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Electron-energy-loss spectra of the Si(100)-(2 × 1) surface exposed to NH_3

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High-resolution vibrational electron-energy-loss spectroscopy has been used to study the interaction of NH_3 with the Si(100)-(2×1) surface. NH_3 is decomposed on the Si(100) surface at 300 K to form the $SiNH_2$ and SiH species. It is proposed that the amino (NH_2) species is bonded to the dangling bond of the Si(100) surface atom. Changes in the adsorbed state of both species under heat treatment are discussed.

I. INTRODUCTION

The interaction of NH_3 with Si surface is of considerable interest not only from the scientific viewpoint but also from the technological application of silicon nitride. Several studies have been made on the interaction of NH_3 with the Si(100) surface by the use of x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, etc.[1–3] Bozso and Avouris[3] have reported that NH_3 is dissociated at 300 K to form the SiNH and SiH species on the Si(100)-(2×1) surface. In the present work, vibrational electron-energy-loss spectroscopy (EELS) has been employed to the study of the adsorbed state of NH_3 on the Si(100)-(2×1) surface. This work is a part of our investigation series on the gas-Si surface interactions [Si(111)-H,[4] Si(111)-N,[5] Si(111)-NH_3,[6] etc.].

II. EXPERIMENT

The experiments were performed by the *in situ* combined techniques of EELS, low-energy electron diffraction (LEED), and Auger-electron spectroscopy (AES) using an ultrahigh-vacuum system with a base pressure of 1×10^{-10} Torr. The EELS spectrometer used for the present study consists of a double-pass 127° cylindrical deflector analyzer (CDA) for the monochromator and a single-pass 127° CDA for the analyzer. For EELS measurements, the primary electron energy E_p of 5.1 eV and the incident angle $\theta_i=65°$ with respect to the surface normal were used. The off-specular measurements were made by rotating the monochromator around an axis which was perpendicular to the incidence plane of the electron beam. The sample used was a Si(100) wafer (*p* type, boron-doped, 1000 Ω cm), and was mounted such that the electron beam scattered along the [011] azimuth. The clean Si(100) surface, showing the sharp (2×1) LEED pattern, was carefully prepared by the standard technique (Ar^+-ion-bombardment–annealing–flashing cycles). No impurities were observed on the clean surface thus prepared within the detection limit of AES. Ammonia was introduced into the vacuum chamber via the 10-mm-diam doser located 8 mm from the sample surface.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the EELS spectrum in the specular mode of the Si(100)-(2×1) surface at 300 K exposed to ~10 L NH_3 [1 langmiur (L) $\equiv10^{-6}$ Torr s], which nearly corresponds to the saturation coverage. Similar spectra were obtained for lower exposures. Losses are observed at ~50, 75, 103, 195, 258, and 414 meV. The off-specular measurements indicated that all losses, except for the 414-meV loss, were mainly dipole excited. It is noted that, in the saturation-coverage region, the (2×1) LEED pattern is observable with the increased background intensity. The 258-meV loss is attributed to the Si—H

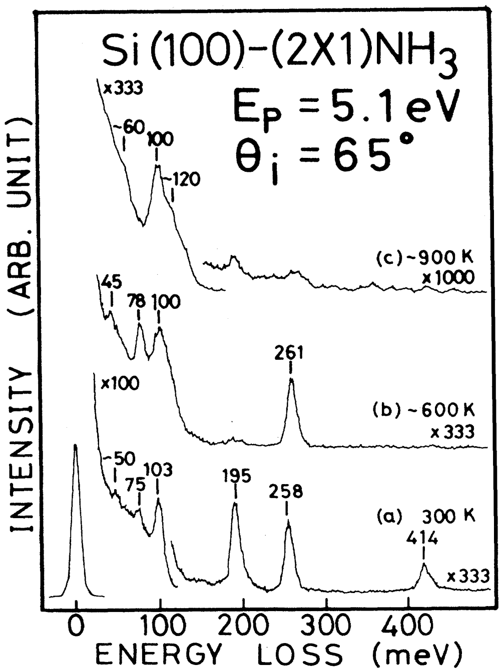

FIG. 1. EELS spectra in the specular mode of the Si(100)-(2×1) surface (a) exposed to ~10 L NH_3 at 300 K; (b) after heating at ~600 K for 2 min; (c) after heating at ~900 K for 2 min ($E_p=5.1$ eV).

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stretching vibration of the SiH species by comparison with the EELS study for the Si(111)-H system.[4] The 103-, 195-, and 414-meV losses are attributed to the Si—N stretching vibration, the NH_2 scissors vibration, and to the NH_2 symmetric- and antisymmetric-stretching vibrations, respectively. These assignments are based on comparison with the infrared-absorption studies of the organosilicic compounds. Organosilazane (R_3SiNH_2) has the Si—N stretching vibration at 103–106 meV, the NH_2 scissors vibration at 190–192 meV, and the NH_2 symmetric-stretching vibration at 422 meV, and the NH_2 antisymmetric-stretching vibration at 431–432 meV.[7] Peri[8] studied the NH_3-exposed dry silica aerogel and observed the NH_2 scissors vibration and the NH_2 symmetric-stretching vibration at 193 and 427 meV, respectively. Thus, it is interpreted that at 300 K NH_3 is partially dissociated to form the $SiNH_2$ and SiH species and that the amino (NH_2) species is bonded to the Si surface with a covalent bond formed between its nitrogen atom and the dangling bond of the Si(100) surface atom. It is difficult to interpret the ~50- and 75-meV losses unambiguously. The ~50-meV loss may tentatively be associated with the NH_2 bending vibration and the 75-meV loss with the NH_2 and SiH bending vibrations.[4,6]

It is noted that the EELS spectrum for the Si(100)-NH_3 system is similar to that for the Si(111)-NH_3 system.[6] For the Si(111)-(7×7)NH_3 system, the losses are observed at 62, 75, 98, 135, 188, 258, and 422 meV, and it is also interpreted that NH_3 is partially dissociated to form the $SiNH_2$ and SiH species. Bozso and Avouris[3] proposed that NH_3 is dissociated into NH and H on Si(100)-(2×1), while on Si(111)-(7×7) it is dissociated into NH_2 and H. We could not obtain any evidence that the imino (NH) species existed at 300 K, because we could not detect that corresponding NH bending mode which was expected at 145–146 meV according to the infrared spectroscopy study of organosilazine [$(R_3Si)_2NH$].[7]

By heating the Si(100) surface (preexposed to NH_3 at 300 K) to ~600 K, the EELS spectrum is varied drastically [Fig. 1(b)]. The 195- and 414-meV losses (NH_2 scissors and NH_2 symmetric- and antisymmetric-stretching modes, respectively) are markedly decreased in intensity. These results suggest that the $SiNH_2$ species are mostly decomposed. The intensity (normalized by the elastic peak intensity) of the 258-meV loss (SiH stretching mode) is only slightly increased ($<10\%$). This is interpreted to indicate that the H atoms produced by the decomposition are partly bonded to the Si(100) surface to form the SiH species, but the majority are desorbed as H_2. The same conclusion has been reached by Bozso and Avouris.[1,3] The shift of the 258-meV peak to 261 meV [compare Figs. 1(a) and 1(b)] is interpreted to indicate that the Si atoms (bonded to the H adatoms) are back-bonded to the N atoms in the subsurface. Similar results are observed for the Si(111)-NH_3 system.[6] The 78-meV loss (which has been measured to be dipole active) is mainly attributed to the bending mode of the SiH species (tilted from the surface normal) on the Si substrate distorted by the penetration of N atoms into the subsurface. The 45- and 100-meV losses are attributed to the symmetric-breathing mode and the asymmetric in-plane bond-stretching mode of the near-planar Si_3N species, respectively, by comparison with the EELS studies for the Si(111)-N (Ref. 5) and Si(111)-NH_3 (Ref. 6) systems. The broad 100-meV peak may include the contribution from the Si—N stretching mode of the residual $SiNH_2$ species.

After heating at ~900 K, losses associated with the surface species containing H atoms are all extinguished [Fig. 1(c)]. This indicates that H atoms are removed from the surface by the desorption of H_2. The 100-meV loss is attributed to the Si_3N species. The ~60- and 120-meV losses are associated with the growth of the silicon nitride.[9] It is noted, after heat treatment at 600–900 K, that the (2×1) LEED pattern is still observable with the background. The 195- and 258-meV losses [Fig. 1(c)] are attributed to the NH_3 adsorption on the surface from the residual NH_3 in the chamber.

IV. SUMMARY

A vibrational EELS study has been performed concerning the adsorption of NH_3 on the Si(100)-(2×1) surface. The NH_3 molecules are adsorbed partially dissociatively to form the $SiNH_2$ and SiH species. The NH_2 and H are bonded covalently to the dangling bonds of the surface Si atoms. The structural model is shown in Fig. 2. In Fig. 2, as the H—N—H bond angle of an NH_3 molecule is 107°, it is assumed that the molecular plane of the NH_2 species is inclined by ~60° from the Si—N bond axis. Considering the near sp^3 hybridization of the surface Si atom, it is also assumed that the Si—N bond is directed ~20° with respect to the surface normal. The structural model is compatible with the surface-normal dipole selection rule[10] which is applicable to all the observed losses except for the 414-meV loss. By heating to ~600 K, the $SiNH_2$ species are mostly decomposed to form the Si_3N species; H atoms produced by the decomposition are partly bonded to the Si surface to form the

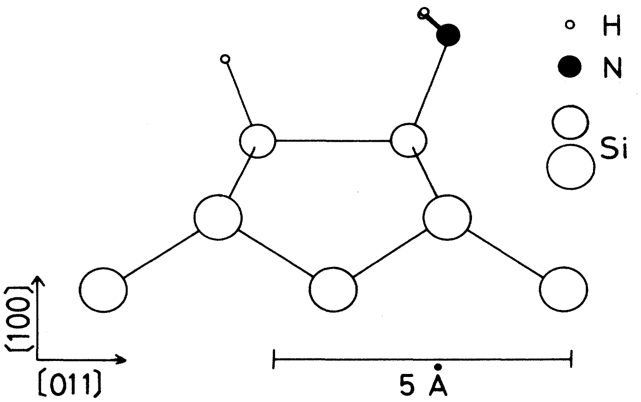

FIG. 2. Schematic of the structural model for the Si(100)-(2×1) surface exposed to NH_3 at 300 K. The adsorbate-induced displacements of Si atoms are not included.

SiH species, but the majority are removed from the surface as H_2. By heating to $\sim$900 K, the H adatoms are completely removed from the surface; the existence of the Si_3N species and the formation of the silicon nitride are observed.

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