Adsorption and thermal decomposition of H_2S on Si(1 0 0)

Ying-Huang Lai [a], Chuin-Tih Yeh [a], Yi-Hsin Lin [b], Wei-Hsiu Hung [b,*]

[a] *Department of Chemistry, National Tsing-Hua University, Hsin-Chu 300, Taiwan*
[b] *Synchrotron Radiation Research Center, Hsin-Chu Science-Based Industrial Park, No. 1, R&D Road VI, Hsin-Chu 30077, Taiwan*

Abstract

Adsorption and thermal decomposition of H_2S on Si(1 0 0)-2 × 1 are studied by means of temperature-programmed desorption (TPD) and X-ray photoemission spectroscopy (XPS) with synchrotron radiation. The H_2S molecule dissociates to form H and HS on the Si surface at adsorption temperature of 115 K. The Si(1 0 0)-2 × 1 surface structure is conserved upon the adsorption of H_2S due to bonding of dissociative H and HS on two Si atoms in a dimer without breaking the Si–Si dimer bond. H_2 and SiS are the only desorption products of thermal decomposition of H_2S with peaks at 780 and 820 K, respectively. On the basis of TPD and XPS results, intermediates involved in decomposition of H_2S and their adsorption configurations are proposed and discussed.
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1. Introduction

Investigation of deposition of sulfur on silicon surfaces is of fundamental importance in chemistry and physics as well as in contexts of doping, passivation and heteroepitaxial growth of group II sulfides [1–4]. As a gaseous source of sulfur, H_2S undergoes thermal decomposition on a Si surface, which produces surface Si hydrides and sulfides [5]. The bonding configuration and the composition upon adsorption of H_2S on Si greatly affect the subsequent chemical reaction of film growth and fabrication, and influence properties of thin films and resulting interfaces. Thus, improved under-standing of adsorption and decomposition of H_2S on the Si surface can provide insight into limitations and merits of H_2S as a source of sulfur for film growth and surface passivation.

According to ultraviolet photoelectron spectroscopy (UPS), initial adsorption of H_2S is dissociative to form surface SH and H species on Si(1 0 0) at 150 K [6]. Previous work of D_2S on Si(1 0 0) with a scanning tunneling microscopy (STM) indicated that the dissociative DS moiety bridged two Si atoms between two dimer rows and the D atom bonded to a Si atom of the neighboring dimer [7]. Saturation of available adsorption sites was accordingly attained at a coverage of 1/3 monolayer (ML) DS and D. Other work by STM showed that adsorption of H_2S on a Si surface was site-selective and temperature-dependent because adsorption was affected by surface reconstruction and thermally activated dissociation

* Corresponding author. Tel.: +886-3-578-0281; fax: +886-3-578-9016/9816.
E-mail address: whung@srrc.gov.tw (W.-H. Hung).

[8]. A theoretical calculation with modified neglect of differential overlap (MNDO) indicated bridged S and on-top H (mono- and di-hydrides) to be the most energetically favored products on dissociative adsorption of H_2S on Si(1 0 0) [9]. Using Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) measurements, Han et al. [10] proposed the reaction intermediates and their adsorption geometries following adsorption and thermal decomposition of H_2S on Si(1 0 0). Their results showed that H_2 was the only desorption product during thermal decomposition of H_2S. As hydrogen desorbed, the AES peak of surface sulfur disappeared at ∼600 °C, attributed to sulfur diffusion into the Si bulk.

Surface sulfur could be deposited after thermal decomposition of H_2S on a Si surface, of interest specifically for passivating a Si surface [11]. However, volatile Si_nS_m molecules are expected to desorb at elevated temperatures because the S–Si bond is stronger than the Si–Si bond [1]. According to TPD measurement, SiS desorbed from a Si surface covered with sulfur [2]. On the basis of STM, desorption of silicon sulfide from the Si surface caused creation of surface vacancies, as observed on oxygen-induced etching of the silicon surface [12,13]. To explain the disappearance of surface sulfur at elevated temperatures, diffusion of surface sulfur into the Si bulk was proposed, instead of desorbing from the surface [10,14].

We investigated adsorption of H_2S on Si(1 0 0) and its subsequent thermal reaction. We characterized the surface composition and monitored the desorption products with TPD and synchrotron radiation X-ray photoemission spectroscopy (XPS), from which we accordingly propose the configuration of adsorption and the mechanism of decomposition of H_2S on Si(1 0 0).

2. Experimental

Experiments were performed in a UHV chamber equipped with a quadrupole mass spectrometer, LEED, and a hemispherical electron-energy analyzer (VSW HA100). The XPS measurements were carried out at the HSGM and LSGM beamlines of the Synchrotron Radiation Research Center in Taiwan; the incident angle of the photon beam was 55° from the surface normal. The photoelectrons were collected with the electron-energy analyzer normal to the sample surface. All XPS data presented here resulted from Shirley background subtraction with a third-order polynomial to each side of the peak in all fits. In order to identify the chemical species on the sample surface, we fitted XPS spectra numerically with Gaussian-broadened Lorentzian functions. The onset of photoemission from an Au foil attached to the sample holder served as the Fermi level.

The thickness of the Si(1 0 0) sample (n-type, 1–10 Ω cm) used in this work was 0.3 mm. To prevent any possible organic residuals, we cleaned the Si surface with acetone, methanol and hot HNO_3 (1 M) in a sequence followed by rinsing with in distilled water. A Ta strip (thickness 0.025 mm) was uniformly pressed between two Si samples with Ta foils at either end, which were in turn mounted on the copper block. The sample could be cooled to 115 K with liquid nitrogen via conduction through the copper block and heated by resistive heating of the Ta strip and the Si samples. The sample temperature was monitored with a K-type thermocouple spot-welded onto a thin Ta foil that was inserted between the two Si samples. The thermocouple did not contact directly to the Si sample surface. The Si surface was cleaned by resistive heating in situ slowly to 1200 K. The H_2S gas (Matheson, 99.5% min) was introduced onto the Si(1 0 0) surface at 115 K by background dosing through a leak valve. As the surface sulfur-containing species generated on adsorption of H_2S could be desorbed, a clean Si(1 0 0)-2 × 1 surface was retained by flashing to 1200–1300 K to remove sulfur adatoms left on the surface after each experimental run. The surface cleanness was verified with LEED and XPS.

3. Results and discussion

Fig. 1(a) shows S 2p XPS spectra collected from a Si(1 0 0)-2 × 1 surface exposed to H_2S at 115 K. Only an S $2p_{3/2}$ binding energy is observed at ∼163.3 eV at all exposures up to 20 L. According to previous UPS and STM measurements [6,7],
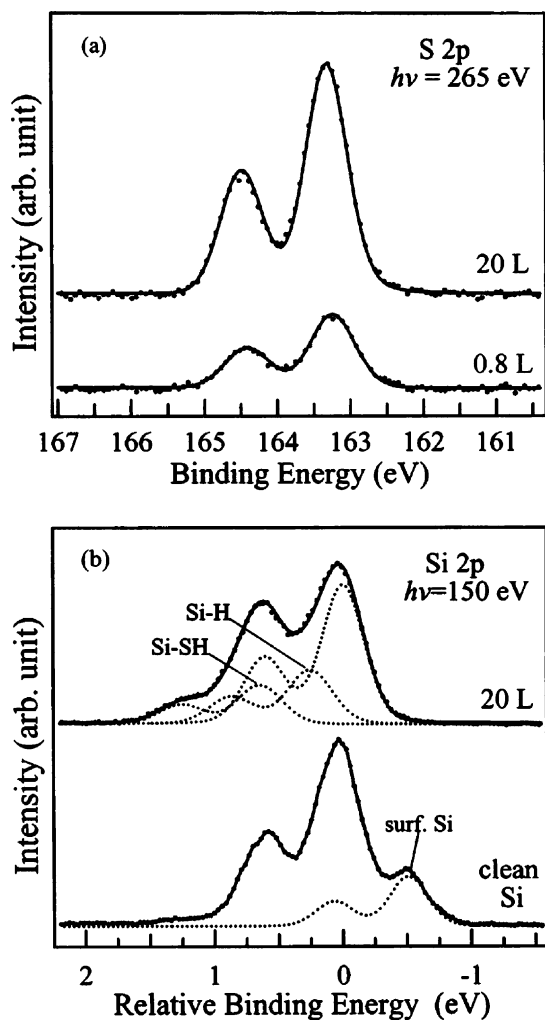
Fig. 1. (a) XPS spectra of S 2p for a Si(1 0 0) surface exposed to H$_2$S (0.8 and 20 L) at 115 K (b) XPS spectra of Si 2p for a clean Si(1 0 0) surface before and after exposure to 20 L H$_2$S at 115 K. Dots represent data collected after background subtraction; solid lines are fitted curves, and various components are shown with dashed lines. The photon energies used to collect these spectra are 150 eV for Si 2p and 265 eV for S 2p, respectively.

H$_2$S dissociates to form H and HS species at 150 K. In our work, there is no significant difference between the binding energies of S 2p for a Si surface exposed to H$_2$S at 115 and 150 K. Thus, this S feature is attributed to surface HS, as discussed further below. No significant change in the S 2p spectrum is observed on further exposure up to 100 L. Hence, the surface is saturated with chem-

isorbed HS and H, and the sticking coefficient for physisorption of H$_2$S is greatly decreased.

Fig. 1(b) shows core-level spectra of Si 2p taken before and after a clean Si surface is exposed to 20 L H$_2$S at 115 K. The Si 2p binding energy is referred to the bulk 2p$_{3/2}$ component so that complication resulting from the variation of surface band bending can be eliminated after adsorption and thermal decomposition of H$_2$S. The Si 2p spectrum of a clean Si(1 0 0)-2 × 1 surface is fitted with four Si 2p components (three surface core-level components shifted with respect to a bulk component) [15]. For simplicity and clarity, only one surface Si component for the clean surface with a chemical shift at −0.5 eV is shown in Fig. 1(b), which has been ascribed to the upward buckled Si of a dimer. This component is gradually attenuated upon increasing exposure of H$_2$S, indicating that a reaction occurs between H$_2$S and surface dimer Si atoms. For the Si 2p spectrum obtained on exposure at 20 L as shown in Fig. 1(b), the curve fits indicates two H$_2$S-induced Si 2p$_{3/2}$ components with chemical shifts at 0.25 and 0.65 eV, respectively. Adsorption of atomic hydrogen is reported to form a Si(1 0 0)-2 × 1–H surface and gives a chemical shift of Si 2p$_{3/2}$ by 0.26 eV relative to bulk Si [16]. Thus, the former component is attributed to a contribution of dimer Si bonded to a hydrogen atom (Si–H), as well as subsurface Si. The Si 2p$_{3/2}$ component with the great chemical shift, 0.65 eV, is attributed to surface Si bonded to the electron-withdrawing SH moiety (Si–SH). The integrated area of Si 2p due to Si–SH is near that of the upward buckled Si atom on a clean Si surface, indicating that the adsorption site (dangling bond) on the dimer Si is saturated by 0.5 ML SH$_{(ad)}$ and H$_{(ad)}$.

An H$_2$S molecule dissociates to form H and HS that bond to two surface Si atoms which might not be in the same Si dimer. The ordered (2 × 1) LEED pattern is maintained after adsorption of H$_2$S at 115 K. We assume that dissociation of H$_2$S occurs mainly at the existing dangling bond without major disruption of the Si surface structure. In agreement with previous work [10], dissociative adsorption of H$_2$S on Si(1 0 0)-2 × 1 is proposed to proceed as shown in Fig. 2(a) and (b). At 115 K, the dissociative H and HS species are likely bound
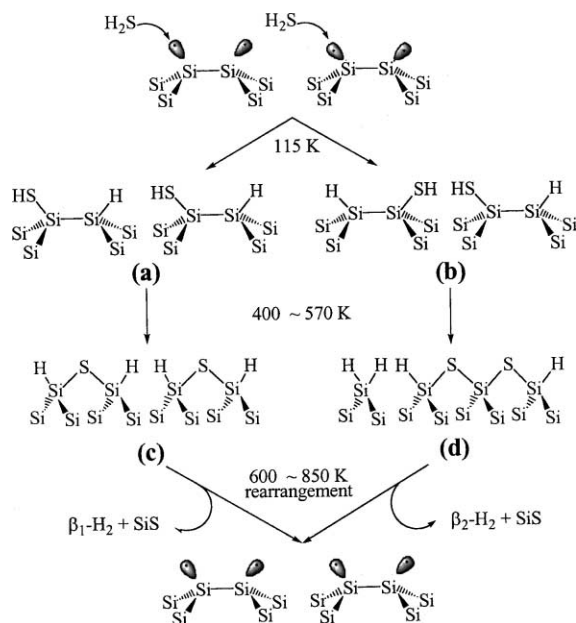
Fig. 2. Schematic diagram of a reaction pathway for H_2S decomposing on a Si(1 0 0)-2 × 1 surface.

Fig. 3. TPD spectra of H_2 ($m/e = 2$) and SiS ($m/e = 60$) collected from Si(1 0 0)-2 × 1 after an exposure to 20 L H_2S at 115 K. The heating rate is about 2 K/s.

to dangling bonds of the Si dimer without breaking of the Si–Si dimer bond, as observed for H_2O and NH_3 on Si(1 0 0) [17–19].

Fig. 3 shows TPD scans taken from a Si(1 0 0) surface exposed to 20 L H_2S at 115 K. To detect possible products evolved during thermal decomposition of H_2S on the surface, we observed several possible fragments. Hydrogen ($m/e = 2$) and SiS ($m/e = 60$) are the only desorption products of H_2S decomposition; desorption of SiS is observed with a feature at 820 K in our work, in contrast to previous results in which no sulfur-containing desorption product was detected [10]. Desorption of SiS is generally observed when a Si surface is exposed to sulfur-containing compounds (e.g. elemental sulfur and alkanethiols) and subsequently annealed to 500–600 °C [2,20]. Desorption of hydrogen exhibits an intense feature at 780 K with a shoulder at ∼680 K. These desorption features resemble the β_1 and β_2 states of hydrogen desorption observed for adsorption of atomic hydrogen on Si(1 0 0), which are attributed to recombination of surface hydrogen in the forms of Si mono- and di-hydrides (HSi and H_2Si), respectively [10]. Thus, our TPD data indicate that H_2S dissociates
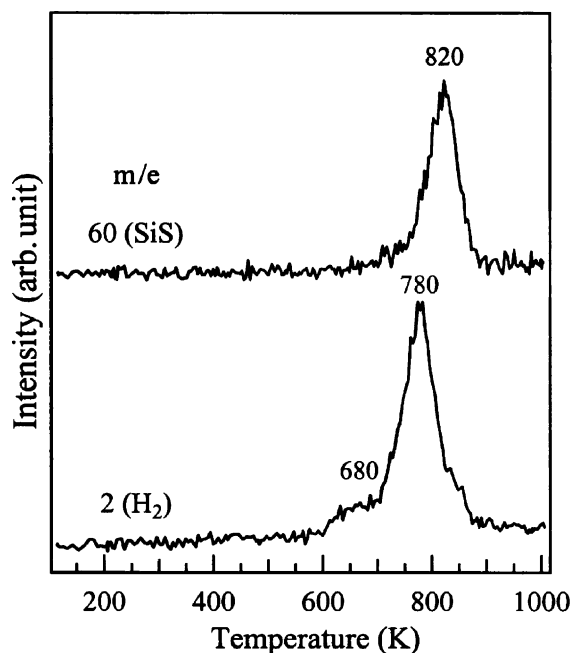
to form Si monohydride with a small proportion of Si di-hydride. At all exposures below 20 L, no molecular desorption of H_2S is detected, indicating that all chemisorbed H_2S decomposes to form surface hydrogen and silicon sulfide.

The thermal evolution of XPS spectra is used to characterize the variation of surface composition during thermal decomposition of H_2S on Si and correlates with TPD results to elucidate the reaction intermediates. Fig. 4 shows core-level spectra of S and Si 2p obtained from a Si(1 0 0) surface that was exposed to 20 L H_2S at 115 K and followed by warming to the indicated temperatures. All XPS spectra were taken at 115 K after the sample was heated to a desired temperature at a linear rate of ∼2 K/s and cooled immediately on stopping the heating abruptly. Upon annealing the sample above 420 K, the intensity of the S 2p peak at 163.35 eV due to HS gradually attenuated and a new peak appeared at 162.65 eV, indicating that the HS species further dissociate to form surface sulfur adatoms ($S_{(ad)}$). At 570 K, all HS species dissociate completely to form surface sulfur. The
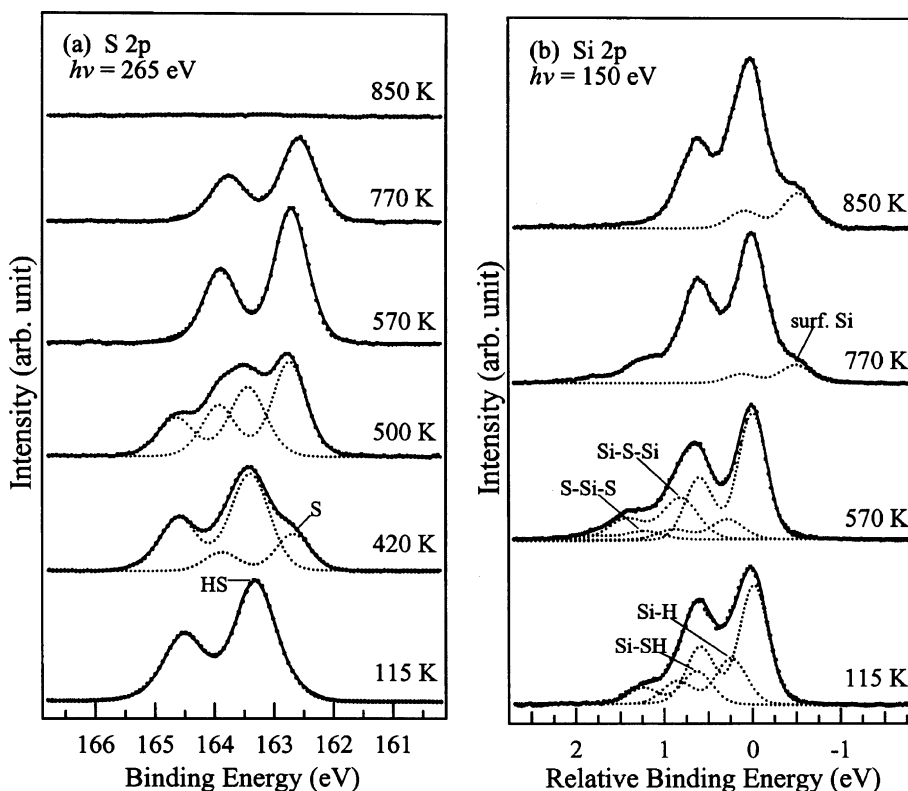
Fig. 4. XPS spectra of (a) S 2p and (b) Si 2p for a Si(1 0 0) surface exposed to 20 L H$_2$S at 115 K and subsequently heated to indicated temperatures.

Si 2p spectrum obtained at 570 K is deconvoluted into three surface components with the chemical shifts of 0.29, 0.86 and 1.22 eV with respect to bulk Si. The latter two peaks with greater chemical shifts are due to S-induced Si 2p$_{3/2}$ components, indicating that adsorption of sulfur adatoms results in surface Si with two oxidation states. Theoretical work indicates that a surface S atom absorbs at a bridge position above the topmost Si atoms, corresponding to the most energetically stable configuration [21]. Accordingly, we propose that the S-induced Si peak at 0.86 eV is due to the surface Si atom bonded to one hydrogen and one bridge-bonded sulfur (HSi–S–SiH) as shown in Fig. 2(c). The formation of HSi–S–SiH can occur via transfer of hydrogen from sulfur to Si on breaking the dimer Si–Si bond. This feature resembles the formation of Si–O–Si, which has been observed during thermal decomposition of surface hydroxyl (Si–OH) [22]. Rezaei et al. [7] concluded

that dissociation of S–H is catalyzed by the Si surface via a concerted mechanism of formation and breaking of bonds that involve surface Si atoms. Dissociation of the S–H species to form the bridge-bonded S is complete at 570 K, which is significantly less than that observed for O–H (~673 K). Hence, the temperatures of bridge-bonded O and S formation are determined mainly through dissociation of O–H and S–H bonds, instead of the Si–Si dimer bond.

The large chemical shift of Si 2p$_{3/2}$ at 1.22 eV is near that observed for Si(1 0 0)-1 × 1–S, in which the surface Si atom is terminated by bridge-bonded sulfur and has an oxidation state of +2 [11]. Thus, the Si 2p$_{3/2}$ component is attributed to a surface S–Si–S species that we propose to form from two adjacent SH, as shown in Fig. 2(d). Accordingly, the Si di-hydride is produced through this reaction pathway, corresponding to the β_2-H$_2$ desorption peak. In addition, the Si 2p$_{3/2}$ compo-

nent with a chemical shift at 0.29 eV is thus attributed to both Si di-hydride and subsurface Si atom.

The integrated S 2p intensity of surface sulfide remains constant until desorption of SiS occurs. Upon annealing the sample to 770 K, the S 2p peak at 162.65 eV assigned to surface sulfur has decreased in intensity. The resulting LEED pattern becomes a diffuse (1 × 1) structure that might result from diffraction of electrons reflected from the bulk. These results indicate that surface sulfur is removed from the surface, which is consistent with desorption of SiS as shown in TPD results. The chemical shifts of S and Si 2p corresponding to the formation of subsurface sulfide is not observed in the XPS measurement. In contrast to a previous report in which the diffusion of sulfur into the Si bulk is proposed, our TPD and XPS measurements indicate that all of surface sulfur is removed from the surface on desorption of SiS [10]. This process is consistent with the argument based on thermodynamics, such that the Si–S bond is stronger than the Si–Si bond and desorption of SiS occurs via breaking of the Si back-bond [1,2]. Finally, annealing the sample to 850 K completely removes surface sulfur and the upward buckled Si of the dimer reappears with a chemical shift of $2p_{3/2}$ at −0.5 eV, as shown in Fig. 4(b). A clean Si surface with a sharp (2 × 1) LEED can be retained, indicating a rearrangement of an H_2S-etched Si surface.

On the basis of TPD and XPS results, we depict the adsorption configuration and thermal decomposition of H_2S on Si(1 0 0)-2 × 1 schematically in Fig. 2. Upon adsorption of H_2S at 115 K, most of dissociative SH and H binds alternatively to dangling bonds of the Si dimer row without breaking the Si–Si dimer bond and preserves a (2 × 1) LEED pattern. It is likely that dissociation of H_2S occurs on two Si atoms of a Si dimer. However, the possibility of dissociation of H_2S on two adjacent dangling bonds of neighboring dimers cannot be excluded [18]. A small proportion of surface SH binds to adjacent Si atoms of two Si dimers, which might facilitate formation of S–Si–S and Si di-hydride (SiH_2) via insertion of sulfur and transfer of hydrogen. The presence of SiH_2 results in desorption of hydrogen at 680 K, which re-

sembles β_2-H_2 observed for the adsorption of atomic hydrogen on Si. Our proposed reaction of H_2S decomposition on Si(1 0 0) is consistent with results of theoretical calculation by the MNDO method, which suggests that bridged S and on-top H (mono- and di-hydrides) constitute the most energetically favorable geometry for dissociative adsorption of H_2S [9]. The surface sulfur becomes removed from the surface by desorption of SiS, instead of diffusion into the bulk.

4. Conclusion

TPD results show that H_2 and SiS are desorbed from a Si surface during thermal decomposition of H_2S. XPS data indicate that dissociative adsorption of H_2S yields surface H and HS on Si(1 0 0) with a small activation barrier at 115 K. The resulting H and HS bind to Si atoms of a dimer and consequently preserve the (2 × 1) surface structure. The dissociaiton of the HS moiety dissociates further to form a Si–S–Si intermediate on breaking the Si–Si bond of a dimer at temperatures above 420 K. Si mono-hydride and di-hydride are proposed to be the surface intermediates, corresponding to desorption features of hydrogen at 780 and 680 K. A small proportion of HS species might dissociate to form an S–Si–S species with formation of Si di-hydride. Compared with previous works on H_2O on Si(1 0 0), our TPD and XPS data indicate many general similarities in the adsorption and thermal reaction of H_2S and H_2O on a Si surface. Finally, as a gaseous source of sulfur in the chemical vapor deposition on a Si surface, thermal decomposition of H_2S produces surface Si–H that is difficult to remove without etching the Si surface via desorption of SiS. This process might result in becoming incorporated hydrogen at the interface between the Si substrate and the grown film.

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