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Dissociative adsorption and thermal desorption of dibromoethylene on Si(1 0 0)2×1: surface mediated dehalogenation and recombinative evolution of HBr

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Abstract

The room-temperature (RT) adsorption of dibromoethylene on Si(1 0 0)2×1 has been investigated by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) mass spectrometry. The C 1s and Br 3d XPS spectra indicate the presence of a mono-σ bonded vinyl bromide adspecies (30%) and a di-σ bonded vinylene adspecies (70%) on Si(1 0 0)2×1, which suggests dehalogenation of dibromoethylene producing one or both Br atoms upon RT adsorption. Annealing the sample to 645 K for 30 min completely removes the vinyl bromide adspecies, leaving behind the di-σ bonded vinylene. Recombinative desorption of HBr from the 2×1 surface has been observed over the temperature range 800–1000 K upon further annealing. The adsorption and desorption behaviour of dibromoethylene on Si(1 0 0)2×1 is found to be consistent with an insertion reaction mechanism, in marked contrast to the cycloaddition reaction mechanism observed for ethylene or acetylene on Si(1 0 0)2×1. The present work illustrates the surprisingly rich chemical activity of the 2×1 surface in facilitating dehalogenation of prototypical halogenated alkenes.

Keywords: Thermal desorption; X-ray photoelectron spectroscopy; Chemisorption; Halides; Silicon; Molecule–solid reactions

Cycloaddition reactions between unsaturated organic hydrocarbons and the Si(1 0 0)2×1 surface have been extensively studied by a variety of surface sensitive techniques and computational methods [1–5], due largely to their potential applications in microelectronics and organic sensors and to their fundamental importance in understanding organosilicon chemistry. As the simplest unsaturated hydrocarbons with a double and triple C–C bond respectively, ethylene and acetylene have attracted considerable attention and their di-σ bonding interactions with the dangling bonds of the Si dimer on Si(1 0 0)2×1 have been well characterized, with carbon atoms undergoing rehybridization from sp^2 to sp^3 and sp to sp^2, respectively [6,7]. In addition, halogen chemistry (of F, Cl, Br) on Si surfaces is of special interest to the semiconductor industry because halogen plasma etching is a critical processing step, on

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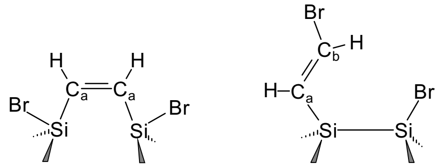
which the industry relies to assure the performance and reliability of Si-based electronic devices. Studies of adsorption and desorption of atomic and molecular chlorine on Si(1 0 0)2 × 1 and Si(1 1 1)-7 × 7 surfaces have revealed that different processes appear to greatly depend on the coverage [8–11]. In particular, Cheng et al. [12] and Koleske and Gates [13] reported that halogen extraction from Si(1 0 0) and Si(1 1 1) is driven by atomic hydrogen via different reaction pathways following the Eley-Rideal and hydrogen-transfer mechanisms, respectively. The combination of the simplest unsaturated hydrocarbon, such as ethylene, with halogens would provide an important family of haloethylenes with unique hybrid properties that are of fundamental and practical interests to silicon surface chemistry. Previous investigations have mainly focussed on metal-catalysed degradation of haloethylenes on low Miller index metal surfaces, including Cu(1 1 0) [14,15], Cu(1 0 0) [16], Pd(1 1 0) [17], and Pt(1 1 1) [18]. In particular, Yang et al. have shown that *cis*-dichloroethylene chemisorbs dissociatively on Cu(1 0 0) to atomic chlorine that remains on the surface up to 900 K and to acetylene that further trimerizes to benzene upon thermal desorption [16]. In contrast, the adsorption of chloroethylene on Pt(1 1 1) is found to follow reaction pathways that resemble that of ethylene on Pt(1 1 1) with the C–C bonds near-parallel to the surface, while the chlorine is observed to recombine with hydrogen to form HCl that leaves the surface near 460 K [16,18].

On single-crystal silicon surfaces with unique directional dangling bonds, the halogen atoms in halogenated ethylenes could open up new reaction pathways, in addition to the addition reactions of alkenes, for potential functionalization of the silicon surface in the development of molecular devices [19]. Recently, we have provided a comprehensive study on the RT adsorption and thermally induced chemistry of a family of chloroethylenes on Si(1 1 1)7 × 7 by using vibrational electron energy loss spectroscopy [20] and extended this investigation to Si(1 0 0)2 × 1 surfaces by X-ray photoelectron spectroscopy as a function of temperature [21]. These studies investigate the effects of molecular symmetry, halogen content, steric effects resulting from different geometry isomerism, etc. on the pertinent chemical processes. To date, there has been no XPS study reported for bromoethylenes on Si or metal surfaces. The present work therefore provides the first study on the thermal chemistry of dibromoethylene on Si(1 0 0)2 × 1 with the goal to identify the similarities or differences in the reaction mechanisms as a result of the change in the halogen atoms, particularly in view of the similarities in the average covalent bond length (bond energy) between C–Br at 1.94 Å (288 kJ/mol) and C–Cl at 1.77 Å (330 kJ/mol) [22].

All the experiments were performed in a home-built dual-chamber ultra-high vacuum system with a base pressure better than 1×10^{-10} Torr [23]. The sample preparation chamber was equipped with an ion-sputtering gun and a four-grid retarding-field optics for both reverse-view low energy electron diffraction (LEED) and Auger electron spectroscopy. The analysis chamber housed a differentially pumped 1–300 amu quadrupole mass spectrometer for TPD studies and an electron spectrometer (VG Scientific CLAM-2), consisting of a hemispherical analyser (100 mm mean radius) and a triple-channeltron detector, for XPS investigation with unmonochromatic Al Kα radiation (with a photon energy 1486.6 eV) from a twin-anode X-ray source. A 14×7 mm^2 substrate was cut from a single-side polished p-type boron-doped Si(1 0 0) wafer (0.4 mm thick) with a resistivity of 0.0080–0.0095 Ω cm. Details of the sample mounting and preparation procedures were described elsewhere [23]. Dibromoethylene (97% purity) was purchased from Aldrich and thoroughly degassed by repeated freeze–pump–thaw cycles, prior to exposure to the Si sample by backfilling the preparation chamber to an appropriate pressure (as monitored by an uncalibrated ionization gauge) with a variable precision leak valve. All exposures (in units of Langmuir, $1\ \text{L} = 1 \times 10^{-6}$ Torr s) were performed at RT and with a saturation coverage unless stated otherwise. A home-built programmable proportional–integral–differential temperature controller was used to provide linear temperature ramping at an adjustable heating rate, typically set at 2 K/s for the present TPD experiments [23]. XPS spectra were collected with an acceptance angle of ±4° at normal emission from the silicon substrate and with a constant pass energy of 50 eV giving an effective energy resolution of 1.4 eV full-width-at-half-maximum (for the Si 2p photopeak). The binding energy scale of the XPS spectra presented in the present work has been calibrated to the Si 2p feature of the bulk at 99.3 eV [24]. Spectral fitting and deconvolution based on residual minimization with the Gaussian–Lorentian peak shape was performed by using the CasaXPS software. For temperature-dependent XPS measurements, the sample was flash-annealed to the preselected temperature and allowed to cool to RT before collecting the XPS spectra.



(c) Vinylene (d) Vinyl Bromide

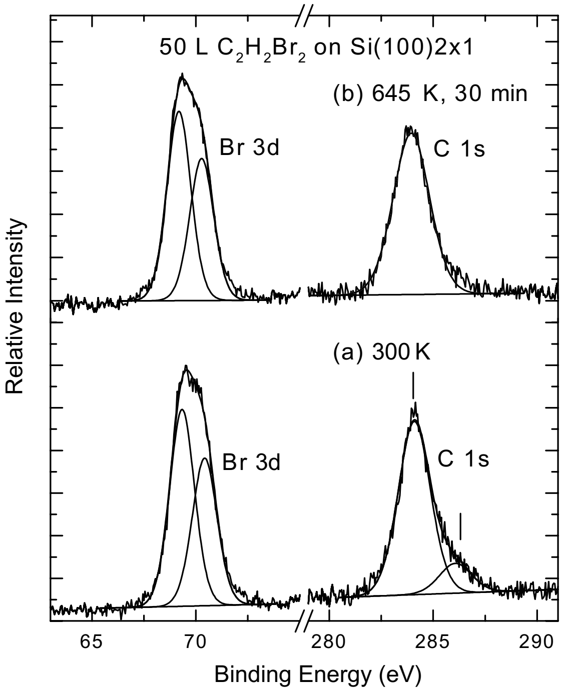


Fig. 1. XPS spectra of the Br 3d and C 1s regions of a 50 L RT exposure of dibromoethylene on Si(1 0 0)2×1 (a) at 300 K and (b) upon further annealing at 645 K for 30 min. Schematic diagrams of the local surface bonding arrangements for (c) the di-σ bonded vinylene adspecies and (d) the mono-σ bonded vinyl bromide adspecies.

Fig. 1 shows the XPS spectra of the Br 3d and C 1s regions of 50 L of dibromoethylene adsorbed on Si(1 0 0)2×1 at RT and upon annealing to 645 K for 30 min. No significant change in the intensity ratio of the C 1s to Si 2p photopeaks has been found for exposure above 10 L, suggesting that a saturation coverage has been reached for the 50 L exposure. The C 1s feature is fitted to two Gaussian lineshapes centered at 284.0 and 286.0 eV (Fig. 1a), which are found to be at the same locations with similar relative intensities as those for dichloroethylene adsorbed on Si(1 0 0)2×1 at RT (not shown) [21]. The similarities in these C 1s spectra suggest that a similar C backbone for the adsorption structures of both dibromoethylene and dichloroethylene on Si(1 0 0)2×1. Using synchrotron-radiation XPS at 391 eV photon energy, Fink et al. also observed two well-resolved C 1s peaks at the same binding energies for 1,2-dichloroethylene adsorbed on Si(1 0 0)2×1 at 80–100 K followed by annealing to 150–200 K [25], but with reverse relative intensities for the two peaks. In spite of the attempt to remove multilayer adsorption by annealing the sample to 150–200 K before XPS measurement, we believe that the stronger intensity found for the peak at 286.0 eV by Fink et al. could be due to physisorption [25]. On the other hand, we hypothesize that the C 1s peaks observed at 284.0 and 286.0 eV correspond to different C local environments with and without direct bonding to a Si surface atom, respectively. In particular, Fig. 1c shows a di-σ bonded vinylene structure with total dehalogenation (with the insertion of two Si surface atoms into the C–Br bonds) giving rise to one type of C local environment (C_a), while Fig. 1d depicts a mono-σ bonded vinyl bromide structure with a single Si surface atom insertion and two different C types (C_a and C_b). The proposed bonding model is similar to that reported for acetylene on Si(1 0 0)2×1 by Taylor et al. [3]. Assuming that the C_a 1s photopeak at 284.0 eV and the C_b 1s feature at 286.0 eV have similar ionization cross sections and that geometric effects with respect to detection are unimportant, we estimate that the relative moiety of the vinylene adspecies (70%) is considerably higher than that of the vinyl bromide adspecies (30%). Upon holding the sample at 645 K for 30 min, the C_b 1s photopeak has evidently been removed (Fig. 1b) while the overall intensity of the C 1s envelope has only been slightly reduced (by 13%). The reduction in the C_b 1s intensity could be attributed to either thermal desorption of the vinyl bromide adspecies or conversion of vinyl bromide to vinylene adspecies. The latter conversion process from a mono-σ bonded structure to a di-σ bonded structure has also been reported for 3-pyrroline adsorbed on Si(1 0 0)2×1 by Liu and Hamers [27]. Evidently, the thermal desorption behaviour of C 1s peak is consistent with the higher stability of the di-σ bonded vinylene adspecies relative to the mono-σ bonded vinyl bromide adspecies, which is also in general accord with the stability of the di-σ bonded structure of acetylene [3].

It should be noted that the LEED pattern remained essentially unchanged from the sharp 2×1 reconstruction (of the clean Si(1 0 0) surface) upon exposure of 50 L of dibromoethylene, which suggests that the adsorption does not affect the dimer row of the 2×1 surface in accord with the proposed adsorption structures (Fig. 1c and d).

To verify our proposed assignment of the C 1s features, we have independently re-measured the XPS spectrum for a saturation coverage of ethylene on Si(1 0 0)2×1 at RT using our aforementioned experimental setup. The corresponding C 1s region reveals a single feature centered at 284.3 eV (not shown), which is characteristic of the di-σ bonded 1,2-ethanediyl adspecies with sp^3 hybridization for the C atoms. Evidently, the C 1s binding energy for vinylene (284.0 eV) shown in Fig. 1 is found to be lower than that for the 1,2-ethanediyl adspecies (284.3 eV) (for ethylene adsorption), which is also in good agreement with that found for acetylene and ethylene adsorption as reported by Fink et al. [25]. The small energy difference of 0.3 eV can be attributed to the difference in the C hybridization between sp^2 (vinylene) and sp^3 (1,2-ethanediyl adspecies). In contrast, the C 1s binding energy for sp^2-hybridized hydrocarbons (such as ethylene) is higher than that for sp^3-hybridized hydrocarbons (such as ethane) in the gas phase [26], in which the type of C hybridization is not as important for the core-level binding energy shift as the electronegativity of the attaching ligands [26]. Apparently, hybridization plays a more prominent role for the C 1s binding energy shift for adsorbed species directly bonded with the surface atoms. It should be noted that Liu and Hamers reported almost the same C 1s binding energy for acetylene (284.1 eV) and ethylene (284.0 eV) adsorption on Si(1 0 0)2×1 with reference to the Si $2p_{3/2}$ peak at 99.4 eV [27], in disagreement with the data of Fink et al. [25] and the present result.

Fig. 1 also shows that there is only one broad feature corresponding to the Br $3d_{5/2}$ and $3d_{3/2}$ photopeaks at 69.2 and 70.3 eV respectively, which indicates no discernible chemical shift arising from the C–Br or Si–Br bond in general accord with the stronger electronegativity of the Br atom (2.8) than that of the C (2.5) or Si atoms (1.8) [28]. The adsorption of Br can be inferred by comparison with our earlier study on ethylene adsorption on Si(1 0 0)2×1. In particular, the present work shows that the corresponding dibromoethylene adsorption gives a similar C 1s to Si 2p intensity ratio, indicating that the saturation moiety of dibromoethylene is also similar to that of ethylene (i.e., one molecule per Si dimer) [29]. Given that there is no vacant dimer site remaining upon formation of the vinylene adspecies, the dissociated Br atoms could only occupy the back dangling bond sites of the Si dimer, as indicated in Fig. 1c. The Si atoms of the dimer could therefore be considered as undergoing an insertion reaction into the C–Br bonds to effect dehalogenation, upon the adsorption of dibromoethylene. It should be noted that a saturation exposure of dibromoethylene to a Si(1 0 0) surface terminated with H or O does not produce any adsorption (not shown), which further supports the aforementioned bonding picture that Si dangling bonds are required. Furthermore, the Br 3d feature does not appear to be greatly affected by annealing to 645 K for 30 min (Fig. 1b) and only minor reduction in its intensity relative to Si 2p is observed. In accord with our proposed bonding model, the mono-σ bonded vinyl bromide adspecies would have undergone desorption at 645 K, reducing the C 1s to Br 3d intensity in a 2:1 proportion. The discernibly less proportional reduction observed in the overall C 1s intensity suggests that conversion from the mono-σ bonded vinyl bromide adspecies to di-σ bonded vinylene adspecies cannot be ruled out.

In order to investigate the desorption process in greater detail, XPS spectra of Br 3d and C 1s regions were collected at RT after sequentially flash-annealing the sample up to a preselected temperature as shown in Fig. 2. In contrast to the earlier result shown in Fig. 1, no detectable change in the C 1s region is observed over the 300–620 K region (Fig. 2b and c). The lack of any intensity reduction in the C_b 1s feature (at 286.0 eV) in the present flash-anneal experiment suggests that desorption of vinyl bromide is a slow process. (This observation is in marked contrast to the small reduction in the C_b 1s intensity found after the prolonged annealing at 645 K, as shown in Fig. 1.) Between 620 and 800 K, a 20% reduction is found in the overall C 1s intensity (Fig. 2c), which is indicative of plausible desorption of vinyl related species. Further flash-annealing to 1230 K does not significantly reduce the overall peak intensity (Fig. 2c) but discernible changes to the peak location are observed (Fig. 2b). In particular, the C_a 1s peak maximum originally located at 284.0 eV (with predominant contribution from vinylene, Fig. 1c) appears to shift to 283.0 eV, which is characteristic of SiC [30], while the weaker C_b 1s shoulder at 286.0 eV (predominantly attributed to vinyl bromide) has now relocated to 284.5 eV, which could be assigned to carbon clusters (Fig. 2b) [31]. These changes are therefore consistent with thermal cracking of the vinylene adspecies and the production of silicon carbides and carbon clusters above 800 K [32]. In addition, unlike the C 1s feature, significant intensity reduction is not observed for the Br 3d feature until the flash-annealing temperature exceeds 800 K as shown in Fig. 2c. Between 800 and 1000 K, the Br 3d peak is found to diminish in intensity by almost 85% and is completely removed above 1200 K, suggesting the total removal of Br-containing adspecies.

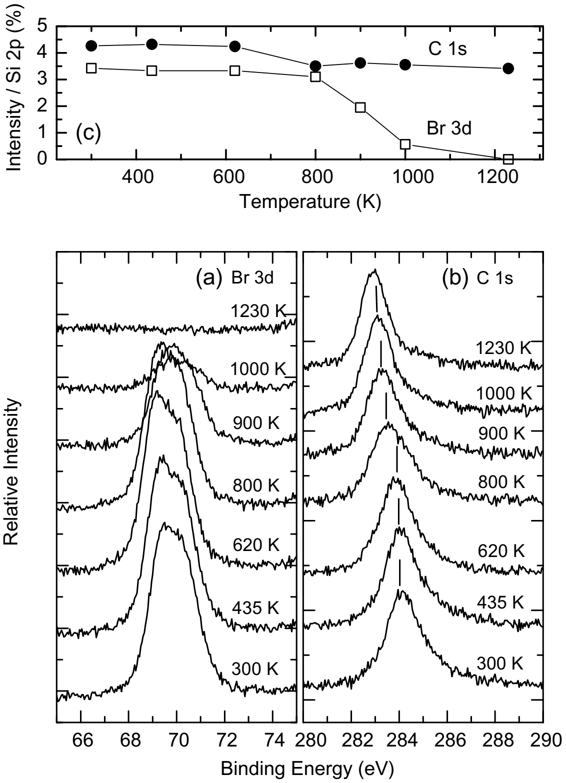


Fig. 2. XPS spectra of (a) the Br 3d and (b) C 1s regions of a 50 L RT exposure of dibromoethylene on Si(1 0 0)2×1 as a function of flash-annealing temperature. The overall intensities of the Br 3d and C 1s XPS features relative to the Si 2p peak intensity as a function of temperature is shown in (c).

Fig. 3 shows the TPD profiles of m/z 80, 28, 26, and 2, corresponding to the parent ions of HBr, C_2H_4, C_2H_2 and H_2 respectively, for a 50 L exposure of dibromoethylene on Si(1 0 0)2×1 at RT. Evidently, the 20% reduction in intensity for the C 1s feature at 284.0 eV observed at 800 K (shown in Fig. 2) is in good accord with the strong desorption peak of m/z 26 at 770 K (Fig. 3c), which indicates the desorption of acetylene arising from vinylene or dehalogenated vinyl bromide adspecies. The desorption temperature for m/z 26 (770 K) is also found to be in agreement with that for acetylene desorption (750 K) reported by Taylor et al. [3]. The weaker TPD feature of m/z 26 at 630 K (and 580 K) (Fig. 3c) is found to occur at the same temperature as the corresponding TPD feature of m/z 28 (Fig. 3b), which suggests a common desorption species. In particular, the m/z 28 TPD features could be attributed to the removal of ethylene likely produced by hydrogenation following a hydrogen exchange reaction with Br in the vinyl bromide adspecies. Given that m/z 28 is one of the most commonly found fragments in any ultra-high vacuum chamber, we cannot rule out the possibility of minor contributions of

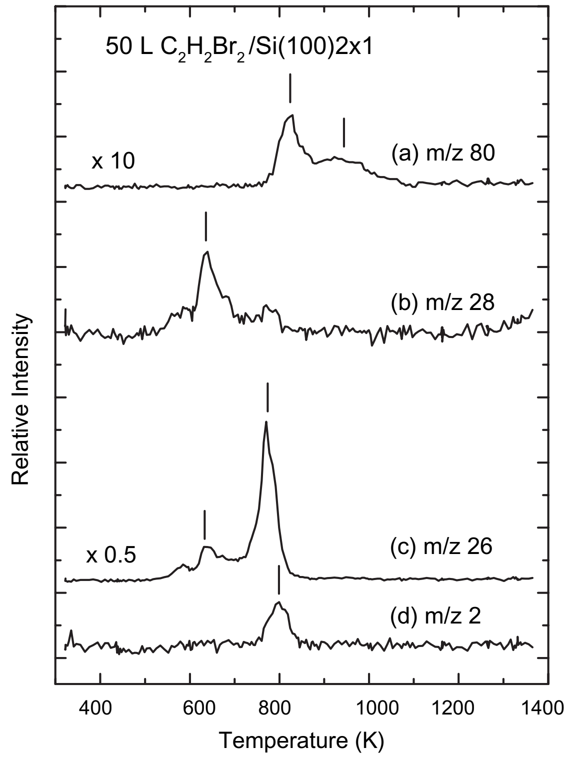


Fig. 3. Temperature programmed desorption profiles of (a) m/z 80, (b) m/z 28, (c) m/z 26, and (d) m/z 2 for a 50 L RT exposure of dibromoethylene on Si(1 0 0)2×1.

hydrocarbon species from the sample environment (e.g. manipulator) during the TPD experiment. The TPD maximum of m/z 2 at 800 K (Fig. 3d) is found to be in good accord with recombinative desorption of H_2 arising from silicon monohydride [32].

The present work also shows for the first time recombinative desorption of HBr via two possible reaction pathways as indicated by the m/z 80 TPD features at 830 K and 950 K (Fig. 3a). In particular, given the similarity of its desorption maximum to that of the m/z 2 TPD feature at 800 K (Fig. 3d), we propose that the m/z 80 TPD feature at 830 K (Fig. 3a) could correspond to recombinative desorption of the Br atoms (dissociated upon dibromoethylene adsorption, Fig. 1a and b) with the surface H atoms. The H atoms on the surface could be due to dissociative adsorption of resident water in the UHV chamber on the Si sample [33] during the sample preparation stage. The weaker m/z 80 TPD feature at 950 K (Fig. 3a) could then be attributed to recombinative desorption of dissociated Br atoms with H atoms dissociated from the hydrocarbon adspecies (vinylene).

The evolution of HBr is found to occur in the same temperature range (800–1000 K) as that for $SiBr_x$ ($x = 1$–4) found in the Si etching process [34], indicating both of these desorption pathways (i.e. HBr evolution and $SiBr_x$ desorption) are thermodynamically viable in this temperature range. However, since no etching products such as $SiBr_x$ is observed in the present work, recombinative desorption of HBr is evidently favoured kinetically likely due to a lower activation barrier. In addition, the mechanism for HBr evolution is different than those reported for atomic H extraction of Br-terminated Si(1 0 0) and Si(1 1 1) surfaces [12,13]. In particular, Cheng et al. proposed an Eley-Rideal mechanism in which a gaseous H atom recombines with an adsorbed Br atom on Si(1 0 0) to form the desorbed HBr [12], while on the Si(1 1 1) surface a more-complex hydrogen-transfer mechanism for HBr evolution has been proposed by Koleske and Gates [13]. In the present case, since both H and Br atoms are available on the surface upon dibromoethylene adsorption, we believe that the Langmuir–Hinshelwood mechanism (i.e., following second-order kinetics) is more consistent with our present data.

In summary, the present work illustrates the general similarity in the RT chemisorption and thermal chemistry involving dibrominated and dichlorinated ethylenes on Si(1 0 0)2×1. Both di-σ bonded vinylene and mono-σ bonded vinyl bromide adspecies are observed upon dehalogenated adsorption on the 2×1 surface at RT, with the Si dimers likely undergoing insertion reactions. The weakly bonded vinyl bromide adspecies is found to desorb upon prolonged annealing at 645 K while further annealing of the more strongly bonded vinylene adspecies leads to the desorption of acetylene at 770 K and the formation of silicon carbide above 800 K. Furthermore, recombinative desorption of the dissociated Br atoms with resident surface H atoms and with H atoms dissociated from vinylene or other cracked hydrocarbon adspecies has also been observed. The present work therefore provides the first experimental evidence for the thermal evolution of HBr on Si(1 0 0)2×1. Like dichloroethylenes [21], no surface etching product is found for dibromoethylenes on the Si(1 0 0)2×1 surface.

Acknowledgements

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