Dynamical behavior of methylchloride on GaAs(001)

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ABSTRACT

The dynamical behavior of methylchloride (CH_3Cl), which is an important precursor in the atomic order etching of III-V compounds, was studied on a GaAs(001)-2x4 surface using a supersonic molecular beam. Direct scattering and trapping/desorption channels of incident CH_3Cl were assigned based on a detailed analysis of incident energy and angle dependence of the scattered molecule. A large energy exchange from translational to rotational modes was observed for directly scattered CH_3Cl. A trajectory simulation was conducted to quantitatively explain the angle dependence of scattered CH_3Cl, energy exchange at collision, and the energy dependence of trapping probability on the surface.

Keywords:
Atom-solid interactions, scattering, Molecule-solid scattering, Gallium arsenide, Chemisorption, Physical adsorption, Methylchloride

I. 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 partly 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 etching molecule and 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 process. 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 etching molecule.

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

In this paper we discuss the surface dynamics of CH_3Cl on GaAs(001) surface by using a pulsed CH_3Cl beam in order to pursue the possibility of an atomic layer etching. In the experiment, the atomically-controlled GaAs(001)-2x4 surface was prepared by 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 time-of-flight spectrum of chemical species desorbed or scattered from the GaAs surface was measured by a rotating quadrupole-mass-spectrometer (QMS).

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II. EXPERIMENTS

The apparatus consisted of a source chamber generating a supersonic molecular beam of CH_3Cl, a mechanical chopper chamber, a target chamber for the GaAs surface, and a quadrupole mass spectrometer (QMS) chamber. The seeded CH_3Cl beam was generated from a 1.1 mm hole of a pulsed valve in a source chamber pumped by a 2,000 l/s turbomolecular pump and was skimmed by a 0.7 mm aperture. The control of translational energy was made by changing the seeding gas and CH_3Cl density. As seeding gases, we used He, Ar, and Xe. The target chamber had a base pressure below 2 x 10^{-10} Torr. Incident beam energy was determined from flight time between a high-speed mechanical chopper and the mass spectrometer. We only measured in-plane scattered angular distribution. The QMS output was sent thorough a preamplifier, followed by a digital oscilloscope or a multichannel scalar.

Measurements were made using a GaAs(001)-2x4 surface. The arsenic-rich 2x4 surface was prepared by molecular beam epitaxy (MBE) followed by cooling from 820 K (the growth temperature) to 570 K in an As_4 flux. The sample was transferred through an ultra-high-vacuum (UHV) tunnel from the MBE chamber to the target chamber. The CH_3Cl supersonic beam was directed at the sample mounted on a temperature variable manipulator that enabled the incidence angle to be controlled within an accuracy of 0.5 degree.

III. RESULTS AND DISCUSSION

A. CH_3Cl /GaAs(001)-2x4 system and QMS fragmentation

To distinguish chemical reactions on the GaAs surface from the fragmentation in the QMS ionizer, we compared the mass spectrum of the surface scattering beam to that of the incident beam. Fig. 1 shows the comparison of CH_3Cl fragmentation patterns (integrated intensity), when a pulsed CH_3Cl beam was injected directly into the QMS and onto the GaAs surface at 773 K. In both mass patterns, the dominant peak appeared at m/e=50, corresponding to CH_3Cl^+. The other important peaks were m/e=35 (parent peak, corresponding to Cl^+) and m/e=15 (CH_3^+). Intensity ratios between these mass peaks showed no difference between the incident beam and the surface scattered beam, indicating that the chemical species scattered from the surface at 773K was assignable to the CH_3Cl molecule. Fragmentation was measured at various surface temperatures below 920K, but no significant changes were seen in the fragmentation pattern.

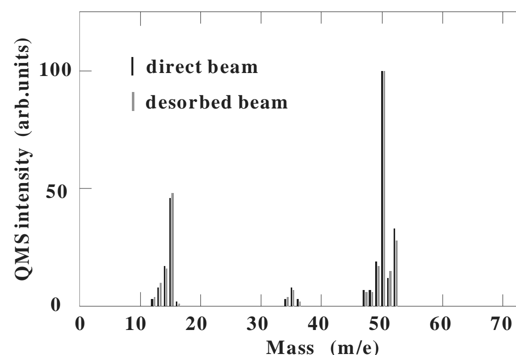

Fig.1 Comparison of fragmentation pattern of CH_3Cl between incident and scattered beams.

Fig.2 shows the temperature dependence of QMS intensities of CH_3Cl^+, when a pulsed CH_3Cl beam was injected onto a GaAs surface with a pulse width of 1.0 ms and an incident energy of 0.056eV. The angle of the incident beam was 60° from the surface normal and the QMS located at the surface normal. The intensity of CH_3Cl^+ showed a constant value below 570K, but it decreased with the surface temperature above 570K. The other fragments in Fig.1 also showed the same temperature dependence as CH_3Cl^+. We could observe no fragments other than those showed in Fig.1 at these high surface temperatures (>570K). This suggests that the incident CH_3Cl molecule took the other reaction passes on the GaAs surface. We observed an evolution of a new strong

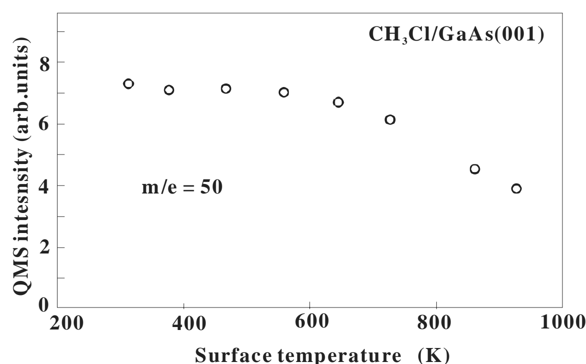

Fig.2 Temperature dependence of CH_3Cl molecule fragmentation.

scattering peak at higher scattering angles at these high surface temperatures, but we will not mention the further discussion on this new scattering peak. From these results, we concluded that CH_3Cl desorbed from the surface without any dissociation below 570K.

B. CH_3Cl TOF spectra

Dynamical properties of scattered CH_3Cl were mainly studied by TOF measurement. According to Hurst [3], the TOF spectrum I_{inc} of an incident beam is basically described as a function of molecular velocity v and as a function of time $t\ (=L/v\ )$.

$$I_{inc}(v)\ dv = A\ v^3\ exp[-\ (v-v_s)^2/\alpha^2]\ dv \quad (1)$$

and

$$I_{inc}(t)\ dt = A'\ t^{-5}\ exp[-\ (L/t-v_s)^2/\alpha^2]\ dt \quad (1)'$$

Here, A and A' are normalization constants and L is flight distance. The stream velocity v_s and the halfwidth α can be obtained from the best fit with the experimental results. Equation(1) can describe both a supersonic velocity distribution (the present case) and a Maxwell-Boltzmann velocity distribution ($v_s = 0$ and $\alpha^2 = 2kT/m$, where T is gas temperature and m the CH_3Cl mass). Considering the degrading of the resolution by the apparatus, we convoluted $I_{inc}(t)$ with the shutter function $S(t)$ and get the TOF intensity $G_{inc}(t)$ of the incident beam onto the sample surface

$$G_{inc}(t) = \int_0^t S(t-\tau)\ \ I_{inc}(\tau)d\tau \quad (2)$$

The shutter function $S(t)$ is mainly determined by the mechanical chopper opening and the incident-beam radii. As QMS is a density-sensitive detector (where signal intensity depends on the length of QMS ionization region), we must multiply $G_{inc}(t)$ by time t to get the detector response

$$F_{inc}(t)\ dt = B\ t\ \ G_{inc}(t)\ dt\ , \quad (3)$$

where B is a normalization constant. The TOF spectrum was compared with equation (3) and v_s and α were obtained from the best fit. The mean velocity of the incident beam was described according to Hurst [18] as

$$\langle v^2\rangle = \alpha^2\ (\ S^2 + 3.5 - 3/(2S^2 + 3)\ ) \quad (4)$$

where $S = v_s/\alpha$ which was fit to the experimental data. The translational energy of incident beam Ei was obtained from the following equation

$$Ei = 1/2\ m_{CH3Cl} \langle v^2\rangle \quad (4)'$$

where m_{CH3Cl} is the mass of CH_3Cl.

The TOF of scattered molecules was measured in the temperature range from 300 K to 500 K. In this range no decomposition of CH_3Cl occurred on GaAs surface and the surface residence time of trapped CH_3Cl was negligibly small (< 10μs). Fig.4 shows the TOF spectrum of CH_3Cl a for an incident energies of 0.056eV. The surface temperature was 300K and the incident and scattered angles were respectively 60° and 45° from the surface normal. In the figure, the zero point in flight time (abscissa) was taken as the time when incident molecules passed the mechanical chopper slot in front of the pulse valve, so the flight time in the figure is the time from the chopper slot to the solid surface, the residence time on the solid surface, the flight time from the surface to the QMS ionizer, the flight time in the QMS, and the electric delay time of signal processing.

The low incident energy spectrum (*Ei=0.056eV*) consists of one broad peak, while the high incident energy spectrum (*Ei=0.176eV*) consists of a sharp peak superimposed on the leading edge of a broad peak. An important feature in the high incident spectra was that the fast sharp peak increased and the broad peak decreased as the CH_3Cl incident energy was increased. The half-width of the sharp peak was about 85 μs, nearly the same as that of the incident pulse (69.4μsec), and was independent of substrate temperature. In contrast, the shape of the broad peak was nearly independent of the incident-beam shape, incident angle and reflected angle, but was sensitive to surface temperature. Assuming that desorbed molecules had a Maxwell-Boltzmann distribution and the surface residence time was zero, we compared the shape of the broad peak with the shape derived from the equation

$$I_{des}(t) = \int_0^t G'_{inc}(\tau)\ \ I_{MB}(t-\tau)\ \ d\tau\ , \quad (5)$$

where $G'inc(t)$ expresses the time-dependent incident beam and $I_{MB}(t)$ is a function derived from the following equations.

$$H_{MB}(v)\, dv = C\, v^3 \exp[-m_{CH3Cl}\, v^2/2kTs]\, dv$$

(6)

and

$$I_{MB}(t)\, dt = D\, t^{-1} H_{MB}(L/t)\, dt$$

(7)

Here, C and D are normalization constants, m_{CH3Cl} is the mass of CH_3Cl, k is the Boltzmann constant, and Ts is the surface temperature. As in Fig. 3, the spectrum was in good agreement with the Maxwell-Boltzmann distribution estimated at 560K (indicated by open circles) except for a longer decay.

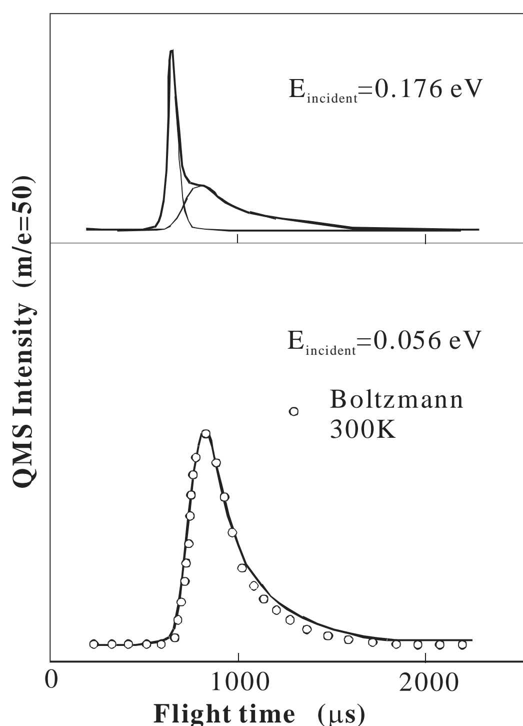

Fig.3 Time-of-flight (TOF) spectra of CH_3Cl reflected from GaAs(001) at 570 K. The variation of incident energy drastically changes the spectrum shape. The sharp spectrum is from direct-inelastic scattering and the broad spectrum is from trapping/desorption.

Fig.4 shows the angular dependence of the scattered beam measured for an incident energy of 0.56 eV and an incident angle of 60˚. Although the plot shows some scatterings, the QMS intensity has a maximum at the surface normal (scattering angle $\theta s = 0$) and the intensity can be expressed by $\cos^{0.82}\theta s$.

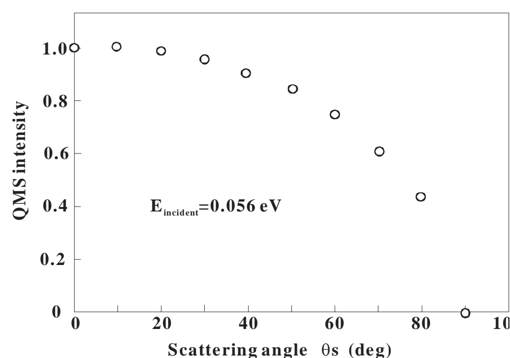

Fig.4 Angle dependence of QMS intensity for the incident energy of 0.056eV.

Fig.6 is a detailed plot of the angular dependence of sharp and broad peak intensities for the incident energy of Ei = 1.76eV. The intensity of the sharp peak increases with the scattering angle, differing from that in the case of an incident energy of 0.56 eV.

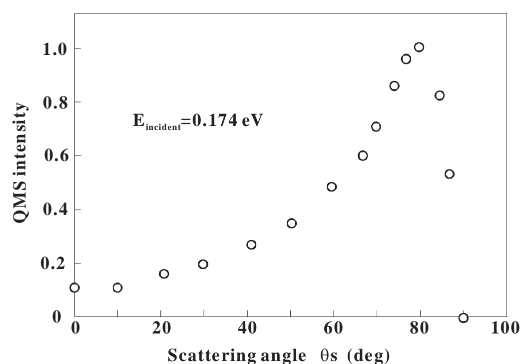

Fig.5 Angle dependence of QMS intensity for the incident energy of 0.174eV.

At a substrate temperature of 570 K, the incident CH_3Cl molecule would have two reaction channels as shown in Fig.6; a tapping/desorption channel with CH_3Cl molecules loosely trapped in a molecular chemisorption well, and a direct inelastic scattering channel with incident CH_3Cl molecules unable to lose sufficiently the translational energy on the surface and be directly scattered from the surface into the vacuum. From above mentioned results, we assigned the desorbed CH_3Cl molecule observed at the incident energy of

0.056 eV was through the former channel (trapping/desorption channel) and that observed at 0.176 eV through the latter one (inelastic direct scattering cannel).

IV. SUMMARY

We studied the dynamical behaviors of CH_3Cl on the GaAs(001) surface by a supersonic molecular beam. Direct scattering and trapping/desorption channels of incident CH_3Cl were analyzed from TOF measurements of scattered CH_3Cl as a function of the incident energy and reflected angle.

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