

Stability and mechanism of selective etching of ultrathin Ge films on the Si(100) surface upon chlorine adsorption

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This work investigates the effect of chlorine termination on the stability and the etching of ultra thin Ge layers on a Si(100) surface, using scanning tunneling microscopy (STM) and synchrotron radiation photoemission spectroscopy. The initial growth of Ge on the Si(100) surface is known to occur layer by layer. The intensities of the Ge $3d$, Si $2p$, and Cl $2p$ core levels, after the chlorine passivation of Ge/Si(100) surfaces, together with the STM images reveal that most of the deposited Ge atoms have been randomly dispersed on the surface layer during initial submonolayer growth. They occupy only $\sim 90\%$ of the surface after a 2-ML (monolayer) coverage. Chlorine termination drastically alters the atomic composition of the surface (dimer) layer and in the thin films when annealing at elevated temperatures occurs. Specifically, Cl termination of the Ge/Si(100) surfaces causes Ge, which initially form Cl-Ge bonds in the surface layer, to move into the subsurface layers after annealing at 650–750 K. Silicon is extracted from the subsurface layers to form Cl-Si bonds. Above 900 K, chlorine is desorbed in the form of SiCl_2 , leaving the initial thin Ge films on the Si(100) surface almost intact.

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I. INTRODUCTION

SiGe alloys, multilayers, and strained SiGe/Si heterostructures are technologically important because they have numerous applications in optoelectronics, as well as wireless and broadband communication.¹ Si/Ge overlayers also serve as a fundamental model system to improve our understanding of semiconductor surfaces and interfaces.^{2,3} The dangling-bond energy of Ge-Ge dimers is less than that of Si-Si dimers, so that a simplified scenario for the growth of Si/Ge overlayers is known.^{4–6} The growth of Ge on the Si(100) surface follows the Stranski-Krastanov growth mode. At a typical growth temperature between 600 K and 1000 K, the first three monolayers will be adsorbed in a layer-by-layer fashion and, therefore, the Ge/Si interface is quite abrupt. In contrast, adsorbed Si atoms diffuse into the subsurface sites when they are deposited on a Ge(100)- 2×1 surface, which leads to a nonabrupt Si/Ge interface.⁷

The chemical etching of semiconductor materials is an important process in the making of integrated circuits and nanoscale devices. Selective etching, whereby an etchant attacks one material, while leaving the adjacent material relatively unaffected, is frequently required in the making of complicated devices. A detailed understanding of the surface reactions that occur during etching and the effect of etchants on thin films is essential to adequately control the fabrication of nanoscale devices.^{8,9} The precise control of the etching rates of different layers in the SiGe systems often involves the use of chlorine, hydrogen chloride, and the related halogen compounds. Chlorinated silicon and germanium compounds, such as SiCl_4 , Si_2Cl_6 , and GeCl_4 , are also commonly used in Si and Ge epitaxy. Hence, the interaction of chlorine atoms with Si/Ge surfaces and interfaces has attracted much attention. Several different techniques, including x-ray photoelectron spectroscopy,^{10–12} temperature programmed desorption,^{13,14} and scanning tunneling

microscopy¹⁵ (STM) have been used to examine the adsorption and thermal desorption of chlorine on Si and Ge surfaces. Previous reports have shown that the Cl_2 molecules on (100) surfaces dissociatively chemisorb on the dangling bonds of surface dimers, and that the thermal removal of Cl from a Si(100)- 2×1 :Cl surface occurs only by the desorption of SiCl_2 (and a small amount of SiCl_4 , Refs. 13 and 14); similarly, the thermal removal of Cl from Ge(100)- 2×1 :Cl proceeds via the desorption of GeCl_2 .¹⁶ This study utilizes both synchrotron radiation core-level photoemission spectroscopy and STM to examine the Cl-terminated ultrathin Ge films on Si(100) surfaces annealed at various temperatures. Si and Ge atoms bonded to Cl will undergo large changes in their Si $2p$ and Ge $2p$ core-level binding energies. The Ge- and Si-shifted Cl $2p$ core-level components are also well separated because of the difference between the charge transfer of the Cl-Si bonds and that of the Cl-Ge bonds. STM yields a direct view of the atomic structure of the surface; photoemission studies of the core levels provide a strong spectroscopic contrast between atoms in different environments. The results demonstrate that Si is segregated to the Ge/Si(100)- 2×1 :Cl surface to form Cl-Si bonds which replace Cl-Ge bonds at around 700 K. Ge in the surface layer moves into the subsurface layers, suggesting that the formation of more hetero-Ge-Si bonds does not increase the energy as much as the stronger Cl-Si bonds reduces it. Above 850 K, chlorine is desorbed in the form of SiCl_2 and therefore, the initial thin Ge film on the Si(100) surface remains nearly intact.

II. EXPERIMENTAL DETAILS

The photoemission spectra were observed at the Taiwan Light Source laboratory in Hsinchu, Taiwan. Synchrotron radiation from a 1.5-GeV storage ring was dispersed by a wide-range spherical grating monochromator. The photocur-

rent from a gold mesh positioned in the synchrotron beam path was monitored to measure the relative incident photon beam flux. Photoelectrons were collected 15° from the surface normal and analyzed by a 125-mm hemispherical analyzer in a μ -metal shielded UHV system. The overall energy resolution was less than 120 meV. The on-axis Si(100) samples were sliced from boron-doped wafers that had an electrical resistivity of around $10 \Omega \text{ cm}$, which corresponds to a dopant concentration of $\approx 1.5 \times 10^{15} \text{ cm}^{-3}$. The initial clean Si(100) surfaces were obtained by Joule heating to $\sim 1450 \text{ K}$ for a few seconds after degassing at $\sim 900 \text{ K}$ for many hours. The Ge deposition, Cl_2 adsorption, and annealing were done *in situ* in UHV conditions. The substrate heating was accomplished by passing a controlled dc current directly through the sample. The Ge deposition on a clean Si(100) sample was performed by atomic layer epitaxy (ALE), i.e., 15-L (1 langmuir = 10^{-6} torr sec) digermane saturating exposure at $\sim 325 \text{ K}$ followed by thermal annealing at 950 K to desorb the hydrogen. Digermane (Voltaix, ultrahigh purity grade, 20% in He) was introduced into the chamber through a precision leak valve. Previous studies have shown the amount of Ge deposited in a adsorption-annealing cycle to be about 0.4 ML (monolayer).¹⁷ Here, 1 ML is defined as the site density for a unreconstructed Si(100) surface, i.e., $5.76 \times 10^{14} \text{ atoms/cm}^2$. Chlorine molecules were introduced to the sample surface through a leak valve and a stainless-steel tube.

III. RESULTS AND DISCUSSION

A. STM results

A clean Si(100) surface is formed by rows of Si-Si dimers with each atom of a dimer having a dangling bond. A chlorine atom prefers to form a single bond. Therefore, upon exposure to a clean Si(100) surface, Cl_2 molecules will be dissociatively chemisorbed onto the dangling bonds to form dichloride (Cl-Si-Si-Cl) species. The dimerized structure remains the same, exhibiting no buckling between the two Si atoms.¹⁵ After 0.4-ML Ge is deposited by 1 ALE cycle, the Ge/Si(100) surface will consist of Si-Si, Si-Ge, and Ge-Ge dimers, and will exhibit an analogous dimer structure to that of the clean Si(100) surface.¹⁷ These three kinds of dimers will be converted into Cl-Si-Si-Cl, or Cl-Si-Ge-Cl, or Cl-Ge-Ge-Cl species after Cl_2 exposure at near room temperature; the Cl-terminated 0.4-ML-Ge/Si(100) surface shows the same apparent 2×1 dimer structure as shown in Fig. 1(a). This high-resolution image reveals two kinds of dimer atoms—one much brighter than the other. A previous report has shown that these brighter and darker atoms correspond to Cl adsorbed on Ge and Si, respectively.¹⁸ The two kinds of chlorine have no obvious order. The coverage of the bright atoms is around 0.33 ML, less than the expected 0.4 ML. This result suggests that, after ALE is performed, some fraction of the deposited Ge atoms are not in the top surface layer to adsorb Cl. Figures 1(b) and 1(c) display images taken after the successive annealing of the Cl-terminated 0.4-ML-Ge/Si(100) surface at 740 K and 1000 K for 1 min. At 740 K , most of the Cl atoms remain on the surface (as indicated by the photoemission results to be discussed in the

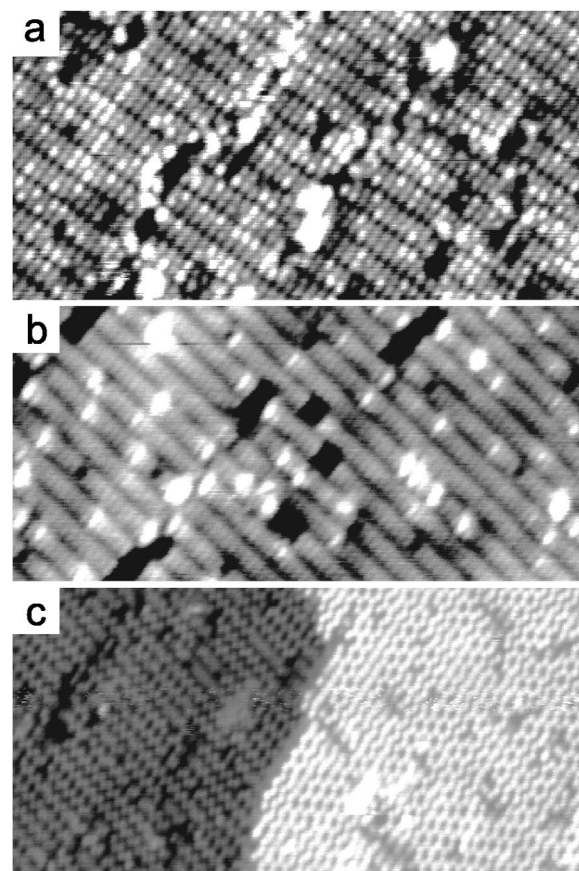


FIG. 1. STM images of the Si(100) surface (a) after 1 cycle of Ge ALE growth and Cl_2 saturation exposure were performed, and the same surface following annealing at (b) $\sim 750 \text{ K}$ and (c) 1000 K . The bright and dark atoms in (a) correspond to Cl adsorbed on Ge and Si, respectively. The bright dimers in (b) correspond to dangling-bond pairs of Ge-Ge dimers. The scanned areas are about $80 \times 160 \text{ \AA}^2$ for (a,b) and $130 \times 260 \text{ \AA}^2$ for (c). The sample bias used was (a) $+2.2 \text{ V}$, (b), (c) -2.0 V .

following section). There are notable vacancy clusters and elongated bright spots each occupying a dimer site. Unlike Fig. 1(a), Fig. 1(b) shows that the surface Cl atoms have the same apparent height, implying that they bond mostly to the same atomic species and that most of the surface species will either be Cl-Si-Si-Cl or Cl-Ge-Ge-Cl, not Cl-Si-Ge-Cl. Figure 1(c) shows that the surface annealed at 1000 K consists of rows of buckled dimers, very similar to the 0.4-ML-Ge/Si(100) surface before Cl termination.¹⁷

B. Photoemission results for the 0.4-ML-Ge/Si(100)- 2×1 surface

High-resolution core-level photoemission spectroscopy can be used to distinguish atoms at nonequivalent sites and in different chemical bonding configurations, according to shifts in their binding energy.¹⁹ Figures 2(a), 2(b), and 2(c) show the respective surface-sensitive Cl $2p$, Ge $3d$, and Si $2p$ core-level spectra (circles), and their decomposition into constituent components from the 0.4-ML-Ge/Si(100)- 2×1 surface and from the same surface after chlorine termination

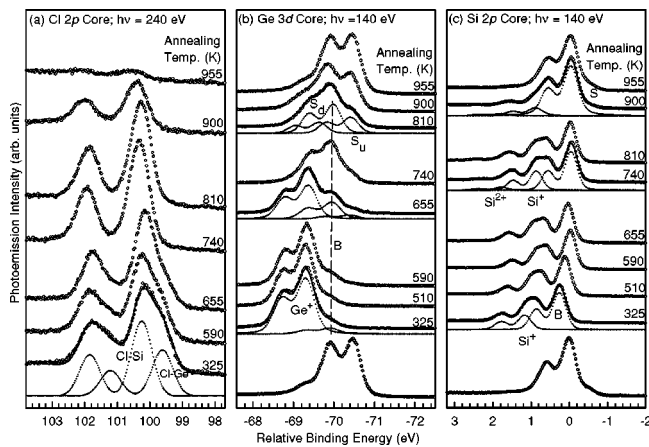


FIG. 2. Photoemission spectra (circles) and fits (solid curves) for the (a) Cl $2p$, (b) Ge $3d$, and (c) Si $2p$ core levels of the 0.4-ML-Ge/Si(100) sample [bottom spectra in (b) and (c)], the same sample after Cl termination at 325 K and successive annealing for 60 s at various temperatures, as indicated. The 0.4-ML-Ge/Si(100) sample was obtained by growing Ge on a clean Si(100) surface with 1 cycle of Ge atomic layer epitaxy. The curves, labeled ClSi, ClGe, Ge^+ , B, S_u , S_d , Si^+ , and Si^{2+} , are a result of decomposition into individual components, each with a pair of spin-orbit-split peaks. The B component is derived from the bulk, while S, S_u , and S_d are associated with the top surface layer. The Cl-Si, Cl-Ge, Si^+ , and Ge^+ components are emitted from the Cl-Si-Si-Cl, Cl-Ge-Ge-Cl, and Cl-Si-Ge-Cl surface species. The B components correspond to Si and Ge in the subsurface region. The relative binding energy of the Si $2p$ core levels refers to the Si $2p_{3/2}$ line of the B component in the bottom spectrum. The relative binding energy of Cl $2p$ and Ge $3d$ refers to the corresponding Si $2p_{3/2}$ line of the B component, to eliminate the band-bending effect.

at 325 K and high-temperature annealing. All fitting was least-squares fitting.^{6,17,19} Each component that consists of a pair of spin-orbit-split doublets is assumed to have the same Voigt line shape. Figure 3 plots the intensities associated with the relevant components. Before annealing at higher temperatures, the Cl $2p$ core level [bottom spectrum in Fig. 2(a)] has two components that correspond to emissions from the Cl atoms attached to Si and Ge (labeled Cl-Si, and Cl-Ge), respectively.¹⁸ The difference between the binding energy of Cl-Si and that of Cl-Ge, 0.64 eV, is rather large when the similar electronic structure of Si and Ge is considered.¹⁹ Without performing detailed corrections for defect effects, the chlorine coverage is nominally 1 ML because each surface atom (Si or Ge) has a dangling bond. The intensity ratio (38:62) of the Cl-Ge and Cl-Si components indicates that the Ge and Si coverage on the topmost surface layer is 0.38 and 0.62 ML, respectively, after 1 cycle of Ge ALE. The corresponding Si $2p$ spectrum [the second from the bottom in Fig. 2(c)] displays two spin-orbit doublets (labeled Si^+ and B). The chemical shift of Si^+ relative to B, which is ≈ 0.91 eV, is consistent with a nominal charge state of +1 for Si directly bonded to Cl.^{12,19} Consequently, the Si^+ component originates from Si directly bonded to Cl, while the B component originates from bulk Si. Similarly, the corresponding Ge $3d$ line shape in Fig. 2(b) includes a dominated Ge^+ component and another discernible B component. Ge atoms

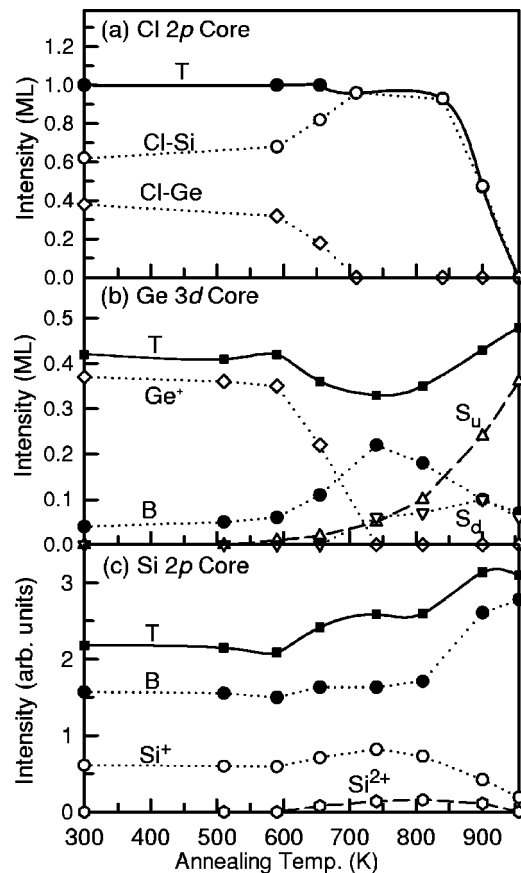


FIG. 3. Evolution of the intensity of the relevant photoemission spectra in Fig. 2. The Cl coverage is scaled to 1.0 ML, the Ge^+ (ClGe) coverage is 0.38 ML, and the Si^+ (ClSi) coverage is 0.62 ML. The dashed and the solid lines are simple guides.

adsorbed on the dimer layer contribute to the Ge^+ component after Cl termination and will, therefore, account for the coverage of the Cl-Ge component (0.38 ML). The intensity of the B component is about one-ninth that of Ge^+ . Accordingly, the amount of Ge atoms that are present under the surface layer during the growth is ~ 0.04 ML if we neglect the effect of layer attenuation. Figure 3 shows that the annealing of the chlorine-terminated 0.4-ML-Ge/Si(100) surface substantially changes the relative intensity of many of the components, i.e., the population of the corresponding atoms in the different thin-film layers. Below 810 K, the total intensity of the Cl $2p$ spectra [curve T in Fig. 3(a)] remains fairly constant, implying that most of the surface chlorine atoms remain on the surface. However, between 590 K and 740 K, the intensity of the Cl-Si component increases at the expense of the Cl-Ge component. When the surface is annealed at more than 740 K, the intensity of the Cl-Ge component vanishes; the corresponding Cl $2p$ spectrum in Fig. 2(a) therefore includes only the Cl-Si component, suggesting that all the surface chlorine atoms are bonded only with Si atoms. The replacement of the surface Cl-Ge bonds with Cl-Si bonds is also evident from the change in intensity of the Ge $3d$ and Si $2p$ spectra as shown in Figs. 3(b) and 3(c). Between 600 K and 740 K the intensity of the Si^+ component increases, while the Ge^+ component gradually vanishes.

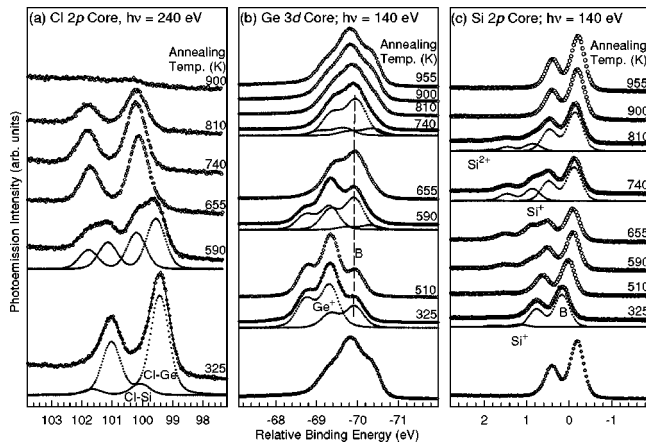


FIG. 4. Photoemission spectra (circles) and fits (solid curves) for the (a) Cl $2p$, (b) Ge $3d$, and (c) Si $2p$ core levels, similar to those in Fig. 2. The only difference is that the beginning sample is covered by a 2.0-ML-Ge layer after 5 cycles of Ge ALE are performed.

After annealing at 740 K, the Ge $3d$ spectrum consists mainly of the B component and two smaller doublets, S_u and S_d . In buckled Ge-Ge or Ge-Si dimers S_u and S_d are commonly attributed to emissions from the up and down atoms, respectively.²⁰ Ge-Ge and Ge-Si dimers are evident in Fig. 1(b) as bright protrusions. Their paired dangling bonds typically allow for a more efficient electron transfer between the tip and the surface, leading to the larger apparent height shown in the STM images.²¹ The Si $2p$ spectra in Fig. 2(c) show that the intensity of Si^+ increases during 810 K annealing and that a new component (labeled Si^{2+}) emerges. The chemical shift of Si^{2+} relative to B, of around 1.82 eV, is consistent with a nominal charge state of +2 for Si directly bonded to two Cl atoms. A theoretical study has found that after 1-ML Si is deposited on a Ge(100) surface, the surface energy of the Si-terminated structure is 0.38 eV/dimer higher than that of the segregated structure, in which Si indiffuses and occupies the second layer while Ge forms the surface layer.²² The same study has also determined that the chlorine passivation of the Si/Ge(100) surface will dramatically reverse 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. Experimental work has verified that the thermodynamic driving force behind the energy differences is sufficiently large to cause the exchange of Cl-Ge bonds with Cl-Si bonds upon thermal activation.²³ Interestingly, the same theoretical approach has found that a 1-ML-Ge film on a Si(100) surface remains thermodynamically stable after chlorine termination, since the Cl-Ge-Ge-Ge-terminated surface is 0.23 eV/dimer less than the segregated (Cl-Si-Si-Cl-terminated) structure.²⁴ The Cl-induced instability (i.e., Si segregation) of ultrathin Ge films on a Si(100) surface found herein suggests that the hetero-Ge-Si bonds formed by the incorporation of Ge into the bulk Si environment will raise less chemical and strain energy than that determined by the aforementioned calculation. Rather, the energy difference between the Cl-Ge and Cl-Si bonds is

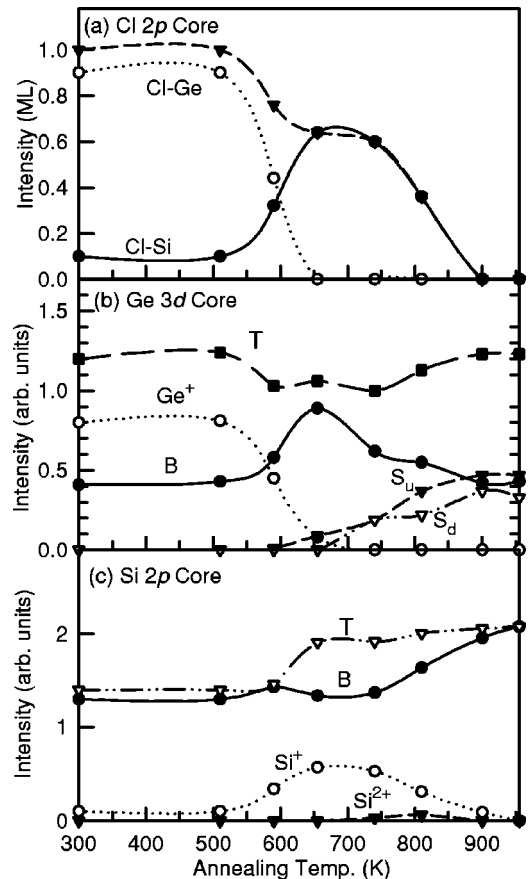


FIG. 5. Evolution of the intensity of the relevant photoemission spectra in Fig. 4. The Cl coverage is scaled to 1.0 ML; the Ge⁺ (ClGe) coverage is 0.9 ML; and the Si⁺ (ClSi) coverage is 0.1 ML. The dash and the solid lines are simple guides.

likely to be the dominant factor driving reactions in the Cl-terminated Ge films, as in the case of Cl:Si/Ge(100).²³

C. Photoemission results for the 2-ML-Ge/Si(100) surface

Since ~ 0.4 ML Ge is deposited on the Si(100) surface during each Ge ALE cycle, the Ge coverage is estimated to be about 2.0 ML after 5 cycles of growth. The Cl $2p$, Ge $3d$, and Si $2p$ core-level photoemission spectra for the 2-ML-Ge/Si(100) sample were also measured and fitted, and the results are shown in Figs. 4 and 5. In Fig. 5, the intensity of the Cl-Ge, Cl-Si, Ge⁺, Si⁺, and B components reveals that the dimer layer of the 2-ML-Ge/Si(100) surface consists of 0.9 ML of Ge and 0.1 ML Si. After the sample is exposed to Cl₂ and annealed at 655 K, the coverage of the surface Cl-Si bonds increases to 0.64 ML (from 0.1 ML) while Cl-Ge falls to 0 (from 0.9 ML). These observations imply that the remaining 0.64-ML chlorine atoms only form Si-Cl bonds, so the rest of the surface mostly consists of Ge-Ge dimers. Unlike the 0.4-ML-Ge coverage, the Cl $2p$ signal drops by about 40% and the Si^{2+} component is negligible. Although the reaction temperature (~ 655 K) is high enough to desorb GeCl₂ on a Cl-terminated Ge(100) surface, chlorine is likely to be desorbed in the form of Cl₂ at this stage, since this temperature is too low for SiCl₂ desorption, and the amount

of Ge atoms is not reduced (as discussed in the following section). The reaction temperature (~ 655 K) is lower than ~ 750 K for the sample with a coverage of 0.4-ML Ge, perhaps because partially recovered Ge-Ge dimers provide additional reaction pathways.

D. Selective Si etching

The etching product GeCl_2 will be desorbed from the Ge(100) surface at ~ 620 K, much lower than ~ 900 K for SiCl_2 to be desorbed from Si(100).¹⁰ In Fig. 2, we see that the Cl 2*p* signals decline above 810 K and vanish at 1000 K. The STM image [Fig. 1(c)], showing rows of buckled dimers, resembles the images taken before exposure to Cl_2 . The Ge 3*d* and Si 2*p* spectra [upper part of Figs. 2(b) and 2(c)] after complete chlorine desorption can be seen to have line shapes that are very similar to those [bottom of Figs. 2(b) and 2(c)] before exposure to Cl_2 at near RT. Furthermore, the integrated intensities of the Ge 3*d* spectra before and after the Cl_2 adsorption and desorption are approximately equal. In the case of 2-ML coverage shown in Fig. 5(a) the integrated Cl 2*p* intensity has fallen significantly at ~ 600 K and fades away at ~ 850 K. However, the line shape and the intensity of the Ge 3*d* and Si 2*p* spectra after complete chlorine desorption [top parts of in Figs. 4(b) and 4(c)] again resemble those before Cl_2 exposure [bottom parts of spectra in Figs. 4(b) and 4(c)]. These findings suggest that the initial thin Ge layers (up to 2 ML) on the Si(100) surface will essentially be the same, before and after all the reactions occur, i.e., chlorine adsorption, Si segregation, exchange of Cl-Ge and Cl-Si, and chlorine desorption. Since the amount of Ge on the Ge/Si(100) surfaces remains the same, the adsorbed chlorine atoms will predominately leave the surface in the form of SiCl_2 (maybe some Cl_2 , but not GeCl_2) during annealing processes. In other words, Si will be preferentially consumed during the etching with Cl_2 molecules of ultra thin Ge films on Si. Similar observations of selective etching

have also been reported for the Si/Ge system.^{23,25} These highly asymmetric Si and Ge etching rates on Ge/Si surfaces are unsurprising, given that there are no Cl-Ge bonds present on the surface above 740 K, even though the grown Ge layers float on top on the relatively sharp Ge/Si interface.

IV. SUMMARY

This study utilizes core-level photoemission spectroscopy and scanning tunneling microscopy to examine the Cl-terminated ultrathin Ge films on Si(100) surfaces after annealing at various temperatures. The two techniques form a powerful surface probing combination. STM can yield a direct view of the atomic structure of the surface; photoemission analysis of the Cl 2*p*, Ge 3*d*, and Si 2*p* core levels can provide a strong spectroscopic contrast between atoms in different chemical environments. The STM images show that a dimerized structure remains the basic atomic building blocks throughout the chlorine termination and annealing processes of the thin Ge films on the Si(100) surface. An increase in the Cl-Si related core-level peaks, the vanishing of the core-level components due to the Cl-Ge species, and the loss of the STM contrast between the Cl-Si and Cl-Ge features clearly demonstrate that Si in the subsurface layers will be segregated to the surface to form Cl-Si bonds that will replace the Cl-Ge bonds at around 700 K. Above ~ 810 K, chlorine is desorbed in the form of SiCl_2 , although the top layer of the initial 2-ML-Ge/Si(100) surface is composed primarily of Ge-Ge dimers.

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