

Chlorine-induced Si surface segregation on the Ge-terminated Si/Ge(100) surface from core-level photoemission

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This study investigated the thermal reactions on the Cl-terminated Si/Ge(100)- 2×1 surface using synchrotron radiation photoemission spectroscopy. Populations of surface Cl-Ge and Cl-Si bonds during annealing are monitored by measuring the intensities of their corresponding Ge $3d$, Si $2p$, and Cl $2p$ core-level components. Experimental results clearly demonstrate that no Si atoms are present on the surface after the deposition of 0.8 monolayer Si on the Ge(100) surface at 730 K and that Cl termination pulls out the indiffused Si of about two atomic layers deep to form Cl-Si bonds upon annealing at 550–690 K. We attribute such chlorine induced Si segregation to a thermodynamic driving force that favors the Cl-Si surface species. Above 680 K, chlorine is desorbed in the form of SiCl_2 , although the top surface layer of the starting Si/Ge(100) sample consists of Ge-Ge dimers only.

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Understanding not only the atomic composition of the surfaces and interfaces, but also the reactions during epitaxy is essential to both fundamental science and technological application in adequately controlling the growth and etch of multilayer structures such as $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ superlattices and heterostructures. Such structures perform well in bipolar transistors and optoelectronic devices.¹ During the growth of Ge on the Si(100) substrate, deposited Ge remains on the surface and the interface is generally believed to be quite abrupt, because the dangling-bond energy of Ge dimers is lower than that of Si dimers.^{2–4} However, this bond energy causes Ge to segregate onto the surface during Si deposition on Ge layers, forming a nonabrupt interface.^{5–7} The Ge segregation can be suppressed during SiGe epitaxy by reducing the energy difference between the Si- and Ge-terminated surfaces. Many studies have shown that the introduction of surfactants and hydrogen passivation of the dangling bonds on Si/Ge surfaces can effectively change the growth modes.^{8–11}

The kinetic effect of H blocking to hinder Ge segregation during the Si deposition onto the Ge(100) surface has been observed in both chemical vapor deposition and molecular beam epitaxy.^{5,9,10} Similar to hydrogen in the formation of single bonds, chlorinated silicon, and germanium compounds, such as SiCl_4 , Si_2Cl_6 , and GeCl_4 , are extensively employed in the Si and Ge epitaxy.¹² Being more chemically aggressive, chlorine is also commonly used in the commercial etching processes.¹² Hence, the interaction of chlorine atoms with Si/Ge surfaces and interfaces has received much attention.^{13–16} Many different techniques, including x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), low-energy electron diffraction (LEED), and scanning tunnelling microscopy (STM), have been used to investigate the adsorption and thermal desorption of chlorine on the Si(100) and Si(111) surfaces.¹³ The results of STM suggest that Cl_2 molecules dissociatively chemisorb on surface dangling bonds and that the Cl-saturated Si(100) surface is wholly composed of the Cl-saturated Si-Si dimers which appear symmetric in the room-temperature STM images.¹⁴ The Cl-saturated Ge(100)- 2×1 surface, exhibiting

a 2×1 LEED pattern,¹⁵ is expected to possess the same symmetric dimers with Cl's saturating the two dangling bonds on each dimer. Relevant studies have reported that thermal removal of Cl from the Cl:Si(100)- 2×1 surface occurs only by the desorption of SiCl_2 and a small amount of SiCl_4 ,¹³ similarly, thermal removal of Cl from Cl:Ge(100), occurs by desorption of GeCl_2 .¹⁶

This study employs synchrotron-radiation core-level photoemission spectroscopy to examine the 0.8-ML-Si/Ge(100) surface and the Cl-terminated 0.8-ML-Si/Ge(100) surface upon annealing at various temperatures. The technique is based on the observation that Si and Ge atoms bonded to surface Cl exhibit large binding energy changes in their Si $2p$ and Ge $2p$ core levels and that the Ge- and Si-shifted Cl $2p$ core levels are well separated due to the difference in charge transfer between Cl-Si bonds and Cl-Ge bonds.¹⁵ Therefore, combining Si $2p$, Ge $2p$, and Cl $2p$ core-level spectra enables the detailed surface compositions and reactions to be determined. Experimental results clearly demonstrate that no Si atoms are present on the top layer after the deposition of 0.8 monolayer Si on the Ge(100) surface at 730 K and that Cl-termination pulls out the indiffused Si to form Cl-Si bonds upon 550–690 K annealing. Above 680 K, chlorine desorbs in the form of SiCl_2 , although the top layer of the starting 0.8-ML-Si/Ge(100) surface consists of Ge-Ge dimers only.

The photoemission experiments were performed in a μ -metal shielded UHV system utilizing a 1.5-GeV synchrotron radiation in the 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 deposition, Cl_2 adsorption and annealing were prepared *in situ* under UHV conditions. Photoelectrons were collected at normal emission angle by a 125-mm hemispherical analyzer. The overall energy resolution was less than 120 meV.

The Ge(100) samples were sliced from commercial *n*-type wafers. After outgassing at ~ 800 K for ~ 12 hours, the

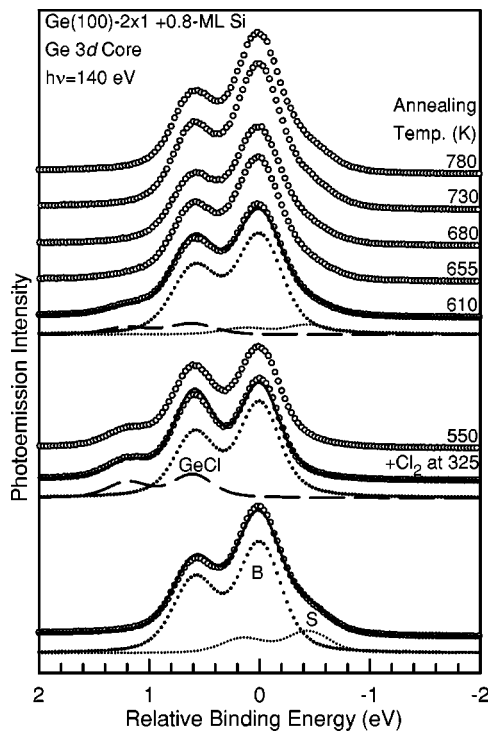


FIG. 1. The Ge $3d$ core-level photoemission spectra (circles) for the starting 0.8-ML-Si/Ge(100)- 2×1 sample (bottom) and the same sample after Cl_2 saturation followed by annealing at various temperatures. The solid curves are fits to the spectra. The curves labeled B, S, and GeCl are the results of decomposition of the spectra into contributions from bulk, the surface, and GeCl species, respectively. The energy zero refers to the $3d_{5/2}$ bulk position for the clean Ge(100)- 2×1 surface.

clean Ge(100)- 2×1 sample was 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 was introduced into the chamber through a precision leak valve in a small dosing chamber. The disilane dosing pressure was around 5×10^{-8} torr. The substrate temperature was varied by controlling the DC current through the samples. The samples' temperature as a function of heating power was measured with an infrared pyrometer and calibrated by attaching a small thermocouple to the center of the back face of an identical test sample. Each annealing lasted for 60 s.

The Si deposition on the clean Ge(100)- 2×1 sample was performed by atomic layer epitaxy (ALE), i.e., 15-L (1 langmuir= 10^{-6} torr s) disilane exposure at ~ 325 K followed by thermal annealing at 730 K. The amount of Si deposited in a cycle is about 0.4 ML,⁵ and therefore, a net deposition of about 0.8-ML Si is estimated after 2 cycles of Si ALE. Here, one monolayer is defined as the site density for unreconstructed Ge(100) surface, i.e., 6.24×10^{14} atoms/cm². Figures 1–3 show the surface-sensitive Ge $3d$, Si $2p$, and Cl $2p$ core-level spectra (circles), respectively, and their least-squares fit (curves) for the starting 0.8-ML-Si/Ge(100)- 2×1 surface, and for the same surface saturated by Cl_2 at 325 K followed by successive annealing to higher temperatures. The fitting was carried out in the

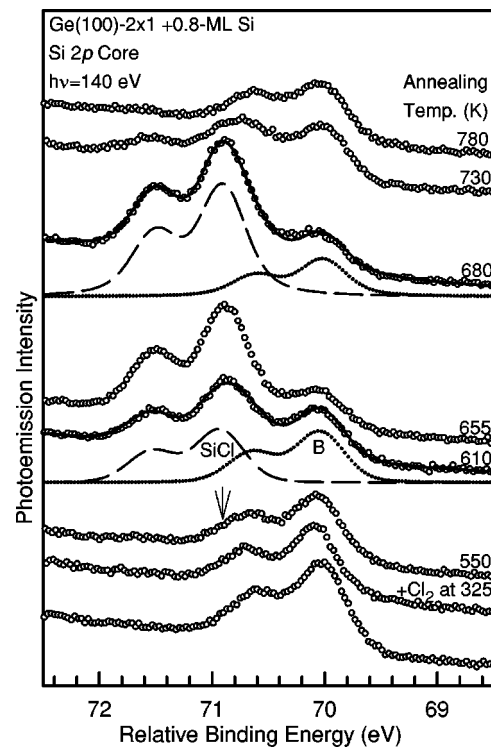


FIG. 2. The corresponding Si $2p$ core-level photoemission spectra (circles) for the starting 0.8-ML-Si/Ge(100)- 2×1 sample (bottom) and the same sample after Cl_2 saturation followed by annealing at various temperatures. To eliminate the band bending effect, the relative binding energy for Si $2p$ refers to the corresponding Ge $3d_{5/2}$ line of the B component in Fig. 1. The curves show the overall fits (solid curves) and the decomposition into bulk and SiCl components.

usual manner.^{5,17} Each component bearing a pair of spin-orbit-split peak is assumed to have the same Voigt line shape.

High-resolution core-level photoemission spectroscopy distinguishes surface atoms in nonequivalent sites and in different chemical bonding configurations according to their corresponding binding energy shifts.¹⁷ The Si $2p$ spectrum for the starting 0.8-ML-Si/Ge(100)- 2×1 surface (bottom spectrum in Fig. 2) exhibits only one spin-orbit-split component (B). The S component typically shown in the spectrum for the clean Si(100)- 2×1 surface is not observed. After Cl saturation, the intensity of the Si $2p$ spectrum is attenuated by the chlorine termination layer by $\sim 20\%$, but its line shape remains largely the same as a single component. Owing to small core-level shifts from different subsurface layers, the line shape of the B component is not particularly narrow. Chlorine has a large electronegativity and its bonding to surface Si atoms shifts Cl $2p$ binding energy by ~ 0.9 and ~ 1.7 eV for the SiCl and SiCl₂ surface species, respectively.^{6,13} Thus, it is visually conceivable that a negligible amount of Cl-Si bounds are present on the top layer of the 0.8-ML-Si/Ge(100)- 2×1 sample and nearly all the deposited 0.8-ML Si atoms indiffuse into the subsurface and bulk environment. This scenario is consistent with the previous reports which suggested that all the Si atoms move be-

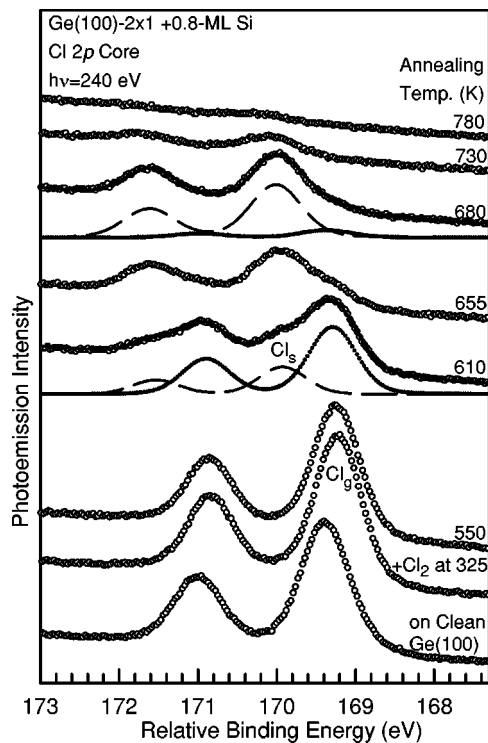


FIG. 3. Cl $2p$ core-level photoemission spectra (circles) for the Cl-terminated Ge(100)- 2×1 , the 0.8-ML-Si/Ge(100)- 2×1 sample and the same sample after annealing at various temperatures. Again, the relative binding energy refers to the corresponding Ge $3d_{5/2}$ line of the B component in Fig. 1. The curves show the overall fits (solid curves) and their decomposition into the Cl_s and Cl_g components.

low the top surface layer and forms a Si-Ge alloy in the subsurface region during both the molecular-beam epitaxy and chemical vapor deposition.^{18,5} The Si indiffusion is further supported by the Ge $3d$ and Cl $2p$ spectra. In Fig. 3, the bottom Cl $2p$ spectrum for the Cl_2 -saturated Ge(100)- 2×1 surface shows one single spin-orbit-split component (labeled Cl_g), which apparently originates from the Cl-Ge surface species. The Cl $2p$ spectrum (second to bottom) for the Cl-terminated 0.8-ML-Si/Ge(100)- 2×1 surface also exhibits one single spin-orbit-split component with a similar binding energy position and, therefore, this component is responsible for the Cl-Ge surface species. The S component of the corresponding Ge $3d$ spectrum (Fig. 1) vanishes upon Cl termination and a component (labeled GeCl) appears at a binding energy 0.61 eV higher than bulk Ge. The new component corresponds to a GeCl species since its binding energy shift is close to the reported value of ~ 0.6 for GeCl.⁶ Upon annealing to 550 K, the Si $2p$ spectrum in Fig. 2 includes a small second component on the higher binding energy side, as marked by an arrow. As the annealing temperature increases to 680 K, the new component (labeled SiCl) grows, while the intensity of the B component falls. The absolute intensities of the SiCl and the B components are plotted in Fig. 4(b). The SiCl component can be attributed to the SiCl surface species, because its binding energy shift of +0.89 eV is close to that found for the SiCl species on the Si(100) and Si(111) surfaces.¹³ During successive an-

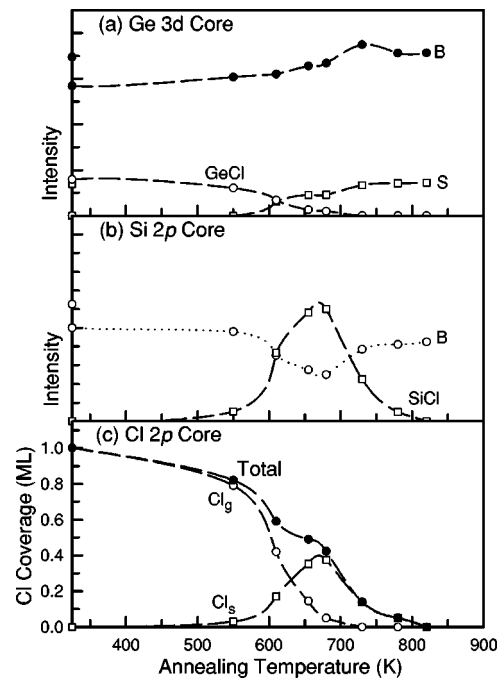


FIG. 4. Intensities of the individual components derived from the (a) Ge $3d$, (b) Si $2p$, and (c) Cl $2p$ core-level spectra. The extra data points at 325 K (on the Y axis) mark the intensities of relevant components before Cl_2 exposure.

nealing to 680 K, the intensity of the GeCl component in the Ge $3d$ spectra (Fig. 1) also decreases, as depicted in Fig. 4(a), and a second component (labeled Cl_s) in the Cl $2p$ spectra (Fig. 3) arises at a binding energy 0.64 eV higher than for Cl_g . The normalized integrated intensities of the Cl_g and Cl_s components in Fig. 3 account for the relative abundance of surface Cl-Ge and Cl-Si species and are plotted in Fig. 4(c). The intensity of the total initial Cl coverage is about 1 ML, as suggested in Refs. 14 and 15.

As Fig. 4(c) depicts, the coverage of Cl gradually decreases to only ~ 0.8 ML at around 550 K. Since Cl-Ge bonds are weak and the etch product $GeCl_2$ desorbs at ~ 620 K on the Cl:Ge(100) surface,¹⁶ a small amount of Cl_2 is likely to be recombinatively desorbed at this temperature range. The Cl coverage decreases more rapidly between 550 and 620 K in the form of Cl_2 or $GeCl_2$.¹⁹ In Figs. 4(b) and 4(c), it is discernible that the intensity evolution of the SiCl component closely resembles that of the Cl_s component in the Cl $2p$ spectra, strongly implying that the formation of the Cl-Si bonds on the surface. Since Cl atoms can only form single bonds and they always terminate the surface. Thus, the formation of the Cl-Si bonds denotes the elimination of existing Cl-Ge bonds, leading to the decrease in the intensity of the GeCl component, as shown in Fig. 4(a). This replacement of Cl-Si bonds with Cl-Ge bonds suggests that the deposited Si atoms, which have indiffused into the subsurface region, must move upwards and undergo place exchange with Ge atoms bonding with Cl. As shown in Fig. 4(c), about 0.5 ML of chlorine atoms remain on the surface at 680 K and mostly bond with Si. Above 680 K, the intensity of Cl $2p$ declines more rapidly, as indicated by the re-

duction in Cl $2p$ intensity. After complete desorption of Cl at 820 K, the integrated intensity of Ge $3d$ remains almost unchanged while that of Si $2p$ is $\sim 33\%$ lower than before Cl adsorption. This means that ~ 0.25 ML of the total (0.8 ML) deposited Si atoms is removed from the sample. Therefore, the desorption product around 700 K is in the form of SiCl_2 . This desorption temperature is appreciably lower than the SiCl_2 desorption peak (~ 830 K) on the $\text{Cl}:\text{Si}(100)\text{-}2 \times 1$ samples, which is likely due to the fact that the surface Cl–Si species are now bonded with the subsurface Ge and that Ge–Si bonds are weaker than that of Si–Si bonds.

For a monolayer Si deposited $\text{Ge}(100)\text{-}2 \times 1$ surface, a theoretical study 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 nonsegregated (Si–Si dimer terminated) surface.⁷ Chlorine adsorption dramatically reverses the situation: 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.⁸ Therefore, thermodynamic forces drive the replacement of the Cl–Ge bonds by Cl–Si, upon thermal activation. The occurrence of the Si–Ge place exchange on the $\text{Cl}:\text{Si}/\text{Ge}(100)$ surface has been similarly observed during atomic hydrogen exposure on the Ge-covered $\text{Si}(100)$ surface.²⁰ To explain the kinetics of the place exchange between Ge and Si, the authors in Ref. 20 proposed a dimer-vacancy diffusion-assisted mechanism, in which the exchange only proceeds via missing dimer vacancies in unit of dimers. Upon 680-K annealing of the Cl-terminated 0.8-ML–Si/Ge(100) sample, Figs. 2, 4(b), and 4(c) show that only about 0.5 ML Si moves to surface to form Cl–Si bonds, whereas, the intensity of SiCl component

is 1.2 times that of the bulk component before annealing. If the simple layer attenuation model is with ~ 3.3 Å escape depth,¹⁷ the Si atoms average moves ~ 2 atomic layers upward to exchange with Ge. Therefore, the exchange mechanism (in which the exchanged Si and Ge layers are next to each other) proposed in Ref. 20 is not applicable here and the atomic detail for the exchange of Cl–Ge and Cl–Si species is not clear at this point. Since both the surface Si and Ge intermixing on $\text{Si}(100)$ ²¹ and Si indiffusion on $\text{Ge}(100)$ ¹⁸ have been found to occur at near room temperature without the introduction of defects, the activation energies of these surface reactions appear much lower than intuitive expectation.

In summary, the chemical-state resolved Ge $3d$, Si $2p$, and Cl $2p$ core-level spectra demonstrate that 0.8-ML deposited Si indiffuses about 2 atomic layers deep on $\text{Ge}(100)\text{-}2 \times 1$ and that the 0.8-ML–Si/Ge(100) surface has a fully Ge-terminated structure. Cl adsorption reverses the Si indiffusion upon annealing. These results are in excellent agreement with recent theoretical findings that the energy for a segregated structure is lower than that of the nonsegregated Si–Si dimer terminated surface and that the Cl–Si–Si–Cl monochloride surface is energetically much more favorable than the Cl–Ge–Ge–Cl surface. Above 680 K, chlorine desorbs in the form of SiCl_2 , although the top layer of the starting 0.8-ML–Si/Ge(100) surface consists of Ge–Ge dimers only.

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