LEED Observation of Methane Monolayer Physisorbed on Ag(111)

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The structure of CH₄ monolayer physisorbed on a Ag(111) surface was observed by LEED. The LEED patterns were recorded with suppressed electron current using a cooled CCD camera in order to minimize the electron stimulated desorption of adsorbed CH₄. The LEED pattern indicated that the lattice of CH₄ molecules forms hexagonal structure in rotationally ordered incommensurate state. Under specific equilibrium condition, intermediate state with the coverage less than unity was found to exist.

1. Introduction

The microscopic structure of the crystalline monolayer of molecules physisorbed on graphite have been studied for various simple molecules by low-energy electron diffraction (LEED).¹⁻³⁾ For metal substrates, especially rare gas layers have been studied.^{1,4,5)} Among metal substrates, Ag(111) surface has been often used for physisorption systems due to its inert nature. On Ag(111) substrate, rare gas atoms adsorb in layer-by-layer manner, which means that the isotherm curve shows a sharp riser from almost zero coverage to full coverage at specific pressure. The rare gas monolayer is known to form a close packed hexagonal structure in azimuthally commensurate relation with the substrate lattice.

The vibrational excitation processes of several kinds of physisorbed molecules have been investigated by electron impact.⁶⁻¹⁰⁾ Generally, excitation cross section is affected by the structure of adsorbed molecules, and the adsorption scheme strongly depends on the characteristics of individual molecule; polar molecules such as carbon dioxide are not likely to show layer-by-layer growth.⁸⁾ On the other hand, CH₄ molecules forms well ordered monolayer.^{9,11,12)} We have measured that the incident energy dependence of elastic or vibrational excitation cross-section (I-V curve) is modulated by diffraction effect that arises from the generation of surface wave diffracted by substrate or adsorbate lattice.^{11,12)} In that experiments, LEED observation of CH₄ layer was insufficient and the analysis of vibrational excitation process on the structural viewpoint remains incomplete.

In the present paper, we present the results of

LEED observation of CH₄ layer physisorbed on a Ag(111) surface at various adsorption equilibrium conditions, and the growth mode specific to CH₄/Ag(111) system is discussed.

2. Experimental

The experimental apparatus is based on an ultrahigh vacuum chamber evacuated by a titanium sublimation pump with a liquid nitrogen shroud, a sputter-ion pump (230 l/s) and a turbo molecular pump (450 l/s). The chamber comprises a sample manipulating system with temperature control, a sputter-ion gun, a LEED optics (Omicron, SPECTALEED) and a high-resolution electron-energy-loss spectrometer (HREELS; LK Technologies, ELS5000). The schematic drawing of the apparatus is shown in **Fig. 1**. Two-fold magnetic shields are installed in the vacuum chamber; outer one covers the LEED and EELS stages and inner one covers only the EELS stage. The sample manipulating system consists of XYZ-translator (Vacuum Generators), a differentially pumped rotational platform (Thermionics, RNN250) and a cryogenic closed-cycle refrigerator (IWATANI, Cryo Mini). The rotational platform is evacuated by a small turbo-molecular pump (70 l/s) and a scroll pump. The substrate is mounted on a sample holder that is connected to the cold end of the refrigerator via a high-purity (6N) copper rod and insulating sapphire crystal plates. A resistive heater and Au-0.07 %Fe vs. Chromel thermocouple are attached on the sample holder for the temperature control. The system enables XYZ-translation, rotation around vertical axis and temperature control of the sample over the range of 20–700 K. A gas handling system was also used for the introduction of Ar or CH₄.

Fig. 1 Schematic diagram of the experimental apparatus.

The ultimate pressure less than 1×10^{-8} Pa was obtained after bakeout procedure for 24–48 hours. The x-ray-aligned and chemically polished Ag(111) substrate was cleaned by standard procedures involving low-energy Ar-ion bombardment and heating cycles, which was repeated until clear diffraction spots could be observed. The layer of CH_4 physisorbed on the Ag(111) substrate was formed under adsorption equilibrium conditions at the substrate temperature ranging from 20 to 50 K. The LEED patterns of CH_4 monolayer were recorded by a liquid N_2 cooled CCD camera (Princeton Instruments). In the course of the experiments, it has turned out that the adsorbed layer is very easy to be disturbed by the incident electron beam. Then to minimize the irradiation effect, the electron source of LEED is activated to emit the electron current of less than 1 nA during only the exposure.

3. Results and Discussion

The typical LEED patterns of CH_4 monolayer are shown in **Fig. 2**. They were recorded at the incident electron exposure of 3nC, which is necessary to obtain LEED patterns with good contrast. The incident energy is 56 eV. Fig. 2(a) was obtained with the CH_4 pressure of 1×10^{-6} Pa and the sub-

(a)

(b)

Fig. 2 LEED patterns of physisorbed CH_4 on Ag(111). (a) was obtained with the CH_4 pressure of 1×10^{-6} Pa and the substrate temperature of 37 K. (b) was obtained with the CH_4 pressure of 5×10^{-6} Pa and the substrate temperature of 43 K.

strate temperature of 37 K and Fig. 2(b) was obtained with the CH_4 pressure of 5×10^{-6} Pa and the substrate temperature of 43 K. Hexagonal spots with similar intensity observable in both figures correspond to the crystal of CH_4 . The patterns indicate that CH_4 crystal forms rotationally ordered incommensurate phase similar to Xe monolayer formed on graphite and Ag(111) substrates. These CH_4 spots could be observed over the incident electron energy range of 30 to 100 eV. The lattice constant of CH_4 monolayer derived from the LEED

Fig. 3 Adsorption condition dependence of coverage derived from the LEED intensity.

patterns is 0.41 nm, which almost coincides with that of bulk crystal of CH₄ (0.42 nm). Though the diffraction patterns are almost same for the two pictures, the ratios of spot intensities of CH₄ peaks to Ag ones are different, which means that the CH₄ coverage in Fig. 2(a) is higher than in Fig. 2(b). The absolute coverage can not be estimated directly from the spot intensity, however, the coverage for Fig. 2(a) is considered to be unity and the coverage for Fig. 2(b) is less than unity due to following experimental results; (1) the ratios of peak intensities of CH₄ to Ag appeared to be similar for wide range of adsorption conditions, i.e. ambient CH₄ pressure and substrate temperature, and (2) if the substrate is cooled further at the constant ambient pressure in 10⁻⁷ ~ 10⁻⁶ Pa range, the spots of both CH₄ and Ag diminishes together while the background intensity goes higher. This means only the first CH₄ layer easily forms single-crystal structure, on the other hand, the succeeding layers become disordered one.

As a result of the observation of LEED patterns indicating the formation of CH₄ crystal over comprehensive adsorption conditions, the ratio of spot intensities of CH₄ to Ag is roughly classified into two categories; typically Fig. 2(a) (type I) and Fig. 2(b) (type II). In Fig. 3, the adsorption conditions showing LEED pattern of each type are indicated as ○ for type I, and △ for type II. The adsorption conditions showing no CH₄ spots are indicated with ×. We did not try to determine the boundary between monolayer and multilayer phases. Fig. 3 exhibits the presence of intermediate phase where less

than monolayer of CH₄ molecules adsorb in incommensurate lattice on Ag(111) substrate in equilibrium with gas phase. This is not the case for the adsorption of rare gas on graphite or metal substrates; rare gasses adsorb in commensurate lattice ($\sqrt{2}$ structure) before the coverage saturates at monolayer. The lattice constants are almost the same for both type I and II, however, more careful analysis leads to the finding that the lattice spacing for type II is 1-2% larger than that of type I. Moreover the intensity profile of CH₄ spots for type II is expanded toward azimuthal direction. This indicates that the lattice direction of crystalline islands tends to have narrow distribution under unsaturated coverage while the lattice spacing remains at a specific value. The slight difference in the lattice constant between monolayer and bulk crystal may cause this translation and deformation of CH₄ spots.

Low energy I-V curves of specular diffraction for CH₄/Ag(111) system have been measured before using HREELS.¹¹⁾ The I-V curve is modulated by diffraction effect, and there is ambient-pressure dependence in the modulation of I-V curves.¹²⁾ The data were measured at the CH₄ pressure of 3×10^{-8} and 1×10^{-7} Pa with the substrate temperature of 43 K. Though the pressure range is lower than in Fig. 3, it could be argued that the phase boundary between monolayer and submonolayer regions in Fig. 3 is extrapolated to the adsorption condition between 3×10^{-8} and 1×10^{-7} Pa with the substrate temperature of 43 K, then the ambient-pressure dependence in the modulation of I-V curve seen in ref.12 arises from the difference of CH₄ coverage.

The difficulty of the LEED observation of physisorbed CH₄ layer is high probability of electron stimulated desorption. If we continued to observe the LEED image at the adsorption condition of type I, the intensity and profile of CH₄ spots changed towards those of type II along with the irradiation of electron beam. The CH₄ spots disappeared after the irradiation of 1 μC at the incident energy of 56 eV. If we assume the size of electron beam in the range of 0.3 to 1 mm on the sample, the desorption yield is estimated at 0.1-1.

4. Summary

LEED patterns of CH₄ monolayer physisorbed on Ag(111) were observed at various adsorption equilibrium conditions. Diffraction spots of CH₄ monolayer crystal were clearly observed at 5×10^{-7} ~ 2×10^{-5} Pa, substrate temperature around 40 K. The diffraction pattern indicates CH₄ crystal forms rotationally ordered incommensurate phase similar

to rare gas crystals. Under specific equilibrium condition, intermediate state with the coverage less than unity exists, which is a different feature than those of rare gas layers.

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