The chamber was installed on the XAFS measurement line using synchrotron radiation at BL9A of Photon Factory in Tsukuba, Japan. A monochromatized X-ray was irradiated on the sample in the NEA activation chamber through a Be window. The Fluorescence X-ray from the sample was detected by 19 elements Ge-Solid-State-Detector (SSD). The XAFS measurement was conducted for the Cs-LIII absorption edge (5.011 keV) by sweeping the incident X-ray energy from 4.8 to 5.4 keV. The electric field of the incident X-ray was polarized normal to the surface. Under the condition, measured XAFS spectra strongly reflected the local structure normal to the surface and were not sensitive to the in-plane structure. The base pressure of the NEA activation chamber was kept at about $3 \times 10^{-8}$ Pa during the XAFS measurement by using ion pump and non-evaporable getter (NEG) pump. As described above, the NEA activation process was conducted several times, and the XAFS measurement was conducted after each activation process. We spent about 15 hours to obtain one XAFS spectrum. QE and Cs-L fluorescence X-ray yield were checked several times during each XAFS measurement. The QE of the NEA surface was different after each activation process. In this paper, we discuss on the NEA surface of the highest and the lowest quantum efficiency.

3. Results of XAFS measurements

Figure 1 shows the change of the measured QE checked using 633nm He-Ne laser during the XAFS measurement. The initial QE of the highest and the lowest QE surfaces was about 3 and 0.05 %, respectively. As shown in Fig. 1, the QE was decreased as usual depending on time. For the highest QE surface, it decayed by about two orders of magnitude and for the lowest one it decayed by about four orders of magnitude during the XAFS measurement. Figure 2 shows the fluorescence X-ray spectra. The solid lines show spectra measured just after the activation process, and the dotted lines are spectra measured after about 15 hours. The peaks observed at about 4.2 keV are Cs-L fluorescence, and the peaks observed at about 5.0 keV are due to the elastically scattered incident X-ray. As shown in Fig. 2, almost no change was observed on the intensity of Cs-L fluorescence peak depending on time, while the quantum efficiency decayed. This result indicated that the decreasing of the QE with time was not caused by desorption of Cs from the surface during the XAFS measurement. Therefore, there must be some structural change on the surface relating to the change of the QE. However, in this work, we assumed that the structural change throughout the XAFS measurement time (for about 15 hours) was smaller than the difference of the structures between the highest and the lowest ones. Since we need the 15 hours to obtain one XAFS spectrum and could not resolve the
structural change faster than that. Figure 3 shows the measured XAFS spectra for the highest and the lowest QE surfaces, and normalized XAFS oscillations are shown in Fig. 4. As shown in Fig. 3 and 4, the quality of the spectra was not so good. It means the amounts of Cs atom on the GaAs surface were very small. Although we could not decide it quantitatively, the amount should be about 1 or 2 atomic layers based on our experience. In spite of the low quality of the spectra, it is found that these two spectra showed different features, which indicated that the structures formed around Cs atom were different for the highest and the lowest QE surfaces. Figure 5 shows the Fourier transformed XAFS spectra comparing with some theoretical calculated ones by using FEFF code [8], which is generally used to calculate XAFS spectra theoretically. The Fourier transformed XAFS spectra are known to reflect the radial distributions of atoms around the X-ray absorbing atom (in this case, it is Cs). Spectra (a) and (b) are measured ones for the highest and the lowest QE surfaces. Other spectra are calculated ones for the model structures showed on the right side in Fig. 5. In the calculations, the distances between atoms were adjusted to represent the two peaks at about 2 and 4 Å as in the measured spectra. It was obvious that the spectra (a) and (b) are different. It indicates again Cs formed different structure on the highest and the lowest QE surfaces. By comparing the measured spectra to the calculated ones, it was found that all the four models did not give a spectrum similar to that of the lowest QE surface. Therefore, we could not discuss on the precise structure of the lowest QE surface now. On the other hand, for the highest QE surface, the Cs-O-As (Model-1) and O-Cs-As (Model-2) models gave the spectra similar to the measured one of the best QE surface. It should be noted that As and Ga was very difficult to distinguish in the XAFS measurement. Therefore, As atoms in the models might be Ga atoms.

4. First principle calculations
Although, it was difficult to analyze the XAFS spectra quantitatively since the quality of the spectra was not good, we tried further consideration on the Model-1 and -2 to find which one is more probable structure. First principle calculations were conducted for the Cs-O-As and O-Cs-As models to find the Cs-O and Cs-As distances that give the minimum energy. In the calculation the positions of Ga and As atoms of GaAs crystal were fixed. Changing the positions of Cs and O, the total energy
was calculated repeatedly. Then the Cs-O and Cs-As distances which give the minimum energy were decided. Figure 6 shows the relationship between the Cs-O and Cs-As distances. As shown in Fig. 6, when we assumed Model-1, the measured and calculated relationships between the Cs-O and Cs-As were very similar. On the other hand, with the Model-2 the measured and calculated results did not agree with each other. Therefore, Cs-O-As structure was more probable than O-Cs-As structure. As mentioned before, the As and Ga atoms were very difficult to distinguish from the XAFS measurement, and the first principal calculations also gave almost the same results for the model with Ga as with As. Therefore, we should conclude that either Cs-O-As or Cs-O-Ga structure might form on the Cs/GaAs surface when the QE was good.

5. Summary
XAFS measurements were conducted for Cs/GaAs NEA surfaces. The fluorescence yield measurement during the XAFS measurement showed that the decrease of Q.E. depending on...
time was not caused by desorption of Cs from surface. The features of the XAFS spectra were
different on the highest and the lowest QE surfaces, which indicated that different structure were
formed on Cs/GaAs surface with the highest and the lowest QE. The discussion on the precise
structure formed on the surface was difficult since the quality of the measured XAFS spectra were not
so good. By combining results from XAFS measurement and the first principle method calculation,
we found a probable structure formed on the highest QE surface can be Cs-O-As or Ga structure. The
results suggested that single atomic layer of Cs was adsorbed on GaAs surface intermediated by O on
the Cs/GaAs NEA surface.

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