STM observation of the chemical reaction of atomic hydrogen on the N-adsorbed Cu(001) surface

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ABSTRACT

Chemical reaction of atomic hydrogen with the N-adsorbed Cu(001) surfaces was investigated at room temperature by scanning tunnel microscopy. At the low exposure of atomic hydrogen, it reacted with the N atoms and turned to be the NH species on the surface. The reaction rate is proportional to the amount of the unreacted N atoms. By increasing the exposure of atomic hydrogen from this condition, the amount of nitrogen species on the surface decreased. This is attributed to the formation of ammonia and its desorption from the surface. The NH species on the surface turn to NH_3 through the surface NH_2 species by atomic hydrogen. Coexistence of the clean Cu surface enhances the rate of ammonia formation owing to atomic hydrogen migrating on the clean surface.

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1. Introduction

Reaction between hydrogen and adsorbed nitrogen on the surfaces has been investigated because of great interest in the synthesis of ammonia. Typical examples are the reactions on Fe(001) [1], Ru(0001) [2], Pt(111) [3], and Rh(111) [4]. In these studies, the ammonia synthesis process on the surfaces can be divided into two. First is the dissociation of H_2 molecules, or generation of atomic hydrogens, and second is their reaction with the adsorbed N atoms. The latter is crucial to understand the chemical reaction process through the synthesis of the ammonia. Although the dissociation of H_2 molecules on the surfaces has been reported on various metal surfaces [5–10], there have been a few studies focusing on the reaction between atomic hydrogen and the N atoms [11,12]. Takehiro et al. [11] reported the reaction of atomic hydrogen on a Ni(110)-p(2×3)-N surface by HREELS. The NH species and ammonia were produced by the reaction of the N atoms with atomic hydrogen at room temperature (RT). This group suggested that activation energy is high from NH to NH_2 species using atomic hydrogen.

Scanning tunnel microscopy (STM) is a powerful tool for investigating chemical reactions on the surface at an atomic level. Previous STM studies have revealed that the reaction processes are highly dependent on the local surface structure and the coverage of the adsorbates. For example, in the case of the oxidation of CO on the O-adsorbed Cu(110) surface [13], the reaction rate of the CO_2 formation is much reduced at

a high coverage of oxygen. This suggests that the diffusion of CO on the Cu regions promotes the oxidation. It is also interesting to investigate the reaction between the atomic hydrogen and N atoms by STM.

In the present study, we have studied the reaction of atomic hydrogen on the N-adsorbed Cu(001) surface at RT by STM. We choose the Cu surface to avoid the reaction through the hydrogen atoms dissociated from hydrogen molecules on the surface [14]. In addition, the N-adsorbed Cu(001) surface has a well-ordered c(2×2) structure and few defects [15]. Therefore, we need not to consider chemical reactions at defects which sometimes behave as active sites of chemical reactions [13].

2. Experimental

The experiments were conducted in an ultra-high vacuum (UHV)-STM system consisting of preparation and STM chambers. The base pressure of the both chambers was better than 1×10^{-10} Torr. The Cu(001) surface was cleaned by cycles of Ar^+ sputtering at 1 keV for 30 min and annealing to 900 K for 15 min in the preparation chamber. To make a nitrogen covered surface, the clean surface at RT was exposed to nitrogen ions using an ion gun at 500 eV and then annealed to 700 K. During the N^+ exposure, the N_2 pressure was kept at 1.0×10^{-10} Torr, and the final nitrogen coverage of the surface was controlled by changing the exposure time. We confirmed the morphology of the N-adsorbed surfaces by STM.

We exposed the N-adsorbed surface at RT to atomic hydrogen produced by thermal dissociation of H_2 molecules with a tungsten filament heated to 2000 K. The filament was placed behind the sample, 5 cm

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away from it, and the sample surface did not see the W filament. Therefore, there was no atomic hydrogen directly from the filament to the sample surface, and contaminations from the filament and the direct effects of its light and heat were minimized. In the present paper, we use the H_2 pressure P_{H_2} during this process as a measure of the atomic hydrogen exposure. The partial pressure of atomic hydrogen is proportional to the square root of that of H_2 molecules [16]. When the pressure of H_2 molecule is 2.0×10^{-6} Torr, the pressure of the atomic hydrogen was estimated to be approximately 1×10^{-7} Torr [17]. All the STM images were recorded in a constant tunneling-current (I_t) mode at RT with a tungsten tip.

3. Results

3.1. Nitrogen adsorption on Cu(001)

Adsorbed nitrogen atoms on a Cu(001) surface occupy fourfold hollow sites of the surface Cu atoms and form a c(2×2) structure [15]. Nitrogen atoms have geometrically almost the same height as the Cu atoms in the first layer [18]. At low coverage, small N-adsorbed islands randomly distribute and are imaged lower than the clean Cu area in STM. The protrusions in the nitrogen-adsorbed regions correspond to the fourfold hollow sites of the Cu lattice. They are often identified as the adsorbed nitrogen atoms for a negative sample-bias voltage (V_B) and the N-free sites for a positive V_B [19]. When the average nitrogen coverage exceeds 0.3 monolayer (ML), the square nitrogen regions of 5 nm × 5 nm in size are aligned along the [100] and [010] directions. Here, ML is defined as the surface density of Cu atoms on the clean Cu(001) surface. The nitrogen atoms are saturated on the surface at the coverage of 0.5 ML and trench-like defects appear as in Fig. 1a. The surface strain is relieved by the lattice expansion toward the trench-like defects [20,21].

3.2. Reaction with atomic hydrogen

When the N-saturated surface was exposed to atomic hydrogen for 1 min with $P_{H_2} = 2.0 \times 10^{-6}$ Torr, protrusions 30 pm higher than the nitrogen atoms were found on the surface as shown in Fig. 1b and c. The protrusions are located on atop sites of the adsorbed N atoms at a negative V_B (Fig. 1c). They never moved during the STM observation.

Their shapes do not correspond to the defect of the N atoms in the N-adsorbed regions [19]. Those protrusions covered about 80% of the surface after the atomic hydrogen exposure for 4 min with $P_{H_2} = 1.0 \times 10^{-6}$ Torr (Fig. 1d), and formed a c(2×2) structure. Considering all the above, we identify the protrusions at a negative V_B to be the NH species as seen in the STM images of the NH species on the Pt(111) [3] and Ni(110) surfaces [12].

After exposure to atomic hydrogen for total 18 min with $P_{H_2} = 1.0 \times 10^{-5}$ Torr (Fig. 1e), the NH species formed small domains of the c(2×2)structure. Approximately 40% of the surface was occupied by the bright areas which were not resolved atomically. The bright areas are identified as clean Cu surfaces because the apparent height between the NH species and the bright area is 40 pm. This value is the same apparent height between the NH species and Cu regions at the N coverage of 0.3 ML, as shown later. With the high exposure of atomic hydrogen, the surface NH species can react with atomic hydrogen, and turn to be the NH_2 species and then NH_3. Since the ammonia molecules desorb from the Cu(001) surface at RT [22], we conclude that the appearance of the clean Cu surface is attributed to formation of NH_3 and its desorption from the surface. The clean surface was found mainly on the center of the terraces, and rarely in the vicinity of steps and trenches. The result can be understood when we consider the motion of the N H species induced by the following reaction process. Unlike the NH species, the NH_2 species on the present surface should be located at the bridge sites as on the Ru(0001) surface [2] and the Cu(111) surface [23]. Then, the NH species produced by the decomposition of the NH_2 species can be on new fourfold hollow sites. Consequently, a part of the NH species apparently move during the atomic hydrogen exposure and can reach the energetically stable sites such as the edge of the trench-like defects where the surface strain is relived. The exposure to atomic hydrogen with $P_{H_2} = 2.0 \times 10^{-5}$ Torr for 10 min resulted in desorption of all the N atoms, and the trench-like defects disappeared. It is noted that no change of the N-adsorbed Cu surface was observed on the surface after the exposure only to hydrogen molecules with $P_{H_2} = 2.0 \times 10^{-5}$ Torr for 15 min.

In all the above experiments, we could not find the protrusions or depressions which can be assigned to the NH_2 species. It is possible that the NH_2 species are on the bridge sites of the Cu surface as observed on the Ru(0001) surface at 7 K [24]. However, there was no protrusion or depression on the bridge site. The results can be interpreted by the
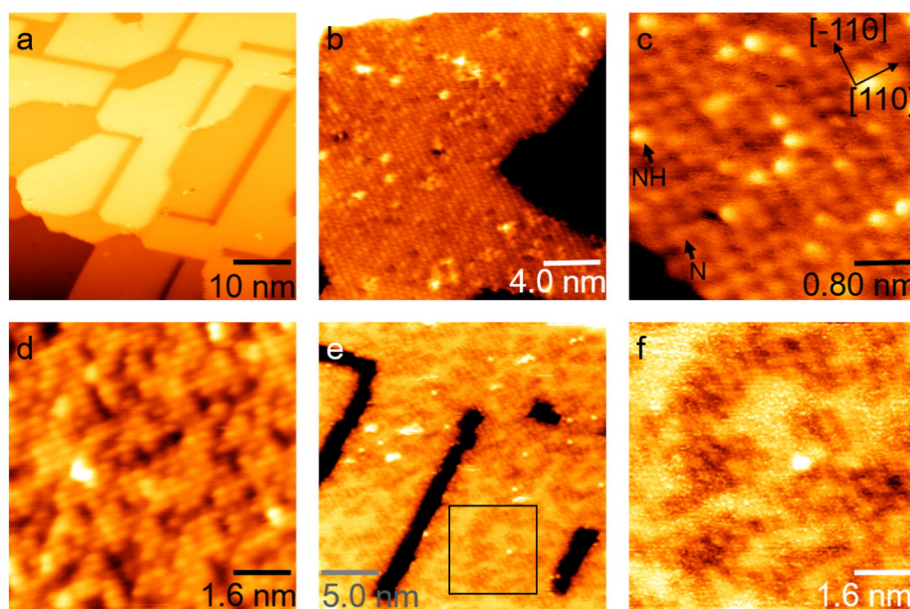
Fig. 1. (a) STM image of the Cu(001) surface with 0.5 ML N atoms ($V_B = -0.5$ V, $I_t = 0.2$ nA) (b–e) STM images after exposure of the surface in (a) to H atoms, (b–c) with $P_{H_2} = 2.0 \times 10^{-6}$ Torr for 1 min ($V_B = -0.5$ V, $I_t = 1.0$ nA), (d) with $P_{H_2} = 1.0 \times 10^{-5}$ Torr for 4 min ($V_B = -0.5$ V, $I_t = 0.2$ nA), (e) with $P_{H_2} = 1.0 \times 10^{-5}$ Torr for 18 min ($V_B = -0.5$ V, $I_t = 1.0$ nA). (f) Magnified image of the area surrounded by solid square in (e).