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Thermal reactions on the Cl-terminated SiGe(1 0 0) surface

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Abstract

Synchrotron radiation photoemission spectroscopy was used to investigate thermal reactions on the Cl-terminated SiGe(1 0 0)-2 × 1 surface. Populations of GeCl and SiCl surface species during thermal annealing are monitored by measuring the intensities of their corresponding Ge 3d, Si 2p and Cl 2p core level components. Experimental results indicate that the initially clean SiGe alloy surface is dominated by Ge–Ge and Ge–Si dimers, and that, after Cl_2 adsorption, thermodynamic forces drive Si in the subsurface region to replace Ge in the GeCl species. Consequently, chlorine desorbs in the form of $SiCl_2$ above ~700 K, leading to etching of Si. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chlorine; Photoemission (total yield); Silicon; Germanium; Thermal desorption

1. Introduction

The understanding of atomic composition of the surface and the reactions during epitaxy is essential to effectively control the growth and etch of multilayer structures, such as $Si_{1-x}Ge_x$/Si superlattices and heterostructures. Such structures offer greatly improved performance for bipolar transistor devices [1]. Because the Ge–Ge dangling-bond energy is lower than that of Si–Si, deposited Ge stays on the surface and the interface during the growth of Ge on the Si(1 0 0) substrate is abrupt [2–4]. However, the dangling bond energy causes deposited Si to diffuse into the subsurface layers, forming a non-abrupt interface during Si deposition on Ge layers [5,6]. The Ge segregation can be suppressed during SiGe epitaxy by reducing the energy difference between the Si- or Ge-terminated surfaces. Many studies have shown that the introduction of surfactants and hydrogen passivation of the dangling bonds on Si/Ge surfaces can, in fact, effectively alter the growth modes [7,8].

Chlorinated silicon and germanium compounds, such as $SiCl_4$, Si_2Cl_6, and $GeCl_4$, are widely adopted in Si and Ge epitaxy [9]. More chemically aggressive, chlorine also plays an important role in the commercial etching processes [9]. Hence, the interaction of chlorine atoms with Si/Ge surfaces and interfaces has received much interest [10–12]. Many different techniques, including X-ray photoelectron spectroscopy, temperature programmed desorption, low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM) have been employed to study the adsorption and thermal desorption of Cl/Si(1 0 0), Si(1 1 1) [10]. STM can be used to study specific

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sites for chlorine chemisorption with atomic resolution and its results show that the Cl-saturated Si(1 0 0) surface is fully saturated dimers that appear symmetric in the room-temperature STM images [11]. The Cl-saturated Ge(1 0 0)-2 × 1 surface, exhibiting a 2 × 1 LEED pattern, is expected to possess the same symmetric dimers, with Cl saturating the two dangling bonds in each dimer [12]. Relevant studies have reported that thermal removal of Cl from the Cl:Si(1 0 0)-2 × 1 surface occurs only by desorption of $SiCl_2$ and a small amount of $SiCl_4$ [10]; similarly, thermal removal of Cl from Cl:Ge(1 0 0), occurs by desorption of $GeCl_2$ [13].

This work employs synchrotron radiation core-level photoemission spectroscopy to investigate the reactions that occur on the Cl-terminated SiGe(1 0 0) surface during annealing at various temperatures. High-resolution core-level photoemission spectroscopy distinguishes surface atoms in non-equivalent sites and in different chemical bonding configurations by corresponding binding energy shifts [12]. In the Cl:SiGe(1 0 0) system, the surface Si and Ge atoms bonded to Cl have large binding energy changes in the Si 2p and Ge 2p core levels. The Ge- and Si-shifted Cl 2p core levels are well separated due to the difference of charge transfer in Cl–Si bonds and that in Cl–Ge bonds [14]. Therefore, combining Ge 3d, Si 2p and Cl 2p core-level spectra enables the detailed surface reactions to be determined. According to our results, thermally activated place exchange of Si and Ge atoms upon Cl-termination at 550–680 K is observed. Above 700 K, only Si atoms are etched away by $SiCl_2$ desorption.

2. Experimental procedure

The photoemission experiments were performed in a μ-metal shielded UHV system utilizing a 1.5-GeV synchrotron radiation in Taiwan Light Source, Hsinchu, Taiwan. Light from the storage ring was dispersed by a wide-range spherical grating monochromator. The photocurrent from a gold mesh positioned in the synchrotron beam path was monitored to relatively measure the incident photon beam flux. The Si growth, Cl_2 adsorption and annealing were prepared in situ in UHV conditions. Photoelectrons were collected at normal emission angle and analyzed by a 125 mm hemispherical analyzer. The overall energy resolution was about 120 meV.

The Ge(1 0 0) samples were sliced from commercial n-type wafers. After outgassing at ~800 K for ~12 h, clean Ge(1 0 0)-2 × 1 samples were obtained by cyclic sputtering with 500-eV Ar^+ and followed by DC Joule heating to ~1000 K for 60 s. Disilane (Voltaix, ultrahigh purity grade) and Cl_2 were introduced into the chamber through a precision leak valve in a small reaction chamber. The substrate temperature was varied by controlling the DC current through the sample and measured with an infrared pyrometer.

3. Results and discussion

The SiGe film is obtained by Si chemical vapor deposition using disilane (Si_2H_6) on a clean Ge-(1 0 0)-2 × 1 sample at 730 K. As estimated, the total amount of Si deposited is around 12 ML (monolayer) by calibrating the intensity of Si 2p to the films grown by atomic layer epitaxy [5]. Here, one monolayer, 6.24×10^{14} atoms/cm^2, is defined as the site density for unreconstructed Ge(1 0 0) surface. Several earlier studies have verified that the deposition of Si leads to a SiGe alloy with the same dimerized 2 × 1 surface structure [5,14,15]. The alloy concentration is not likely spatially uniform, but this uncertainty does not affect the experiment on thermal reactions since the data for different amounts (4–12 ML) of Si deposition show similar results to that presented here [16]. Figs. 1–3 display the surface-sensitive Ge 3d, Si 2p, and Cl 2p core-level spectra (circles), respectively. The figures also show corresponding fits (curves) obtained by least-squares method for the starting SiGe(1 0 0)-2 × 1 surface, and for the same surface saturated by Cl_2 at 325 K, followed by successive annealing to higher temperatures as indicated. Following the standard procedure [3,5], each component in the fitting includes a pair of spin–orbit-split peaks and is assumed to have the same Voigt line shape riding on a smooth background.

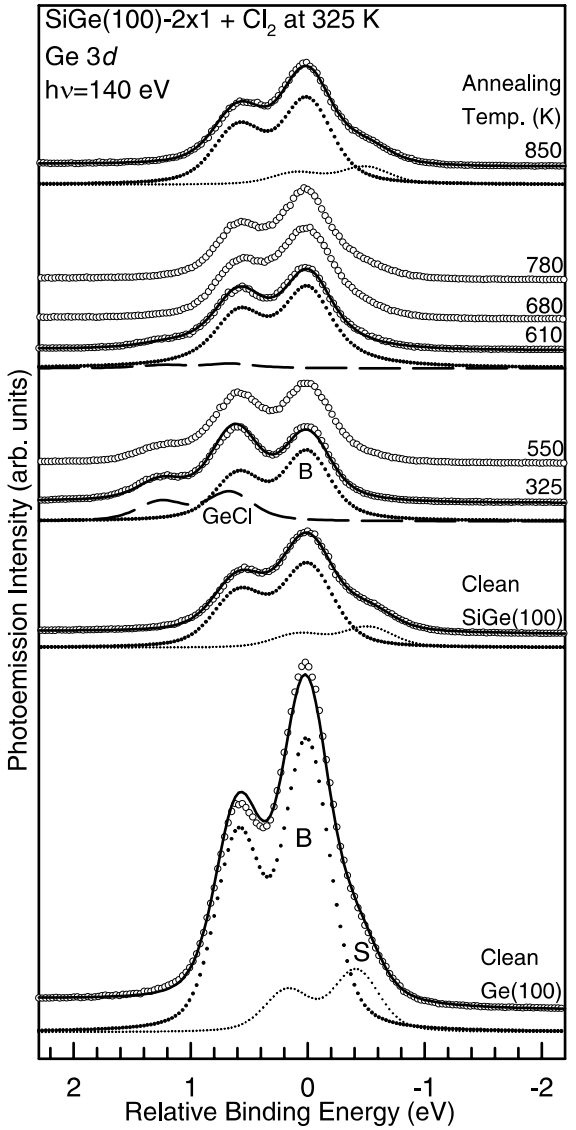

Fig. 1. Ge 3d core-level photoemission spectra (○) for the Ge(1 0 0)-2 × 1 surface; the SiGe(1 0 0) alloy surface obtained by depositing 12-ML of Si at 730 K, and the same surface after Cl_2 saturation followed by annealing at various temperatures. The solid curves are fits to the spectra. The curves labeled B, S, and GeCl are the results of decomposition of the spectra into contributions from bulk, surface, and GeCl species, respectively. The energy zero refers the $3d_{5/2}$ bulk position for the Ge(1 0 0)-2 × 1 surface.

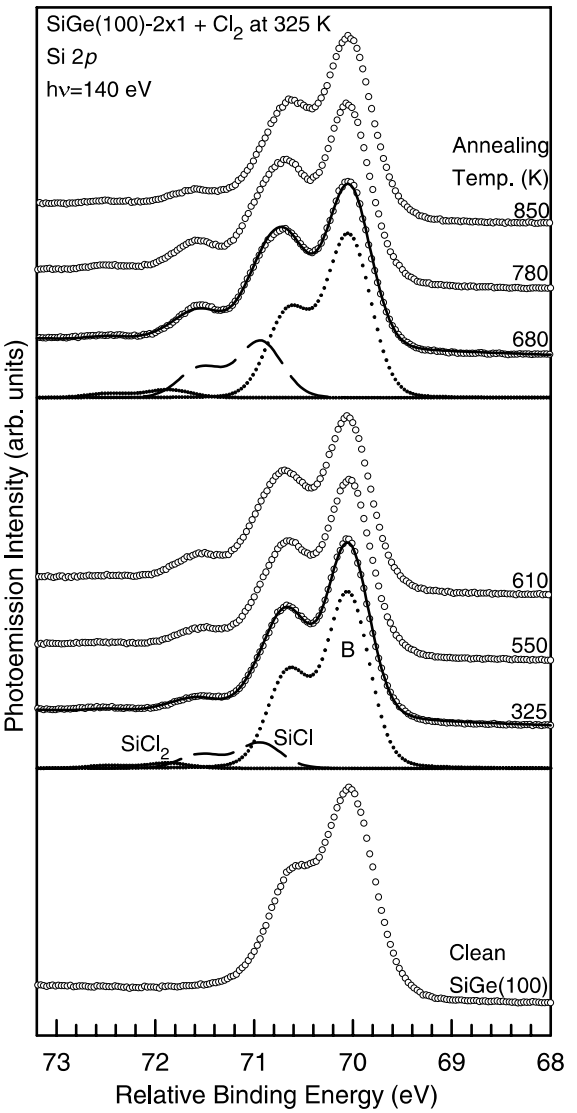

Fig. 2. The Si 2p core-level photoemission spectra (○) for the SiGe(1 0 0)-2 × 1 surface, and the same surface after Cl_2 saturation followed by annealing at various temperatures. To eliminate the band bending effect, the relative binding energy for Si 2p refers to the corresponding Ge $3d_{5/2}$ line of the B component in Fig. 1. The curves show the overall fits (—) and the decomposition into SiCl and $SiCl_2$ components.

Two spin–orbit-split components are employed to fit the bottom two Ge 3d spectra in Fig. 1, for the initial Ge(1 0 0)-2 × 1 sample and the same sample after growing 12-ML Si, respectively. The bulk (B) and the surface (S) components correspond to emission from the bulk and the up atoms of the top dimerized layer, respectively [5,17,18]. The energy zero in Fig. 1 refers to the $3d_{5/2}$ bulk

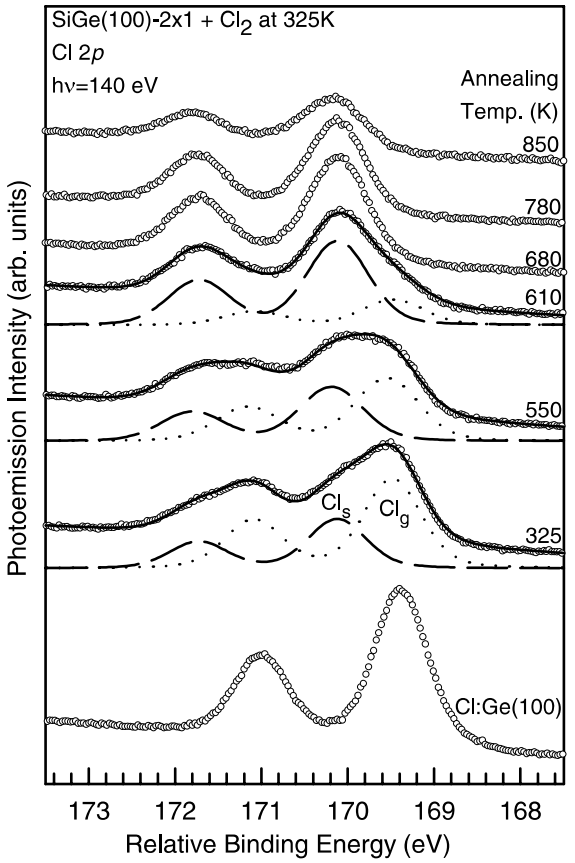

Fig. 3. Cl 2p core-level photoemission spectra (○) for the Cl-terminated SiGe(1 0 0)-2 × 1 surface after annealing at various temperatures. The relative binding energy refers to the corresponding Ge $3d_{5/2}$ line of the B component in Fig. 1. The curves show the overall fits (—) and their decomposition into the Cl_s and Cl_g components.

position for the Ge(1 0 0)-2 × 1 surface. The intensity of the bulk component is significantly reduced following the growth of Si, since much Ge in the bulk is then replaced by Si. The intensity of the S component is not as large as that for the clean Ge(1 0 0)-2 × 1 surface, in part due to a large defect density on the surface [5].

In Fig. 2, the Si 2p spectrum obtained after Si deposition shows one broad spin–orbit-split component, which may originate mainly from the bulk atoms, subsurface atoms, and some down-atoms in the surface dimers. The S component typically shown in the clean Si(1 0 0)-2 × 1 and Ge(1 0 0)-2 × 1 surfaces [3,5] is not observed, indicating that few Si atoms are in the up-atom position in the surface dimers. Two components appear on the higher binding energy side of the B component following Cl saturation. Their binding energy shifts are 0.89 and 1.82 eV, close to those found for SiCl and $SiCl_2$ surface species, respectively [10, 14]. Thus, the two components are responsible for SiCl and $SiCl_2$. Similarly, a new component in the corresponding Ge 3d spectrum (Fig. 1) appears at a binding energy 0.66 eV higher than for bulk Ge. This new component corresponds to the GeCl species since its binding energy shift is close to the reported value of ~0.6 for GeCl [12,14].

The relative populations of Si and Ge atoms on the surface can be directly deduced from the Cl 2p spectra. In Fig. 3, the bottom Cl 2p spectrum for the Cl_2-saturated Ge(1 0 0)-2 × 1 surface shows one single spin–orbit-split component (labeled Cl_g), which originates from the GeCl surface species. After Cl_2 adsorption onto the SiGe(1 0 0) surface, the Cl 2p spectrum includes a second component (labeled Cl_s) appeared at binding energy 0.64 eV higher than for Cl_g. The Cl_s component is caused by the SiCl and $SiCl_2$ species, whose presence is indicated by the corresponding Si 2p spectrum. Decomposition of the second to bottom spectrum in Fig. 3 shows that the intensity ratio of Cl_s and Cl_g is ~0.5, indicating that the number of Ge atoms on the surface is about twice that of Si.

Upon successive annealing to a higher temperature, the SiCl component in the Si 2p spectra (Fig. 2) and the Cl_s component in the Cl 2p spectra grow, while the intensities of the GeCl components in the Ge 3d spectra (Fig. 1) and the Cl_g component fall. At 680 K, the Cl 2p spectrum consists of only the Cl_s component; the GeCl peak in the Ge 3d spectrum vanishes. Cl atoms can only form single bonds and they always terminate the surface. Therefore, the above observations together indicate that the Si atoms originally present in the subsurface region are exchanged with Ge atoms that bond to Cl. A theoretic study of a Ge(1 0 0)-2 × 1 surface grown with a monolayer of Si showed that the energy for a segregated structure, in which Si occupies the second layer while Ge–Ge dimers float to the surface, is 0.38 eV/dimer lower than that for the non-segregated (Si–Si dimer

terminated) surface [4]. Another study showed that chlorine adsorption dramatically reverses the situation [15]: the Cl–Si–Si–Cl monochloride surface is energetically favored over the Cl–Ge–Ge–Cl surface (with Si in the second layer) by 0.3 eV per dimer. Therefore, thermodynamic forces govern the replacement of the Cl–Ge bonds by Cl–Si, upon thermal activation.

Cl atoms start to notably desorb above ~700 K as shown by the reduction of Cl 2p intensity. The integrated intensity of Si 2p is ~13% lower after complete desorption of Cl at ~920 K than before Cl adsorption and thermal annealing. The integrated intensity of Ge remains almost unchanged. Moreover, $SiCl_2$ desorption is generally observed at ~830 K for the Cl:Si(1 0 0) surface [10]. Therefore, the desorption product is primarily $SiCl_2$ on the SiGe alloy film, which is also highly consistent with the above finding that surface Cl atoms largely bond to Si at high temperatures.

4. Conclusions

In summary, high resolution core-level photoemission with synchrotron radiation was used to examine the Cl-terminated SiGe(1 0 0) alloy surface. Chemical-state resolved Ge 3d, Si 2p, and Cl 2p spectra reveal the detailed surface processes which occur during sequential annealing at elevated temperatures. Experimental results show that the initially clean SiGe(1 0 0) surface consists largely of Ge–Ge and Ge–Si dimers with Si atoms in the down-atom position. After Cl_2 saturation followed by thermal activation at 550–680 K, Ge atoms that bond to Cl are exchanged for Si in the subsurface region and ClSi becomes the majority surface species. This result agrees closely with the theoretical finding that the energy corresponding to a segregated structure is lower than that corresponding to the non-segregated Si–Si dimer-terminated surface. It agrees also with the theoretical finding that the Cl–Si–Si–Cl monochloride surface is energetically much more favorable than the Cl–Ge–Ge–Cl surface. Above 700 K, chlorine desorbs in the form of $SiCl_2$, resulting in a net etching of Si.

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