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### SURFACE PREPARATION OF NEA-GaAs(100) BY HCI-ISOPROPANOL ETCHING FOR STM OBSERVATION

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Negative electron affinity (NEA) surface receives low energy nearly equal to band gap energy of a semiconductor to be emitting an electron because that lowers the vacuum level than the conduction band minimum. Especially NEA-GaAs surfaces show distinct natures such as high spin polarization, low emittance, short pulse availability, high intensity and so on. NEA surface are made by adding Cs and oxygen alternatingly onto the clean surface of GaAs. Scanning tunneling microscopy (STM) is used to investigate surface morphology of the GaAs(100) surfaces prepared by the HCl-isopropanol (HCl-iPA) treatment and annealing in ultrahigh vacuum (UHV). The method indicates improvement in surface quality of the GaAs(100).

#### I. Introduction

Negative electron affinity (NEA) photocathodes are expected to be one of next generation electron emission sources, since NEA-GaAs surfaces show distinct natures such as high spin polarization, low emittance, short pulse availability, high intensity and so on.<sup>1-5)</sup>. NEA surface receives low energy nearly equal to band gap energy of a semiconductor to be emitting an electron because that lowers the vacuum level than the conduction band minimum. NEA surface are made by adding Cs and O<sub>2</sub> alternatingly onto the clean surface of GaAs or GaN and other III - V materials<sup>6-9)</sup>.

NEA has been studied by many scientists since Scheer et al. first reported on an NEA study on p-type GaAs(110) in 1965<sup>6</sup>. Several structural models have been proposed for NEA surfaces<sup>10-14</sup>. Su *et al.*<sup>11</sup> have proposed double dipole model that a work function of the surface can be reduced by an electric double layer formed in the interface between GaAs-O-Cs and Cs<sup>+</sup>-O<sup>-2</sup>-Cs<sup>+</sup> layers. Burt *et al.*<sup>12</sup> have shown cluster model in which electron are spatially confined by Cs<sub>11</sub>O<sub>3</sub> clusters forming on the surface. As a result, work function for the surface can be reduced. James and Uebbing *et al.*<sup>15-19</sup> have given heterojunction model, which brings down the vacuum level; alkali metal layers and p-type III-V compound semiconductor layers form hetero junction. Hayase<sup>20</sup> *et al.* have discussed in situ observation of the NEA formation process by surface photo-absorption (SPA) technique<sup>21,22</sup>, and have suggested that surface reaction processes sof Cs and oxygen on the surface of NEA.

However, the detailed processes of NEA surface and mechanism of reduced work function are still unknown at present. It is essential to comprehend the detailed surface states and processes of NEA-activated surfaces for practical application of electron emitting

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materials using NEA surfaces. Recently, Hirao *et al.* have investigated adsorption structures of Cs on the As- terminated (2×4) (100) GaAs surface in detail by  $STM^{23}$ ). They found that the initial adsorption of Cs atoms occurs around the step sites in the form of Cs clusters and that the size of clusters is reduced by successive exposure to O<sub>2</sub>, indicating that the As-terminated (2×4) surfaces are relatively stable in compared to Ga-terminated surfaces and are not broken by the Cs clusters adsorption.

It is considered that Ga plays an important role in the functioning of the NEA surface, and we have studied actual adsorption structures of Cs on Ga-terminated (100) GaAs surfaces by using STM. However, it is extremely difficult to obtain a flat Ga-terminated surface without epitaxial growth system in vacuum condition, because NEA-activated surfaces usually require the GaAs substrate temperature to be increased as high as 600°C to remove the native Ga oxide from the surface while the As oxide evaporates at  $450^{\circ}$ C. As a result, after thermal treatment at 600°C, GaAs surface will be highly rough and it is difficult to obtain smooth Ga-terminated (100) GaAs surface which is capable of observing adsorption structures of Cs using STM.

The other techniques, such as arsenic decapping and ion sputtering, have been also employed widely to produce the well-defined GaAs(100) surfaces<sup>24-32)</sup>. Among them various chemical treatments of GaAs face have been shown to provide the clean and oxide-free surface after annealing in ultrahigh vacuum (UHV)<sup>33-42)</sup>. In this work, we prepared the GaAs(100) surfaces by the HCl-isopropanol (HCl-iPA) treatment and annealing in UHV to study adsorption structures of Cs on the Ga-terminated GaAs(100) during the NEA activation process using STM.

#### **II. Experimental**

Figure 1 shows a schematic picture of STM system consisted of the load lock chamber, the preparation chamber, and the STM chamber. Samples were cut from epi-ready p-type Zn-doped GaAs(100) wafers. The HCl-iPA treatment of the substrates was performed in a nitrogen-filled glove bag which was connected to load lock chamber, following a procedure utilized by Tereshchenko et al.<sup>41,42)</sup>. The etching of the GaAs samples was carried out in 3 M solution of HCl in isopropanol for 120 s. The wet etching method removes the oxidized film, and the Ga atoms were eliminated leaving the As-capped layer. Then they were rinsed in isopropanol for 50 min for transporting preparation and blown by nitrogen. After introduction into the vacuum chamber without atmospheric exposure, the samples were degassed in UHV at 300 °C for 12 h, a thick As-capped layer desorbed from the GaAs(100). After that, the samples were annealed to induce the surface reconstruction process, and characterization and annealing of surfaces were carried out in the UHV system with a base pressure below  $1.0 \times 10^{-8}$  Pa. The annealing temperature was elevated up to 500°C. All STM measurements were done after cooling the sample to room temperature. STM using mechanically polished Pt-Ir tips was used in the constant current mode with a tunneling current of 0.60 nA and a sample bias voltage of -2.0 to -2.3 V.



Fig.1 Schematic picture of the UHV-STM system equipped with NEA activation system and glove box.

#### **III. Results and Discussion**

Figures 2(a) and 2(b) show typical filled-state STM images of the HCl-iPA GaAs(100) surface after the degassing at 300°C for 12 hours, and after the subsequent annealing at 500°C for 3 minutes, respectively. Random terraces, which are separated by single steps or multi-steps of GaAs, can be observed in the STM images. The both images exhibit the presence of like the (4×2) ordered domains where bright and dark rows run along the (011) direction. At present, (4×2) surface reconstruction structure was not observed, but the pretreatment condition for successful STM observation of flat Ga-terminated GaAs(100) surface was established.



Figure 2: GaAs(100) surface after the HCl-iPA treatment : STM images of the HCl-iPA GaAs(100) surface after the annealing at 100nm×100nm (a), and 50nm×50nm (b). The crystallographic directions are marked by white arrows, and both images exhibit presence of bright and dark rows run along the (011) direction. The image (a) was taken at -2.3 V of sample bias voltage with a tunneling current of 0.60 nA, and the image (b) was taken at -2.0 V with 0.60 nA.

#### **IV. Summary**

We prepared the GaAs(100) surfaces by the HCl-iPA treatment and annealing in UHV. Random terraces, which are separated by single steps or multi-steps of GaAs, can be observed in the STM images. It is found that the obtained GaAs(100) surfaces makes STM observation possible. it is still necessary for the experiment to make concerted efforts to collect more information for specifying etching, heating conditions and substantiate and confirm what such information indicates. Relation of surface adsorbate structures and actual electron emission nature of NEA-GaAs will be discussed.

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