The Precursor Mediated Chemisorption of Vinyl Bromide on Si(100)c(4×2)

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We investigated the adsorption states and the reaction of vinyl bromide (CH_2=CHBr) on Si(100)c(4×2), using high-resolution electron energy loss spectroscopy. We found that the chemisorption of this molecule occurs via a precursor state and a vinyl bromide molecule is di-σ bonded to the Si dimer on Si(100)c(4×2) in the chemisorption state. The precursor species are observed in the temperature range from 58 to 90 K. Judging from the vibrational spectra, we conclude that the structure of the precursor state is a three-atom intermediate state (π complex). The activation energy and the preexponential factor of the reaction from the precursor state to the chemisorption state are estimated to be 27.3 kJ/mol (283 meV) and 1.5×10^{13} s^{-1}, respectively. The activation energy decreases with increasing the vinyl bromide coverage owing to the steric repulsion.

1. Introduction

In recent years, a large number of studies have been reported for organic molecules on semiconductor surfaces, concerning both the fundamental scientific interest and the application to molecular scale devices.[1,2] Understanding the reactions of organic molecules with the Si(100) surface is an essential prerequisite for constructing hybrid organic molecule/silicon devices.

Since the discovery of the cycloaddition reaction of alkene and alkyne molecules to the Si(100) surface[3,4] (di-σ bond formation to the Si dimer), the reaction mechanism has been a long standing problem under debate. A few experimental studies have reported on the reaction mechanism of unsaturated organic molecules adsorbed on Si(100). Liu and Hamers proposed two possible models for the di-σ bond formation of ethylene on Si-(100) by infrared spectroscopy.[5] One model is the radical mechanism; first, the π bond of the ethylene molecule is broken to form a radical intermediate state (Figure 1a), followed by the formation of a second Si−C bond. The other model is a three-atom intermediate state model as a precursor state (Figure 1b), and the precursor ethylene molecule becomes chemisorbed on Si(100) forming di-σ Si−C bonds. The later reaction mechanism is also supported by the temperature programmed desorption (TPD) spectroscopy results by Kiskinova and Yates.[6] Lopinski et al. reported that alkene molecules should be chemisorbed on Si(100) by a similar adsorption process via a single Si−C bonded radical species (Figure 1a) on the basis of their scanning tunneling microscopy (STM) results.[7] Theoretical calculations indicate that the three-atom intermediate state (π complex) is a stable precursor state of ethylene,[8] cyclopentene,[9,10] and 1,3-cyclohexadiene[11] on Si(100), but the diradical intermediate state is proposed in the case of acetylene on Si-(100).[12] However, a precursor state for chemisorption has not been identified as a stable species experimentally yet.

In this study, vinyl bromide (CH_2=CHBr) molecules are adsorbed on Si(100)c(4×2). The Br atom of this molecule is

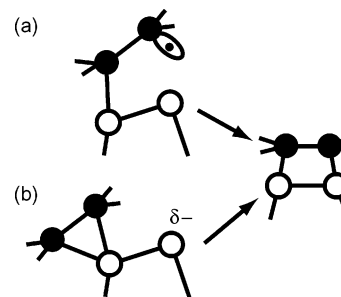* Corresponding author. Fax: 81-471-36-3474. E-mail: yoshinobu@issp.u-tokyo.ac.jp.

Figure 1. Previously proposed models for the adsorption process of alkene on Si(100).[5] (a) Diradical intermediate model and (b) a three-atom intermediate model.

substituted for one of the hydrogen atoms in ethylene. A precursor state may be observed, if it becomes more stable by the substituent Br effects. In addition, the precursor state could be observed at lower temperatures.

In the present paper, we report the high-resolution electron energy loss spectroscopy (HREELS) study on the adsorption states of vinyl bromide as a function of temperature and coverage. At 58 K, precursor species were observed as a stable state. From 83 to 90 K, the reaction of di-σ bond formation from a precursor species was spectroscopically observed as a function of time. Thus, we studied the reaction kinetics from the precursor state to the chemisorption state by time-dependent HREELS spectra and kinetic parameters were obtained.

2. Experimental Section

The experiments were performed in an ultrahigh vacuum chamber with a base pressure less than 1×10^{-10} Torr. This chamber housed an HREELS spectrometer (LK Technologies ELS5000), low energy electron diffraction (LEED) optics, and a quadrupole mass spectrometer (QMS). For HREELS measurements, an energy resolution of 16 cm^{-1} (direct mode) and an incidence angle θ_i of 60° with respect to the surface normal were used.

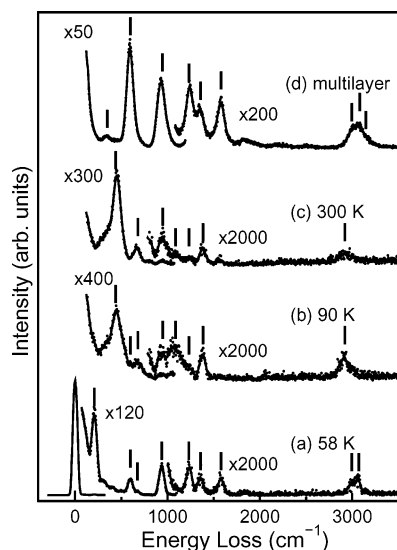To measure a sample temperature, a U-shaped clip made by a Ta tube was attached to the Si sample. W26%Re/W5%Re

Figure 2. HREELS spectra of the vinyl bromide exposed to the Si surface at (a) 58 K and (b) 90 K (15 shots ≃ nearly saturation). (c) Annealing at 300 K after 10 shots of vinyl bromide dosed on Si(100)c-(4×2) and measured at 90 K. (d) Multilayer spectrum of vinyl bromide at 90 K. All spectra were measured in the specular mode. The primary electron energy, E_p = 5.0 eV.

TABLE 1: Assignments of Observed HREELS Peaks (cm^{-1}) of Adsorbed Vinyl Bromide at 58 and 90 K, and the Multilayer of Vinyl Bromide on Si(100)c(4×2), Together with the Observed Vibrational Peaks of Vinyl Bromide in Solid Argon[20]

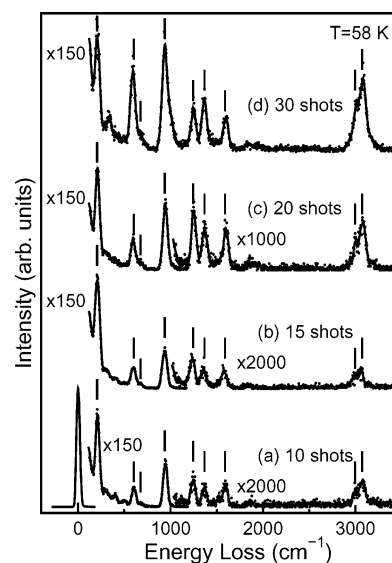| mode	C_2H_3Br/Si(100) at 58 K	C_2H_3Br/Si(100) at 90 K	multilayer on Si(100)	in solid argon[a]
hindered mode	208			
C=C−Br in plane			339	344
ν_{SiBr}		(439)		
ρ_{tCH}	599	600	594	583
ν_{CBr}				609
hindered mode	675			
ν_{SiC}		688		
C=C−H out of plane	938	947	930	941
ν_{C-C}		1087		
CH$_2$ rock	1233	1228	1233	1256
CH$_2$ deformation	1350	1382	1349	1371
$\nu_{C=C}$	1572		1580	1602
ν_{CH} (sp^3)		2920		
ν_{CH} (sp^2)	2996		2996	3024
ν_{CH} (sp^2)	3070		3056	3082
ν_{CH} (sp^2)			3145	3115

^{a} IR measurement.[20]

Figure 3. HREELS spectra of vinyl bromide on Si(100)c(4×2) as a function of exposure at 58 K in the specular mode. E_p = 5.0 eV.

thermocouple wires were inserted in this tube to prevent direct contact of the thermocouple material to the sample surface.[13] The conversion from EMF (mV) to temperature (K) was obtained from the empirical formula of Sandstrom and Withrow[14] and Mitchell et al.[15] In addition, the measured EMF was calibrated by the desorption temperature of the multilayer Xe (73 K)[16] and multilayer water ice (155 K).[17] The sample was cooled at 90 K by liquid nitrogen, at 58 K by liquid helium, and at 79 K by solid nitrogen. From 83 to 88 K, using He gas bubbling through the liquid nitrogen,[18] we could control the temperature from 83 to 88 K by changing the flow rate of He gas with the accuracy of ±0.4 K.

A p-type (B-doped, 3−5 Ω cm) Si(100) wafer was cleaned by being outgassed at ∼900 K for 12 h, flashed up to 1500 K several times, and cooled slowly from ∼1000 to 90 K. After this treatment, the c(4×2) LEED pattern was observed at 90 K. Before the adsorption experiments, we confirmed that the Si(100) surface was clean by measuring the HREELS spectra. Vinyl bromide (CH$_2$CHBr) molecules were introduced onto the surface by means of a pulse gas dosing system. The exposure was controlled by changing the number of shots at a constant gas pressure.

3. Results and Discussion

3.1. Adsorbed States as a Function of Temperature. Parts a and b of Figure 2 show the HREELS spectra of vinyl bromide molecules adsorbed on Si(100)c(4×2) at 58 and 90 K, respectively. The spectrum of Figure 2c was measured at 90 K after the Si substrate was exposed to vinyl bromide molecules at 90 K, followed by heating to 300 K. Distinct differences are observed among the spectra of Figure 2 a−c. Thus, the adsorption state changes depending on temperature. As a reference, the HREELS spectrum of the vinyl bromide multilayer on Si(100)c(4×2) was measured (Figure 2d). The assignment of the vinyl bromide multilayer is made from a comparison with the vinyl bromide IR spectra in cryogenic matrixes.[19,20] All the observed peaks and the assignments of the spectra in Figure 2 are summarized in Table 1.

In the spectrum at 58 K (Figure 2a) an additional peak is observed at 208 cm^{-1} and a shoulder loss is observed at 675 cm^{-1} as compared with the spectrum of the multilayer (Figure 2d). First, the internal bonds of the vinyl bromide molecule are not cleaved, because all the characteristic loss peaks for the multilayer are observed in the spectrum at 58 K (Figure 2a). Next, we try to assign the peaks at 208 and 675 cm^{-1}. Figure 3 shows the HREELS spectra at 58 K as a function of coverage. All the loss peaks at 58 K increase in intensity with increasing coverage, up to 15 shots of vinyl bromide. However, above 20 shots, the peaks at 208 and 675 cm^{-1} remain constant in intensity. On the other hand, the other peaks increase in intensity above 20 shots. Thus, vinyl bromide molecules are condensed on Si(100)c(4×2) above 20 shots. Because the peaks at 208 and 675 cm^{-1} increase in intensity until the multilayer of vinyl bromide molecules starts to develop on Si(100)c(4×2), these peaks originate from the direct interaction between the vinyl bromide molecule and the Si surface. Hence, we attribute the peaks at 208 and 675 cm^{-1} to the hindered translational/rotational modes between the vinyl bromide molecule and the Si surface.

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Although the peaks of external modes are observed, all the peaks of internal modes located at nearly the same positions in the multilayer spectrum. In fact, the ν_{CH} blue shifts to 14 cm^{-1} and the ν_{CC} red shifts to 8 cm^{-1} in the peak position. Thus, we conclude that the structure of the adsorption state at 58 K for vinyl bromide on Si(100)c(4×2) should be similar to that of free vinyl bromide. Similar observations were reported for weakly adsorbed alkene molecules. For example, in ethylene/Pd(110),[21] the internal vibrational modes of ethylene nearly the same position as those of gaseous ethylene; the ν_{CH} red shifts to 10−30 cm^{-1} and ν_{CC} red shifts to 100 cm^{-1}. In addition, the hindered modes are observed at 280, 335, 380, and 530 cm^{-1} due to the interaction between the ethylene molecule and the metal surface. In this system, the occupied π orbital of ethylene interacts with the unoccupied d_{z^2} orbital of metal;[22] the ethylene molecule donates π electrons to the metal substrate. We suppose that the vinyl bromide molecule is π bonded to the down dimer Si atom in the adsorption state at 58 K; the donation of π electron occurs to the electron deficient down dimer atom.[23] Thus, the vinyl bromide molecule is weakly π bonded to the Si surface (π complex).

Next, we try to assign the vibrational peaks of vinyl bromide on Si(100)c(4×2) at 90 K (Figure 2b). The peak at 1580 cm^{-1}, which can be attributed to the stretching mode of a C=C double bond, disappears in the spectrum at 90 K. In addition, a new peak is observed at 1087 cm^{-1}, which is attributed to the stretching mode of the C−C single bond. Hence, the C=C double bond of vinyl bromide is reacted when vinyl bromide molecules are adsorbed on Si(100)c(4×2) at 90 K. The peaks around 3000 cm^{-1} in the spectra of Figure 2 are attributed to the CH stretching mode. In the spectrum of the multilayer, the CH stretching modes are observed at 2996, 3056, and 3145 cm^{-1}, whereas in the spectrum at 90 K they are observed around 2920 cm^{-1}. Generally speaking, CH stretching modes with sp^3-hybridized carbon are somewhat lower in energy (below 3000 cm^{-1}) than those with sp^2-hybridized carbon (above 3000 cm^{-1}).[24] Thus, the hybridized state at 90 K is sp^3, indicating that the C=C double bond of vinyl bromide is reacted. The peak at 688 cm^{-1} could be attributed to the SiC stretching mode, because this mode was observed at 670 cm^{-1} when ethylene molecules were adsorbed on Si(100)c(4×2).[3] We conclude that the vinyl bromide molecule reacts with the Si dimer to form di-σ Si−C bond, because the double bond is reacted, the hybridization state becomes sp^3, and the Si−C bond is formed.

The peak at 439 cm^{-1} in the spectrum at 90 K is attributed to the SiBr stretching mode, because this mode of the silyl halides was observed at 430 cm^{-1}.[25] Thus, the C−Br bonds of adsorbed vinyl bromide molecules are partly dissociated at 90 K. Note that the C−Br dissociation reaction proceeds up to 300 K, where a stronger peak is observed around 439 cm^{-1} (Figure 2c).

The adsorption kinetics was investigated as a function of temperature and time. Figure 4 shows a series of time-dependent HREELS spectra at 87 K. All the peaks in the spectrum of Figure 4a are similar to those in the spectrum at 58 K (Figure 2a). Thus, initially most of the vinyl bromide molecules are weakly adsorbed on Si(100)c(4×2). On the other hand, the spectrum of Figure 4d is similar to the spectrum at 90 K (Figure 2b), which represents vinyl bromide chemisorbed on Si(100)c-(4×2). The peak at 208 cm^{-1} decreases in intensity, which indicates the population of the weakly adsorbed species (π complex) decreases. On the other hand, the peak at 1087 cm^{-1} increases in intensity, which indicates the population of chemisorbed species increase. These results are interpreted to indicate
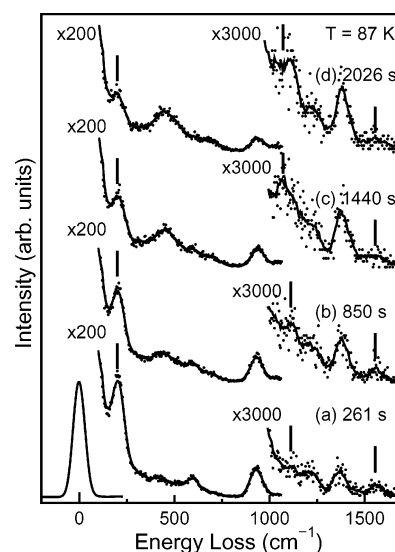

Figure 4. Series of HREELS spectra of vinyl bromide on Si(100)c-(4×2) at 87 K in the specular mode as a function of elapsed time. Elapsed time after the dose is indicated in this figure. At the indicated time, each spectrum starts to be measured. The acquisition time of each HREELS spectrum was 270 s. E_p = 5.0 eV.

that the adsorption state at 58 K is a precursor for the chemisorption (di-σ species) at 90 K.

We note that the di-σ bonded species and the dissociative adsorbed species are mixed at 90 K. When the C−Br bond of vinyl bromide is dissociated on the Si surface, the peak of the SiBr stretching mode is observed at 439 cm^{-1}. The area intensity of this peak may indicate the amount of the dissociated species. After the Si substrate is annealed at 300 K, the intensity of this peak becomes stronger than that at 90 K (Figure 2b). This result indicates that adsorbed vinyl bromide molecules are further dissociated, even after the peak at 208 cm^{-1} almost disappears at 90 K. Therefore, we conclude that the dissociation of the adsorbed molecules do not occur directly from the precursor state, but the consecutive reaction occurs from the precursor to the di-σ species followed by the dissociation. In fact, the peaks at 208, 1572, and 3070 cm^{-1} disappear and those at 1087 and 2920 cm^{-1} appear in the spectrum at 90 K. Thus, most of the C=C double bond of the vinyl bromide molecules are reacted to form di-σ bond at 90 K.

Previously, a radical intermediate state (Figure 1a) and a three-atom intermediate state (Figure 1b) were proposed as a possible precursor state. According to theoretical calculations,[8−10] the length of the Si−C bond in the three-atom intermediate state is 2.4−2.5 Å and that in the radical intermediate state is 1.9−2.0 Å. When alkene molecules are di-σ bonded to the Si dimers, the length of the Si−C bond is about 1.9 Å by theoretical[8−10] and experimental results.[26] Thus, the length of the Si−C bond in the radical intermediate state is nearly equal to that in the di-σ chemisorption state, where a covalent bond is formed between a C atom and an Si atom and the hybridization state of C is near sp^3. On the other hand, in the three-atom intermediate state, the length between an Si atom and C atoms is longer than that in the di-σ chemisorption state. Hence, the interaction between the C atoms and the Si atom is weak, which indicates the hybridization state of C is near sp^2. Judging from the observed ν_{CH} and ν_{CC}, the hybridization state of the precursor is near sp^2. This result supports the structure of Figure 1b.

The adsorption state at 58 K is a precursor state for the formation of di-σ bond with the Si surface. To the best of our
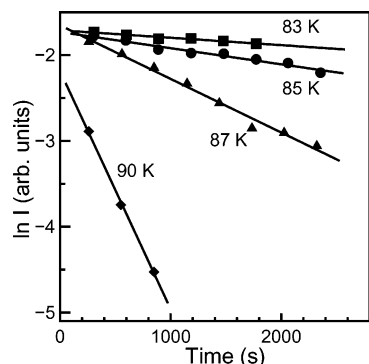
Figure 5. Integrated intensity of the 208 cm^{-1} peak as a function of elapsed time at several selected temperatures. The solid line indicates the least-squares fits of the experimental data points.

knowledge, this is the first spectroscopic observation of the precursor state of alkene on Si(100)c(4×2) as a stable species.

3.2. Kinetic Measurement Using Time-Dependent HREELS. We measured a series of HREELS spectra after vinyl bromide adsorbed on Si(100)c(4×2) at a fixed temperature between 83 and 90 K, as a function of elapsed time after vinyl bromide was dosed on Si(100)c(4×2).[27] Figure 4 shows a series of time-dependent HREELS spectra at 87 K. The indicated time in Figure 4 represents the start time of measuring each HREELS spectrum after the vinyl bromide exposure on Si(100)c(4×2) at $t = 0$ s. Note that it took about 270 s for each spectrum. The peaks at 208, 599, 938 and 1572 cm^{-1} decrease in intensity and the peaks at 439 and 1087 cm^{-1} increase as a function of elapsed time.

The vinyl bromide molecule at the precursor state proceeds to the chemisorption (di-σ bond formation), and the desorption might occur. However, because no molecular desorption was observed from the Si surface by heating to 150 K by QMS measurements, the desorption path of vinyl bromide from the Si surface can be ruled out. Thus, the precursor state proceeds to the di-σ chemisorption state as a first-order reaction.

To determine kinetic parameters from the precursor state to the chemisorption state, we must estimate the amount of the precursor state species. The peak at 208 cm^{-1} is observed only when vinyl bromide molecules are weakly adsorbed on Si(100)c-(4×2) as the precursor state. In addition, the peak intensity at 208 cm^{-1} is proportional to the exposure of vinyl bromide at low temperature (see Figure 3). Thus, we can safely assume that the area intensity of the peak at 208 cm^{-1} is proportional to the amount of the precursor species, and we can estimate the relative amount of the precursor state. Note that the peak at 208 cm^{-1} is integrated after subtracting the background of the elastic peak from each spectrum.

Here, the area intensity of the peak at 208 cm^{-1} is represented by I, with the rate constant (k) from the precursor state to the chemisorption state and the elapsed time (t). Because this reaction is a first-order reaction, the rate equation is obtained by $\ln I = -kt + C$. The constant, C, represents the initial intensity ($t = 0$) of the peak at 208 cm^{-1}. Figure 5 shows the relation between the elapsed time and the area intensity of the peak at 83, 85, 87, and 90 K, respectively. These data can be fitted by the above equation, and the rate constant k is determined at each temperature. Note that the fitting line at 90 K intercepts at a different position in the y axis, because reaction have already started during the exposure of gaseous molecules.

Figure 6 shows the Arrhenius plot between the substrate temperature and the rate constant. Here, we estimate the
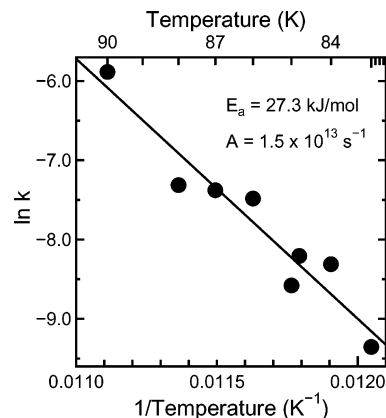

Figure 6. Arrhenius plot of the rate constants for the reaction from the precursor state to the chemisorption state. E_a and A represent the activation energy and the preexponential factor, respectively.
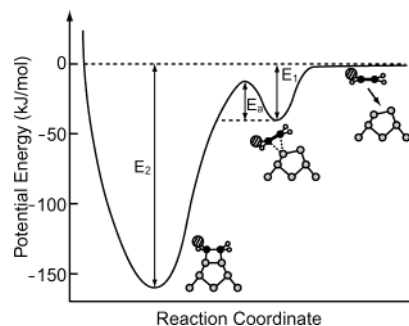

Figure 7. Potential energy diagram for the chemisorption reaction of vinyl bromide on Si(100)c(4×2). E_a, E_1, and E_2 represent the activation energy, the adsorption energy of the precursor state, and that of the di-σ chemisorption state, respectively.

activation energy (E_a) to be 27.3 kJ/mol (283 meV) and the preexponential factor to be 1.5×10^{13} s^{-1}, respectively.

According to the present results, as well as previous theoretical calculations and experimental results, the potential energy profile for the chemisorption reaction of vinyl bromide on Si-(100)c(4×2) may be depicted. In the theoretical calculations,[10,28] the adsorption energy of the precursor state for alkene molecules on Si(100)c(4×2) is 34.7−39.6 kJ/mol (360−410 meV) and that of the chemisorption state (di-σ bond) is 126−157 kJ/mol (1310−1630 meV). According to the TPD result,[29] the chemisorption energy of C_2H_4 on Si(100)c(4×2) is 159 kJ/mol (1650 meV). On the basis of these results, the potential energy profile is constructed in Figure 7. Here, we assume that the adsorption energy of the precursor state is ∼39 kJ/mol (∼0.4 eV) and that of the chemisorption state is ∼155 kJ/mol (∼1.6 eV).

Lopinski et al. reported that the adsorption of 2-butene on Si(100) should proceed via a single Si−C bonded radical species.[7] Lu reported that the chemisorption occurs via a diradical state, which follows a π complex precursor in ethylene on Si(100).[8] However, the present study indicates that a singlet diradical intermediate state does not exist as a stable state. In the case of C_2H_4 on Si(100), the activation energy was estimated to be 3.8 kJ/mol (39 meV).[29] Comparing the activation energy of C_2H_4 on Si(100) with that of vinyl bromide on Si(100), the activation energy of vinyl bromide on Si(100) is much larger. According to the theoretical calculations, the activation energy from the precursor state to the chemisorption is 24.3 kJ/mol (252 meV) in ethylene/Si(100)[8] and 7.7 kJ/mol (80 meV) in cyclopentene/Si(100).[10] Although the calculated activation energy depends on the models, the activation energy of vinyl bromide is larger than those of ethylene[8] and cyclopentene[10]
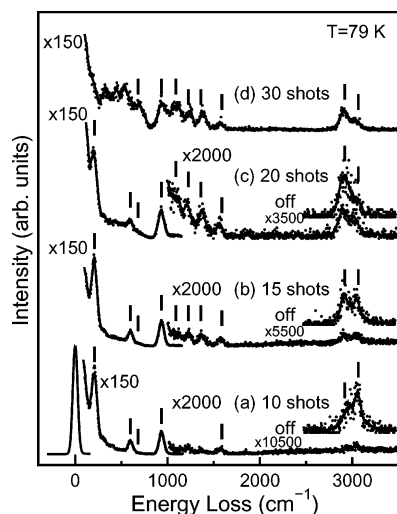
Figure 8. HREELS spectra of vinyl bromide on Si(100)c(4×2) as a function of exposure at 79 K in the specular mode. The spectra in the off-specular mode ($\Delta\theta = 10°$) from 2500 to 3500 cm^{-1} are also shown in these figures (a)−(c). E_p = 5.0 eV.

on Si(100). In fact, around 90 K no precursor species were observed in ethylene[3] and cyclopentene[30] on Si(100)c(4×2), experimentally.

3.3. Intermolecular Interaction between Adsorbed Species. Figure 8 shows a series of HREELS spectra at 58 K as a function of vinyl bromide exposure. As mentioned before, all vinyl bromide molecules are weakly adsorbed on Si(100)c(4×2) (the precursor π complex) initially, and the multilayer is formed at larger exposure at 58 K.

Figure 8 shows the HREELS spectra at 79 K as a function of vinyl bromide exposure. Most peaks monotonically increase in intensity up to 15 shots, similar to the case at 58 K. However, above 20 shots, the HREELS spectra change drastically. The peaks at 208, 600, 947, and 3070 cm^{-1} decrease and the peaks at 439 and 2920 cm^{-1} increase in intensity.

These results indicate that the adsorption state of vinyl bromide on Si(100)c(4×2) at 79 K changes when the coverage of vinyl bromide becomes high. The amount of the precursor species (π complex) decreases with increasing coverage, because the 208 cm^{-1} peak decreases in intensity. By comparing the spectrum at 79 K (Figure 8d) with that at 58 K (Figure 3d), the peaks at 688, 1087, and 2920 cm^{-1} appear when the exposure is high. The double bond of vinyl bromide is reacted, because the 1087 and 2920 cm^{-1} peaks are attributed to the stretching mode of the C−C single bond and the sp^3 CH stretching mode, respectively. The SiC bond is also formed, judging from the appearance of the 688 cm^{-1} peak (the SiC stretching mode). Thus, by increasing the coverage of vinyl bromide, part of the vinyl bromide molecules become di-σ bonded to the Si dimers at 79 K.

When the coverage is low, the reaction rate is estimated to be below 1.5 × 10^{-5} s^{-1} at 79 K using the present empirical results. Assuming that the reaction rate is the same at higher coverage, the adsorption state of vinyl bromide on Si(100)c-(4×2) should be the precursor state. However, part of the adsorbed vinyl bromide molecules become di-σ bonded to the Si dimers at 79 K, though such a reaction does not occur even at high coverage at 58 K. The possible reasons for this reaction are discussed as follows: (i) If the reaction is induced simply by the kinetic energy of incoming molecules, this reaction does not depend on the substrate temperature. However, the phenomena depend on the temperature. Thus, the reaction is not

induced by the kinetic energy. (ii) When 10 shots of vinyl bromide are dosed on the Si surface, the peak at 3070 cm^{-1} becomes larger than that at 2920 cm^{-1} in intensity. As the coverage increases, the relative intensity of the peak at 2920 cm^{-1} becomes larger than that of the peak at 3070 cm^{-1}. Thus, the population of di-σ bonded vinyl bromide molecules becomes larger. The steric repulsion between nearby adsorbed molecules becomes effective with increasing coverage and may induce this reaction. Thus, we conclude that when the coverage is high, the potential energy profile changes by the steric repulsion and the activation barrier decreases; thermally activated vinyl bromide molecules become di-σ bonded to the Si dimers at 79 K.

The potential energy change at higher coverage is also suggested by the previous theoretical calculations. In the case of cyclopentene/Si(100), the chemisorption energy at 0.5 monolayer (ML) is 41.5 kJ/mol (430 meV) more stable than that at 1.0 ML, and the precursor state at 0.5 ML is 58.9 kJ/mol (610 meV) more stable than that at 1.0 ML.[10] Thus, the precursor state does not exist as a stable state at 1.0 ML. This instability occurs due to the repulsive interaction between the adsorbed cyclopentene molecules. A similar situation is expected when vinyl bromide molecules are adsorbed on Si(100)c(4×2). When the coverage of vinyl bromide molecules increases, both the adsorption energy of the precursor state and the chemisorption state decrease by the repulsive interaction. As a result, the activation energy decreases, and the precursor molecules proceed to the di-σ chemisorption state.

Finally, we roughly estimate the activation energy from the precursor state to the chemisorption state at high coverage. At 79 K, the precursor almost disappears within 180 s; the reaction kinetics from the precursor state to the chemisorption state could not be followed by HREELS. Thus, we could estimate that the lower limit of the reaction rate at 79 K is 2.2 × 10^{-2} s^{-1}.[31] On the other hand, at 58 K, the reaction does not proceed at least for 30 min. Thus, we could estimate that the upper limit of the reaction rate at 58 K is 1.1 × 10^{-5} s^{-1}.[32] Assuming the same preexponential factor in the Arrhenius formula, the activation energy is limited to 20.1 < E_a < 22.4 kJ/mol. Therefore, the activation energy from the precursor state to the di-σ chemisorption state is about 6.0 kJ/mol (62 meV) smaller than that at low coverage owing to the steric repulsion.

4. Conclusion

The adsorption states of vinyl bromide on Si(100)c(4×2) were investigated by HREELS measurements. The weakly adsorbed precursor state is stable at 58 K. The di-σ chemisorption state is dominantly observed at 90 K, followed by the dissociation of the C−Br bond. As the precursor state, we propose a π complex species, where the molecule is most probably π bonded to the down dimer atom on Si(100)c(4×2). By measuring the time-dependent HREELS spectra at a constant temperature between 83 and 90 K, we have determined that the preexponential factor of the reaction from the precursor state to the chemisorption is 1.5 × 10^{13} s^{-1} and the activation energy for this reaction is 27.3 kJ/mol (283 meV). At higher coverage, the steric repulsion between adsorbed vinyl bromide molecules decreases the activation barrier from the precursor state to the chemisorption.

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(32) More than 98% of the adsorbed molecules are still in the precursor state 30 min after the exposure at 58 K. Hence, the reaction rate should be less than 1.1×10^{-5} s^{-1}.