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DRASTIC CHANGE OF QUANTUM EFFICIENCY OF NEA-GaAs SURFACE AFTER SUCCESSIVE THERMAL PRETREATMENTS AND CONTRIBUTION OF ITS SURFACE ORIENTATION

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Quantum efficiency (Q.E.) evolution on p-type GaAs surfaces during the negative electron affinity (NEA) activation process has been discussed based on repeated sequence of the thermal pretreatments and the NEA activations. We have realized higher Q.E. by the pretreatment at various temperatures in combination with the successive NEA activation process. It is considered that existence of surface residues lead to formation of efficient electron emission sites during NEA activation. We have also discussed surface morphological effects for Q.E.

I. Introduction

Alkalimetal atoms adsorption on semiconductor surfaces has attracted considerable interest, and especially the Cs/GaAs system has been intensively studied because it can produce negative electron affinity (NEA) surface with advantages in electron sources. The NEA surface lowers the vacuum level at the surface of semiconductor below conduction band minimum of the bulk. The first demonstration of NEA nature was reported by Sheer and Van Laar1). NEA photocathode was realized by the Cs adsorption on the cleaved (110) p-type GaAs single crystal. Later, Turnbull and Evans have reported that the increase electron emission, and stable photoemission were achieved by alternating supply of Cs and O_2 on GaAs(110) surface (Yo-yo method) 2).

NEA GaAs photocathodes activated by Cs and O_2 have advantages in application for photoemitters with narrow energy spreading compared with wide gap semiconductor photocathodes, *e.g.* large quantum efficiency than metal photocathodes, highly polarized electron beam, high infrared sensitivity, and so on. The use of GaAs/GaAsP strained superlattice structure to photocathode has been reported by Nakanishi *et. al.*3,4) and the spin polarization has reached to 92%. For these remarkable advantages, NEA-GaAs photocathodes have been studied mainly in the field of accelerator physics since 1970's5).

On the other hand, their electronic properties and detailed surface processes are still not understood and several plausible models about NEA surfaces have been proposed6~9). Thickness of the NEA layer is estimated within a few monolayers on GaAs surface and is easily degraded. These problems should be solved for the application of photoemission source, however these sensitive surfaces are difficult to discuss actual surface characteristics. Furthermore, it is well known that the GaAs(100) surface has various reconstructed structures. For example, GaAs(100) annealed at 550℃−600℃ shows a Ga-rich (4×2)/*c*(8×2) structure which is explained by existence of Ga dimers on overlayer in contrast to (1×1) structure at GaAs(110) surface10). GaAs(100) annealed at ~450℃ shows an As-rich (2×4)/*c*(2×8) structure10), and an

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excess As absorption induces a *c*(4×4) structure[11)]. Thus, it has been difficult to explain the NEA formed on GaAs(100) substrate.

In this paper, we describe the pretreatment temperature dependence on the maximum quantum efficiency (Q.E.) during the successive NEA activation process.

II. Experimental

Details of the experimental setup and procedure have been previously reported[12)] and reviewed here briefly. All experiments were performed in an ultrahigh vacuum system below then 3×10^{-8}Pa by using an ion pump and a Ti sublimation pump. Under these vacuum conditions, NEA surfaces were not contaminated by residual gases during experiment. Zn-doped p-type GaAs(100) ($\sim1\times10^{19}$cm^{-3}) substrates were used, and the sample was mounted on the temperature-controlled sample holder. Sample temperature was elevated by resistive heating of a Ta wire heater. Sample temperature was measured by a chromel-alumel thermocouple in contact with the backside of the sample holder. The system is equipped with a Cs dispenser (SAES-getters) and a variable leak valve for Cs and O_2 supply during the NEA activation process, respectively. Sample was biased at -40V for photoelectron extraction, and the illumination source was a laser diode with 650nm of wavelength and 20μW of output power.

We repeatedly carried out the sequence of thermal pretreatments and NEA activations for the same GaAs(100) sample with keeping ultrahigh vacuum environment. The sequence is schematically shown in Fig. 1. At first, the GaAs(100) sample was pretreated at various temperatures of 530℃, 580℃, 480℃ or 630℃ for an hour. After the pretreatment, the sample was cooled down to room temperature (R.T.) by natural cooling. Subsequently, the NEA activation was performed by Yo-yo method, where Cs and O_2 were alternately supplied until the saturation of Q.E. During the NEA activation, *in situ* observation of Q.E. was done. When the sequence had been completed, GaAs(100) surface was again refreshed by thermal pretreatment, and activated by Yo-yo method as same as the above sequence.

The Q.E. value was calculated simply from the ratio of the illumination light power and the corresponding photocurrent. We did not consider reflectance of substrate, diffusion, tunneling surface potential barrier explained by Spicer's three-step model[13)] and any other effects.

In the present study, we finally performed 118 times of the sequence. Surface morphology after 118 times of the sequence was observed by scanning electron microscopy (SEM). Prior to the SEM observation, the sample was exposed to air for transfer to SEM.

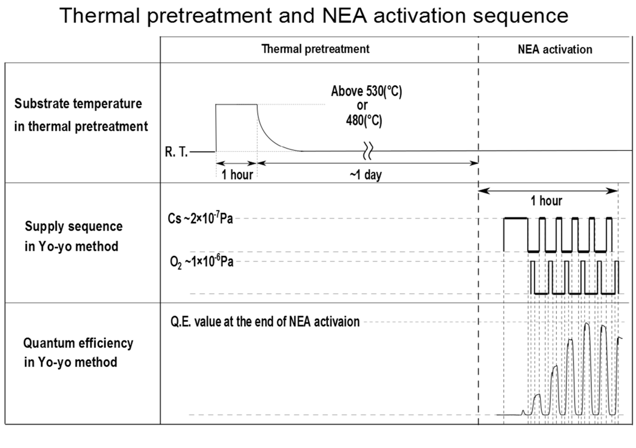

Fig. 1 Schematic diagram of thermal pretreatment and NEA activation sequence. GaAs(100) surface was pretreated by above 530 ℃ high temperature or 480 ℃ low temperature on an hour respectively. Then NEA activation process was carried out.

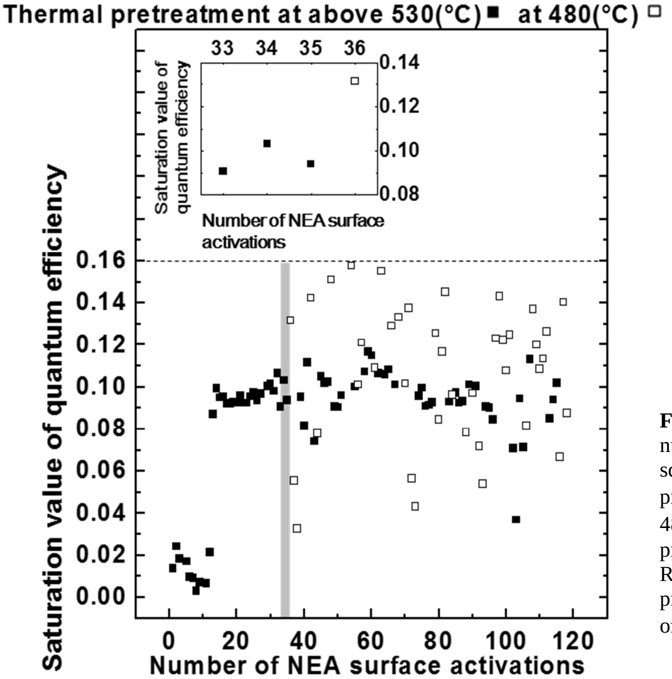

Fig. 2 Quantum efficiency as a function of number of NEA surface activation cycles. Solid squares and open squares indicates surface pretreatment temperature above 530℃ and 480℃ respectively before the NEA activation process. All NEA activation was carried out R.T. after cooling down from surface pretreatment. The inset emphasized increasing of Q.E. after 480℃ low temperature condition.

III. Results and Discussion

Figure 2 shows a Q.E. vs number of the sequences. When the Q.E. value showed saturation, we concluded that the NEA activation was completed.

Up to ~15 times of the sequence, the pretreatment temperature was fixed at 530℃, and increased to 580℃. These processes provided stable Q.E. values of almost 10%, and this condition do not have any dispersion of Q.E. value.

After repetition of the sequence, the pretreatment temperature was lowered to 480℃, then the Q.E. value drastically increased. However, the repetition of sequence with low temperature pretreatment condition abruptly give rise to degradation of Q.E. It is of interest that when the pretreatment was done again at 580℃, the Q.E. recovered to the stable value of 10%.

Figure 3 shows the SEM image of GaAs(100) surface after 118 times of the sequence. Many fourfold symmetrical facets structures were formed. We consider that the first drastic increase of Q.E. after ~15 times of the sequence might be caused by appearance of the Ga-rich surface due to the increase of temperature from 530℃ to 580℃ during thermal pretreatment. It is known that the Ga-rich surface is provided by thermal pretreatment of 550℃-600℃ for GaAs(100) surface, and the NEA nature is achieved by existence of Cs-Ga bonding. Higher pretreatment temperature of 580℃ provided an atomically clean Ga-rich surface, and the Q.E. value of 10% was observed as shown in the Fig. 2. When the pretreatment temperature decreased down to 480℃, the Q.E. clearly increased in the following 1st sequence. It is explained that specific surface residues such as Cs, O, and/or Cs sub-oxide may induced the sufficient NEA activation. However, the repetition of same pretreatment condition of 480℃ in the 2nd or 3rd sequence resulted in abrupt degradation of the Q.E. Within 2nd or 3rd sequence, excess residues remained at surface which may suppressed the NEA activation.

In Fig. 3, formation of crystal facets with {110}-oriented pyramidal structure was observed. 118 times of surface pretreatments and the NEA activations yielded the surface morphological change due to the thermal etching by adsorbed species. It is expected that different type of electron emission sites were activated from the initial GaAs(100) surface.

IV. Conclusions

The specific sequences which include a low temperature surface pretreatment, led higher Q.E. during NEA activation were discussed. It is probably due to the formation of efficient electron emission sites by the reaction of residual species after the thermal pretreatment of 480℃ with newly supplied Cs and O_2. 118 times of sequence with the thermal pretreatments and the NEA activations may induced surface changes comparatively different from initial (100) oriented-surface. Nevertheless, the actual effect due to these changes has not been understood at present, and further investigation is required.

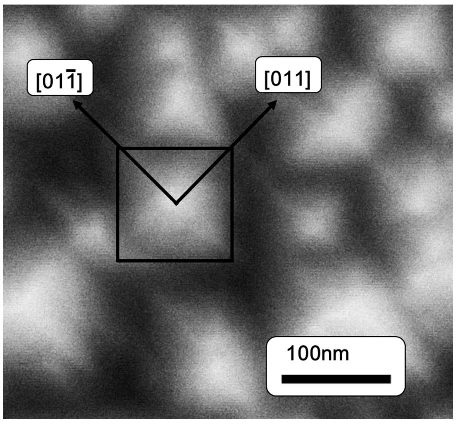

Fig. 3 SEM image of GaAs(100) surface after 118 times of surface pretreatments and NEA activations. Fourfold symmetrical facets were formed different from substrate orientation.

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