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Etching reaction of methylchloride molecule on the GaAs (0 0 1)-2 × 4 surface

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Abstract

Adsorption process of methylchloride (CH_3Cl) on the GaAs (0 0 1)-2 × 4 surface was studied by a scanning tunnelling microscopy (STM) measurement. The arsenic rich 2 × 4 surface, which was prepared by molecular beam epitaxy (MBE), was exposed to a supersonic molecular beam of CH_3Cl with a kinetic energy of 0.06 eV. New bright spots appeared on the CH_3Cl exposed surface. They were largely observed at the ''B-type'' step edge and divided into two types according to their locations. It was suggested that new spots were due to weakly adsorbed CH_3Cl molecules without any dissociation. The adsorption mechanism of CH_3Cl molecule was also studied by an ab initio Hartree-Fock calculation, which explained the experimental results well.
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Keywords: GaAs; Etching; Adsorption; STM; Hartree-Fock

1. Introduction

An atomic layer epitaxy for compound semiconductors such as GaAs, InAs and GaP has achieved great success in semiconductor technology [1]. On the contrary, an atomic layer etching, which removes a few mono-layers with atomic scale accuracy from the surface, is still difficult in spite of great efforts in semiconductor-process technology. This difficulty is due to the lack of the basic knowledge of the surface reactions between the etching precursor and the crystal surface. In many previous studies on the etching chemistry between the etching molecule and the solid surface, the atomically controlled surface (so-called well-defined surface) has not been used and therefore the resulting data is not effective in the atomic layer etching technology. It is important in the development of the atomic layer etching process that the fundamental etching process should be analyzed between the atomically controlled solid surface and the energy-controlled molecule.

Chlorine molecule is often used as an important molecule in the etching of micron-order depth for semiconductor crystals such as silicon and compound semiconductors. However, chlorine molecule cannot be used for the atomic layer etching because it reacts violently with the semiconductor surface and the etching depth is not controlled in the atomic level [2]. We should explore the other precursors for the atomic layer etching, which proves to be a less violent and ''soft'' reaction with the semiconductor surface. Methylchloride (CH_3Cl) and ethylchloride (C_2H_5Cl) are important candidates for the precursor of atomic layer etching in semiconductors.

In this paper, we discuss the adsorption mechanism between methylchloride and the GaAs (0 0 1) surface by a scanning tunnelling microscopy (STM) analysis. In the experiment, the atomically controlled GaAs (0 0 1)-2 × 4 surface was prepared by the molecular beam epitaxy (MBE), and an energy-controlled CH_3Cl beam, which was produced by a supersonic technique, was impinged on the GaAs surface. The surface reaction was also studied by an ab-initio Hartree-Fock calculation. In the calculation, the adsorption energy of CH_3Cl molecule onto the GaAs surface was studied. The calculated result explained well the STM observation of CH_3Cl adsorbed surface, which suggested an important role in the chemical reactions at the step edge of GaAs (0 0 1) surface.

2. Experimental procedure

Fig. 1 shows the block diagram used in this experiment. The surface was prepared by the conventional MBE growth, where

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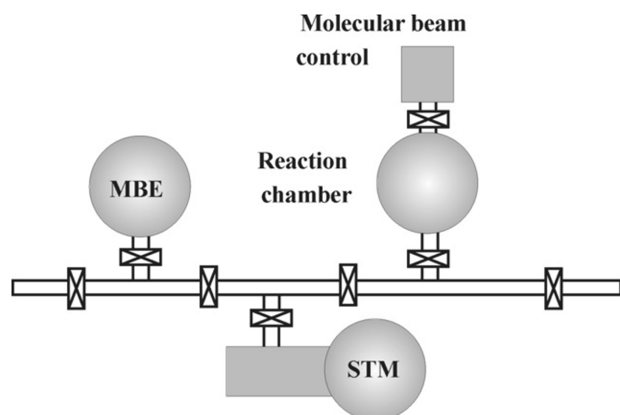

Fig. 1. Experimental apparatus in the experiment. MBE chamber, reaction chamber and STM chamber are connected by the vacuum tunnels in order to avoid the surface degradation.

gallium and metallic arsenic were used as source materials. The epitaxial layer was grown on a silicon doped GaAs (0 0 1) with the electron density of (2–3) $\times$ 10^{18} cm^{-3}, since the (0 0 1) surface had been utilized for most of the GaAs electronic devices. The surface with GaAs (0 0 1)-2 $\times$ 4 reconstruction was studied in the experiment. This surface structure, which is easily obtained by MBE, is relatively stable and the atomic structure is well known [3]. The structure of the grown layer is shown in Fig. 2. The silicon doped GaAs epitaxial layer with the electron density of (1–5) $\times$ 10^{17} cm^{-3} was grown and followed by the growth of the unintentionally doped GaAs with the thickness of 28 nm (100 atomic layers). The surface structure was monitored by a reflection-high-energy-electron-diffraction (RHEED) and the surface was an arsenic-rich 2 $\times$ 4 structure during the epitaxial growth. The RHEED pattern showed a so-called streaky feature, which suggested the atomically flat surface. After the growth, the sample was transferred by a load lock system from MBE chamber to STM chamber through the vacuum tunnel for the observation of the surface atomic structure. The base pressure of the system was $<1 \times 10^{-8}$ Pa.

The STM measurement was done by Omicron VT-STM and the sample temperature was 300 K (room temperature). A tungsten tip was mainly used in the STM measurement. Images

Epitaxial GaAs (undoped) 28nm
Epitaxial GaAs (Si doped) 100nm n = 1 - 5 x 10^{17} cm^{-3}
Substrate GaAs (Si doped) n = 3 x 10^{18} cm^{-3}

Fig. 2. Sample structure of GaAs. The substrate was silicon-doped n^+ GaAs (0 0 1) and the epitaxial GaAs was grown under the arsenic-rich growth condition.

were recorded with the tunnelling current in the range of 0.1–1.0 nA. The negative or positive polarity of the applied voltage was used for images of filled or unfilled surface electronic states, respectively. The obtained signal was processed by the Omicron SCALA system.

The sample was transferred through the vacuum tunnel from the STM chamber to a reaction chamber, after the clean surface of GaAs (0 0 1) was confirmed to show 2 $\times$ 4 reconstruction. The structure of the reaction chamber was the same as the already reported one [4]. In the reaction chamber, the surface was exposed to energy controlled methylchloride (Matheson) by a supersonic-molecular-beam method. In this experiment, 100% methylchloride gas was used without any seeding gas. The kinetic energy of the incident molecule was 0.06 eV that was measured by the time-of-flight measurement. The incident angle of the methylchloride beam was the surface-normal. The total dose of injected methylchloride molecules was controlled by the opening time of an electro-magnetic gas pulse valve and the gas pressure, and was in the range of (5–9) $\times$ 10^{16} mole-molecule/cm^2, which was two orders higher than the atomic density of GaAs (0 0 1) surface. The methylchloride exposed GaAs sample was again loaded into the STM chamber though the transferred tunnel and the STM measurement was carried out at 300 K.

3. Ab-initio Hartree-Fock calculation for adsorption sites of CH_3Cl/GaAs (0 0 1)-2 $\times$ 4

In order to analyze the experimental results, an ab-initio Hartree-Fock (HF) calculation was carried out for the adsorption energy of methylchloride on the GaAs (0 0 1)-2 $\times$ 4 surface. The cluster used in this calculation was formed by 24 gallium atoms, 32 arsenic atoms, 62 hydrogen atoms for terminations, and 1 methylchloride molecule. The surface cluster involved an atomic step (so-called B step). For gallium and arsenic atoms, the effective core potential (ECP) approximation was used in the HF molecular orbital method [5]. The ECP is generated in the valence region which allows the eigenvalue of the corresponding pseudo-orbital equation to provide the same orbital energy as the self-consistent HF method. For the hydrogen atom, Slater-type function, STO-3G, was used. The GAUSSIAN 98 computer package was employed, with three primitive Gaussian functions being used to fit each Slater-type atomic orbital [6].

4. Results and discussion

4.1. STM image of a clean GaAs (001)-2 $\times$ 4 surface

Fig. 3 shows a small-area STM image of a clean GaAs (0 0 1)-2 $\times$ 4 surface. In this measurement, the tip bias voltage and the tunnelling current were -2.0 V and 0.2 nA, respectively (the filled states STM image). Fig. 3 shows a typical arsenic rich 2 $\times$ 4 surface with the characteristic arsenic dimer rows in the $[\bar{1}\,1\,0]$ direction separated 1.6 nm. In this reconstruction, arsenic passivates the second layer gallium atoms, and the arsenic atoms form dimers that arrange themselves. The widely

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