24A1 BM - (WR-SGM) XPS, UPS

Adsorption and Thermal Reactions of H_2O and H_2S on Ge(100)

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The thermal evolution of XPS spectra was used to characterize the variation of surface composition during the thermal decomposition of H_2O on Ge(100), and was correlated with TPD results to elucidate the reaction intermediates. Figure 1 shows O 1s spectra for a Ge surface at 105 K exposed to H_2O for 50 s, and subsequently annealed to various temperatures. All XPS spectra were recorded for samples at 105 K after a sample was heated to a desired temperature and cooled abruptly. Upon annealing the sample to 170 K, the O 1s component at 533.8 eV due to physiorbed H_2O disappeared because of molecular desorption. The intensity of the O 1s signal at 532.1 eV due to surface OH increased, indicating the decomposition of chemisorbed H_2O molecules to form more surface OH species. At 270 K, all chemisorbed H_2O desorbed intact or dissociated to form OH and H. On further annealing to 500 K, a new O 1s feature appeared at 530.5 eV, attributed to surface O formed on dehydrogenation of surface OH. According to the previous DFT calculations, the O atom was proposed to reside on a bridge site between two Ge atoms. The temperature of OH decomposition on Ge(100) is similar to that observed on Si(100); this observation disagrees with an expectation from a calculation that the Si–H bond does not dissociate at temperatures below 670 K. Upon annealing to 600 K, the signal of O 1s at 532.1 eV due to OH disappeared and only O was left on the surface. The total integrated intensity of the O 1s signal decreased significantly because most OH recombined with surface H to desorb H_2O in this temperature range as shown by the TPD data. If the integrated intensity is proportional to the coverage of O-containing species on the surface, about 70 % of surface OH underwent re-combinative reaction. When the sample was annealed to 700 K, the intensity of O 1s further decreased because the O adatom evolved from the surface with desorption of GeO. The surface O was removed completely from the surface at 770 K and a clean Ge surface was regained.

The adsorption and thermal decomposition of H_2O and H_2S on Ge(100) were studied with temperature-programmed desorption (TPD) and X-ray photoelectron spectra (XPS) using with synchrotron radiation. At 105 K, H_2O molecules either absorb molecularly or dissociate to form surface OH and H for exposures of all durations. Chemisorbed H_2O dissociates to form surface OH on annealing to 270 K, whereas H_2S dissociates to form surface SH and H on an initial exposure and further adsorbs molecularly on protracted exposure to the surface at 105 K. The calculation with density-functional theory (DFT) shows that H_2S undergoes dissociative adsorption with a negligible barrier (2.1 kJ mol^{-1}) but H_2O dissociates with a larger barrier (26.8 kJ mol^{-1}). On annealing to 550 K, surface OH mainly recombines with surface H to evolve H_2O, but a small proportion of surface OH decomposes to form surface O and H. Most surface SH undergoes decomposition to form surface S and H at 520 K. Figure 2 shows DFT calculation shows that surface OH has an activation energy for decomposition greater than for recombination with surface H, whereas activation energies for decomposition and recombination of surface SH show the reverse order. Surface H resulting from the dissociation of H_2O and H_2S is thermally activated to combine and to desorb as H_2 at 620 K. For H_2S, a small proportion of surface H recombines with surface S to desorb as H_2S. Finally, surface O and S are removable from the surface with desorption of GeO at 710 K and GeS at 695 K, respectively.

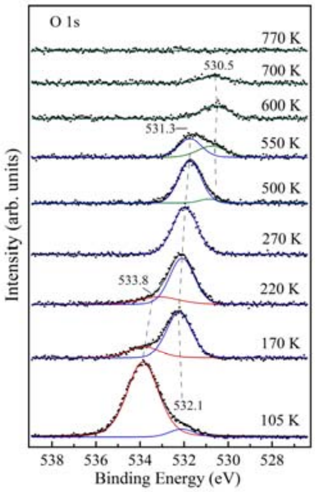

Fig. 1: XPS spectra of O 1s for a Ge(100) surface at 105 K exposed to H_2O for 50 s and subsequently heated to the indicated temperatures.

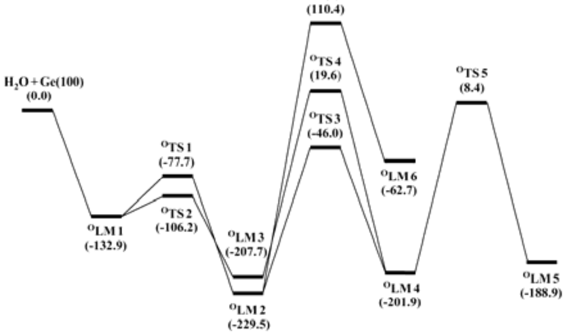

Fig. 2: Potential-energy surfaces for adsorption and reactions of H_2O and on Ge(100). ^{O}LM and ^{O}TS denote reaction intermediates and transition structures of H_2O on Ge(100), respectively. The numbers in parentheses specify the potential energies (kJ/mol) of ^{O}LM and ^{O}TS. All potential energies of ^{O}LM and ^{O}TS are referred to the H_2O molecule separated from the cluster surface.