Electronic and geometric structure of methyl oxirane adsorbed on Si(1 0 0)2 × 1

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Available online 12 July 2007

Abstract

Electronic and geometric properties of the adsorbate–substrate complex formed upon adsorption of methyl oxirane on Si(1 0 0)2 × 1 at room temperature is reported, obtained with synchrotron radiation-induced valence and core-level photoemission. A ring-opening reaction is demonstrated to occur, followed by a five-membered ring formation involving two of the Si surface atoms bound to a surface dimer. Core-level photoemission spectra support the ring-opening reaction and the Si–O and Si–C bond formation, while from the valence spectra a more extended molecular fragmentation can be ruled out. We discuss the most likely geometry of the five-membered ring.

PACS : 79.60.−i; 79.60.Dp; 78.70.Dm

Keywords: Adsorption; Electronic structure; Geometrical structure; Semiconductors

1. Introduction

In the last two decades, since the blooming of the semiconductor industry and microelectronic techniques, the Si(1 0 0)2 × 1 surface has been intensively studied as one of the most technologically important surfaces [1]. In the framework of devising sensors for bio-, organic and inorganic molecules, and as a new kind of support for molecular reactions [2,3], the study of physical and chemical adsorption processes of single molecules on Si(1 0 0)2 × 1 is of utmost importance.

Furthermore, the interaction between organic molecules and silicon surfaces has drawn increasing attention, since current technology demands smaller and smaller functioning units, and their manufacturing in microelectronics involves many steps in which such interaction is important [4,5]. In addition, researchers have developed reaction pathways between organic molecules and Si to synthesize SiC or diamond films. To further improve a fine control on the molecular level, a more fundamental investigation of molecular adsorption phenomena on semiconductor surfaces is needed.

Following the surface reconstruction, the highly reactive asymmetric Si dimers characterize the surface. All surface physics and chemistry processes are related with the dangling bonds of the Si dimers. The physical and chemical adsorption of various organic molecules containing the N atom, CN, C=O, C–OH, C–C radicals and aromatic groups on Si(1 0 0)2 × 1 was studied intensively and the [2 + 2], [4 + 2] cycloaddition reaction between the dimers and molecules are investigated by many works [2,6–10]. Other functional groups such as alcohol (–OH), amine (–NH_2), and halide also provide potential sites for bonding to the Si substrate [11]. A recently reported experiment on adsorption of 2,3-butandiols on Si(1 0 0) has evidenced an adsorption reaction where two –OH groups of 2,3-butanediol bond to each Si dimer atom to make a stable six-membered ring-shape structure as a consequence of O–H bond cleavage [12].

Epoxy chemicals, especially the ethylene oxide and methyl oxirane (propylene oxide), are also very important species for chiral chemical industry, drug production, polymer industry

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and semiconductor industry, in particular in what concerns functionalization and deposition of dielectric thin film. Although few studies have been reported for the chemical behavior of some epoxy molecules on the Si(1 0 0)2 × 1 surface [13], the reaction mechanism of the epoxy group with the Si dimers is still not clearly understood.

Methyl oxirane, (CH_3–$CHOCH_2$), has recently received a new surge of attention in the literature due to its chiral nature, and to the possibility of observing chiral effects by means of synchrotron radiation-related techniques, also in connection with the availability of circularly polarized light at some synchrotron radiation facilities. We have already reported about chiral effects shown by another chiral molecule, 2,3 butandiol, on Si(1 0 0) [12,14] and studies on methyl oxirane on Si(1 0 0) with circularly polarized light are currently under way in our research groups [15].

In the present work, to gather information on the chemical adsorption of methyl oxirane on the Si(1 0 0) surface, we have investigated this system with synchrotron radiation-induced valence and core photoemission, using linearly polarized light, therefore the focus is on electronic and geometrical structure results rather than on chiral properties.

The core-level spectra are informative of the chemical reaction taking place between the epoxy ring and the more reactive sites on the Si surface, namely the dangling bond-bearing Si atoms of the dimer units. By comparison with the C 1s spectra of the isolated methyl oxirane molecule, we can deduce that, while in the free species two of the three unequivalent carbon atoms are bound to the oxygen atom, in the adsorbed species only one C–O bond remains. The analysis of the Si 2p core lines indicates the bonding of the open chain fragment to the Si surface, since we can notice upon adsorption the disappearance of the spectral features related to the dimer atoms and the appearance of new features consistent with Si–O and Si–C bond formation. We can conclude that the most likely bonding situation implies the formation of a five-membered C–O–Si–Si–C ring.

From photoemission data only, it is not immediate to assess which carbon atom is actually bound to the surface (the methylene, CH_2, or the methine, CH, one). We speculate that the most likely surface reaction implies the breaking of the molecular O–CH_2 (methylene C) bond and the formation of a five-membered ring with a CH_2–Si surface bond, on the ground of preliminary near edge X-ray absorption spectroscopy (NEXAFS) measurements and theoretical calculations. Further experimental and theoretical work is in progress to support this hypothesis.

2. Experimental

Experiments were performed on beamline I511 [16], MAX-lab, Lund, Sweden, which is equipped with a UHV system for electron spectroscopy and X-ray emission studies of surfaces and surface-adsorbate system. The base vacuum of both the preparation chamber and the analysis chamber is in the low 10^{-10} ∼ high 10^{-11} Torr range. The photoelectron kinetic energy is detected by a Scienta R4000 dispersive-type of analyzer which is positioned at 45° with respect to the E vector of the synchrotron beam.

(*R*)-(+)-methyl oxirane was deposited on single-domain Si(1 0 0)2 × 1 surfaces at room temperature. We had one of the two possible enantiomers available, although under our experimental conditions (namely the use of linearly polarized light) it is not possible to distinguish between the two chiral isomers. Exposures were in the 1 0 Langmuir range to ensure saturation coverage. The p-type single-domain Si surfaces obtained by a 5° miscut were installed on a sample holder with a 7° grazing incidence angle with respect to the light beam. The width of the two-atom-high terrace of the Si(1 0 0)2 × 1 surface is about 8.5 dimers [17]. Orientation of the Si dimers was checked by LEED. The (*R*)-(+)-methyl oxirane was bought from Fluka with purity better than 99.0% and it was cleaned with repeated freeze-thaw-pump cycles.

The C 1s and Si 2p core level and valence level photoemission spectra were obtained at different electron emission angles (45° and normal emission). NEXAFS spectra around the C K-edge were measured for different angles (0°, ca. 45° and ca. 90°) between the E vector and the surface plane. With the sample holder above described it is possible to measure NEXAFS spectra with the E vector at exactly 0° with respect to the surface plane, and also we use two different sample mountings rotated by 90° with respect to each other to allow in-plane measurements with the E vector parallel or perpendicular to the surface dimers. However, with the light beam at fixed grazing incidence on the sample it is not possible to measure NEXAFS spectra with the E vector at exactly 90° with respect to the surface, therefore our measurements at 90° and 45° are to be intended as "minus the grazing incidence angle" which is 7°. We choose to take the spectra in intermediate position by moving by 45° with respect to the grazing incidence position, to emphasize the difference with the spectra taken at ca. 90°. We consider the difference irrelevant, also taking into account the fact that the light polarization is not exactly 100%. The beam damage was ruled out by recording core-level spectra before and after the NEXAFS measurement.

3. Result and discussion

In Fig. 1 we show the C 1s photoelectron spectrum for methyl oxirane on Si(1 0 0) obtained at a photon energy of 350 eV and at normal emission. We have performed measurements also an emission angle of 45°, with changes not significant for the present discussion. A C 1s photoelectron spectrum of free methyl oxirane obtained at a photon energy of 340 eV is reported for sake of comparison [18], and the binding energy scale is aligned to the gas-phase value. We notice that there are three peaks related to the three carbon atoms in different chemical environments in both cases. However, for the free molecule there is one peak at lower binding energy, clearly related to the carbon atom of the methyl group, and two close peaks at higher binding energy assigned to the carbon of the CH_2 moiety (methylene carbon) and to the carbon bound to one H atom and to the methyl group (methine carbon). In the present case, there is only one peak at higher binding energy

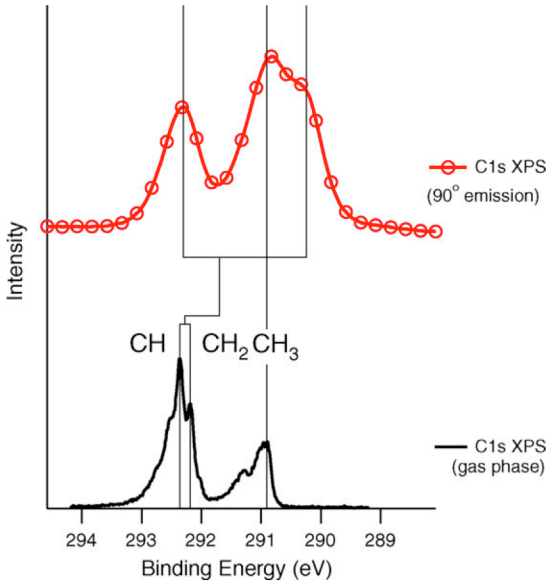

Fig. 1. Top curve: C 1s core-level photoemission spectrum of methyl oxirane on Si(1 0 0)2 × 1 recorded at a photon energy of 350 eV and in normal emission. Bottom curve: gas-phase spectrum obtained at 340 eV photon energy [18]. The spectral assignment for the free molecule in order of increasing binding energy is the following: C 1s emission from carbon of the methyl group, carbon of the methine group, carbon of the methylene group, respectively.

and two overlapping peaks at lower binding energy. This is a clear indication of a ring-opening reaction, since it is explained by the fact that on the Si surface only one carbon atom keeps the bond to the oxygen atom.

In Fig. 2 we report the Si 2p core-level spectra, obtained at a photon energy of 150 eV. We measured Si 2p spectra at two emission angles (normal emission and 45°), with no significant difference, so in the figure we show the data at 45°. For the clean surface, we show a deconvolution in the various surface and bulk components analogous to the literature one [19], while for the adsorbate-covered surface we have obtained a deconvolution which clearly shows new features appearing and some surface features disappearing. In particular, upon adsorption of a saturating amount, the low-binding energy feature, known to be related to the up Si atom in the dimer [19], disappears completely on the right side. Instead, a new component replaces it at the high-binding energy region. Since the energy shift for the new high-binding energy component is consistent with the expectation of a Si bonded to an O atom [20], this is readily assigned to such a bond. Furthermore, another new component is evident in the region of the second layer atoms, which can be related to Si–C bond formation [21]. Therefore, by combining the C 1s and Si 2p results, we conclude that the most likely occurrence is that the ring opens, the oxygen atom and one of the carbon atoms bond to the dangling-bonds of the Si atoms of a surface dimer, and thus a Si–Si–O–C–C five-membered ring is formed.

The valence spectra of the clean and adsorbate-covered surface are reported in Fig. 3. Again we have performed measurements at normal emission and 45°, with no significant changes, therefore we show the results at 45° and a photon energy of 63 eV. We show also a valence spectrum of the free molecule obtained at a photon energy of 60 eV for sake of comparison [18]. The molecular nature of the adsorbate is clearly revealed. Clean Si(1 0 0) (top curve) shows the known features related surface and bulk states [22]. The adsorption of methyl oxirane causes a remarkable change where the whole range of the spectrum exhibits peaks due to molecular orbital-related transitions. We can clearly see the disappearance of spectral features related to the surface states and the appearance of quite intense spectral features related to the adsorbate. In particular, in the binding energy region 15–25 eV three intense well-separate peaks are observed which can be related to similar features in the free molecule valence spectrum [18], therefore hinting for the adsorbate not undergoing further fragmentation beside the ring-opening reaction described above.

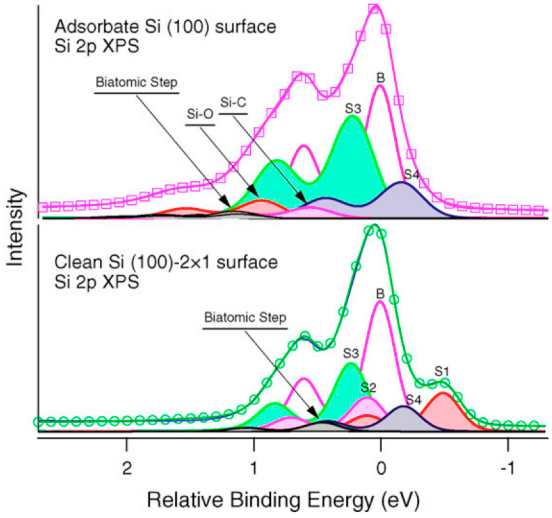

Fig. 2. Si 2p core-level spectra of clean and methyl oxirane-covered on Si(1 0 0)2 × 1 recorded at a photon energy of 150 eV and 45° emission. From top: deconvolution of the spectrum of the adsorbate-covered surface in components related to the atoms of the surface reconstruction with different environments, same for the clean surface [19], raw data.

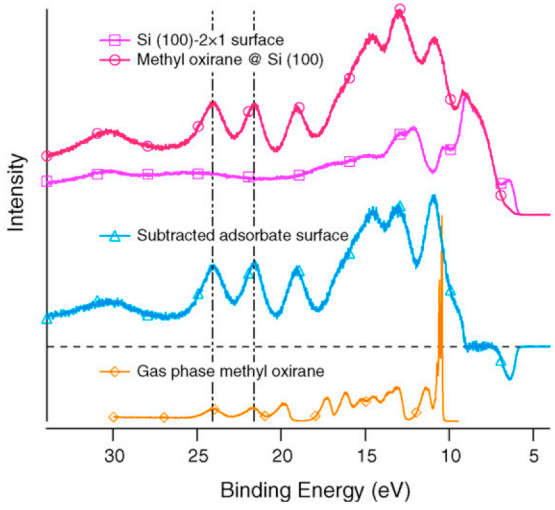

Fig. 3. Valence spectra of clean and adsorbate-covered Si(1 0 0)2 × 1 recorded at a photon energy of 63 eV and 45° emission. From top: adsorbate-covered surface, clean surface, difference spectrum, gas-phase at 60 eV photon energy [18].

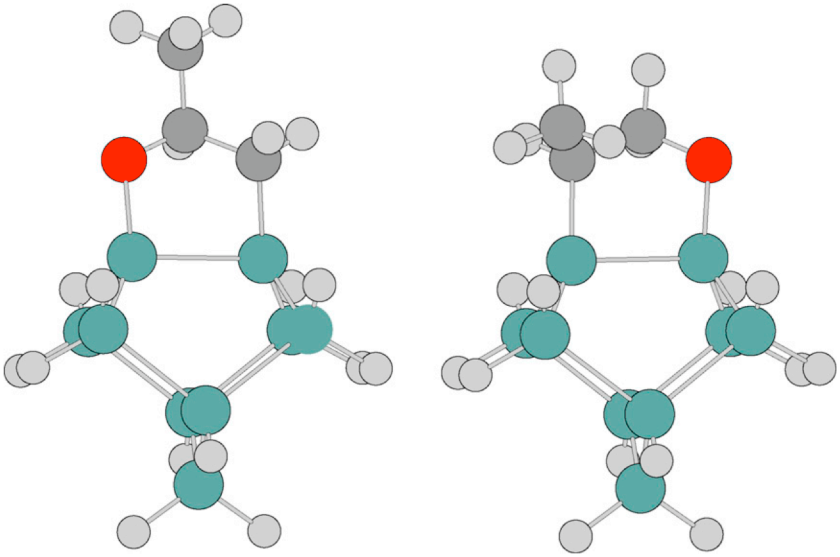

Fig. 4. A sketch of the two five-membered rings which can be formed as a consequence of the ring-opening reaction and the formation of bonds between the open molecular chain and the dangling bonds of the Si dimer atoms. The difference resides on which of the C–O bonds is broken during the surface reaction.

It is a bit more speculative to assess which one of the C–O bonds is broken. Although the three-membered ring-opening/five-membered ring formation reaction is clearly documented in the photoemission results, we have no direct evidence on which one of the C–O bonds in the epoxy ring is broken to permit the subsequent cycloaddition reaction. A sketch of the two different five-membered rings corresponding to the O–CH_2, respectively O–CH–CH_3 bond breaking is reported in Fig. 4. The geometries have been optimized by AM1. Preliminary calculations by DFT with basis B3LYP/6-31G have been performed, which will be reported in detail elsewhere [23], and which do not show important differences in term of geometry and electron distribution compared to the AM1 results.

In a recently published paper, DFT calculations have been performed for the systems methyl oxirane-X(1 0 0) (X = C,S,Ge). [24]. The two possible five-membered rings corresponding to the breaking of either one of the C–O bonds (see Fig. 4) have been compared, and it has been concluded that the ring-opening reaction implying the breaking of the O–CH bond is more probable, in terms of potential barrier, although the energy difference between the two pathways is very small, and actually the ring formed after the O–CH_2 bond breaking is more stable.

We can tentatively verify this hypothesis with some preliminary NEXAFS data. A full experimental and theoretical NEXAFS analysis will be reported elsewhere [23]. In Fig. 5 we show the NEXAFS spectra around the C K-edge for the adsorbate-covered surface. Due to the peculiar geometry of the Si(1 0 0)2 × 1 reconstruction, we have obtained NEXAFS data on two sets of samples, one mounted with the dimers parallel to the E vector when in-plane, and the other one with the dimers perpendicular to the in-plane E vector. This mounting has been used in previous works [25], and allows us to distinguish subtle details on the molecular

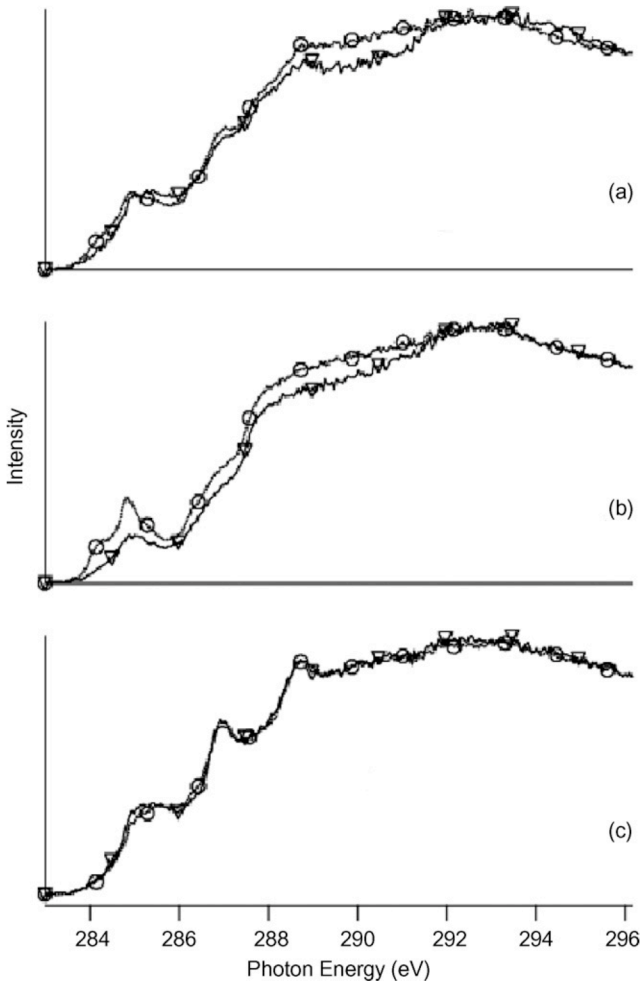

Fig. 5. NEXAFS spectra around the C K-edge. The (a–c) labels refer to angles between the E vector and the surface plane of 0°, 45° and 90°, respectively. For each angle two spectra are shown, corresponding to the different orientation of the dimers (see text).

orientation for the states which lie parallel to the surface plane, but can have different orientations with respect to the dimers. Therefore, in Fig. 5 we show the two sets of data at 0°, 45° and 90° angles between the E vector and the surface plane for the two different sample mountings (see Section 2 for a more detailed description of the experimental geometry).

We have obtained preliminary calculations on the nature and charge distribution of the empty states of this system. According to those, the LUMO is mainly localized on the O–C–C part of the five-membered ring, and the spectral features at higher photon energies correspond to excitation to empty states with mainly C–Si antibonding character and CH–CH_3 antibonding character. Looking at the angular dependence of the NEXAFS features around 287 and 289 eV, which are related to the latter higher-lying empty states, and not to the LUMO, we can observe that their angular distribution is typical of molecular orbitals lying perpendicular or almost perpendicular to the surface. According to the above assignment, this finding hints to the formation of a five-membered ring where the orientation of the C–Si bond and of the CH–CH_3 bond are perpendicular to the surface, in turn supporting the hypothesis of the O–CH_2 bond being actually broken during the surface reaction (see Fig. 4).

On the ground of the above-mentioned considerations, we favor the O–CH_2 bond-breaking pathway, although the other alternative is also consistent with the photoemission results alone. Furthermore, we cannot rule out the simultaneous presence of both species. Further NEXAFS experimental and theoretical analysis is in progress to confirm this preliminary assessment on the geometry of the adsorbate–substrate complex.

4. Conclusion

We have obtained C 1s and Si 2p core-level and valence-level photoemission results for the methyl oxirane-Si(1 0 0)2 × 1 substrate–adsorbate complex at room temperature and saturation coverage. From the C 1s spectra, we gain evidence of the occurrence of a ring-opening reaction. From the Si 2p spectra, we deduce the existence of Si–O and Si–C bond formation. From the valence spectra, we observe that the molecular chain does not undergo further fragmentation after the ring-opening step. The geometry of the resulting surface species cannot be directly assessed by photoemission data, but on the ground of preliminary NEXAFS results we favor a five-membered Si–Si–O–C–C ring with the CH_2 group bonded to a surface Si atom and the CH_3 group perpendicular to the surface plane.

Acknowledgment

The valuable support of MAX-lab staff during measurements is gratefully acknowledged.

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