

行政院國家科學委員會專題研究計畫期中報告

應用染色法研究晶體表面結構與複雜表面上反應的物理機制(1/3)

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計畫編號：NSC 92 - 2112 - M - 009 - 039

執行期間： 92年8月1日至93年7月31日

計畫主持人：林登松 教授 交通大學物理研究所

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計畫參與人員：楊鎧民、謝明峰、吳俊緯、林昌廷、馮世鑫、鄭人夔、張君黛 交大物理所

一、進度與結果簡要說明

本年度我們主要研究重點在以同步輻射核心層光電子激發術及配合穿隧效應顯微鏡 STM 之實空間影像來研究 Chlorine 在 Ge/Si(100)-2x1 樣品上的選擇性侵蝕現象。我們得到是很好的數據，也已分析完畢，其中一些結果已發表”Stability and Mechanism of Selective Etching of Ultra Thin Ge Films on the Si(100) Surface Upon Chlorine Adsorption” (Physical Review B, 2004)，部份結果報導如下。我們目前也完成同步輻射核心層光電子激發譜研究 HCl 在 Si(100)面的列解吸附，正在檢視 STM 之 HCl/Si(100)-2x1 表面在吸附氯化氫過程的實空間影像，探討各種反應模型，並嘗試 Monte Carlo Simulation 以對這些有趣的資料有更好的了解後，完整報導發表。其他嘗試性的困難工作如 UHV non-contact AFM 對 SiO₂ 薄弱之研究也都積極進行中。

二、一些數據與簡要分析

This study applies both synchrotron radiation core-level photoemission spectroscopy and scanning tunneling microscopy to elucidate the Cl-terminated ultra thin Ge films on the Si(100) surface upon annealing at various temperatures. The core-level photoemission measurement is based on the observation that Si and Ge atoms bonded to Cl undergo large changes in binding energy in their Si 2p and Ge 2p core-level and that the Ge- and Si-shifted Cl

2p core levels are 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 surface atomic structure; photoemission studies of the core levels provide strong spectroscopic contrast between atoms in different environments. The results demonstrate that Si segregates to the surface to form Cl-Si bonds in replacement of 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 by as much as the stronger Cl-Si bonds reduces it. Above 850K, chlorine desorbs in the form of SiCl₂ and therefore, the starting thin Ge film remains nearly intact on the Si(100) surface.

A. STM result

The clean Si(100) surface is formed by rows of Si-Si dimers and each atom on a dimer has a dangling bond. A chlorine atom prefers to form a single bond. Therefore, upon exposure to a clean Si(100) surface, Cl₂ molecules dissociatively chemisorb onto dangling bonds of Si-Si dimers and the dichloride (Cl-Si-Si-Cl) species forms. The dimerized structure remains

the same and exhibits no buckling between the two atoms in a dimer [1]. After 0.4-ML Ge is deposited by one cycle of ALE, the Ge/Si(100) surface consists Si-Si, Si-Ge, and Ge-Ge dimers and exhibits analogous dimer structure with that of the clean Si(100) surface [1]. These three kinds of dimers, upon Cl₂ exposure at near room temperature, are simply converted into Cl-Si-Si-Cl, or Cl-Si-Ge-Cl, or Cl-Ge-Ge-Cl species; the Cl-terminated 0.4-ML-Ge/Si(100) surface apparently shows the same 2x1 dimer structure as displayed in Fig. 1(a). As this high-resolution image reveals, two kinds of dimer atoms are present - one is much brighter than the other. A previous report has shown that the bright and dark atoms correspond to Cl adsorbed on Ge and Si, respectively [1]. The two kinds of chlorine have no apparent ordered arrangement. The coverage of the bright atoms is around 0.33 ML, less than the expected 0.4 ML. This result suggests that a fraction of the deposited Ge atoms after ALE is performed are not on the top surface layer to adsorb Cl.

Figures 1(b) and 1(c) display the real space images formed after successively annealing the Cl-terminated 0.4-ML-Ge/Si(100) surface to 740K and 1000K for 1 min. At 740 K, most Cl atoms remain on the surface (as indicated by the photoemission results to be discussed in the next section). Notably, there are vacancy clusters and some elongated bright spots each occupy a dimer site. Unlike Fig. 1(a), Fig. 1(b) shows that atoms in dimers have the same apparent height, implying that surface Cl atoms bond mostly to the same atomic species and that most dimers are either Cl-Si-Si-Cl or Cl-Ge-Ge-Cl, but not Cl-Si-Ge-Cl. Also revealed by Fig. 1(b) are the bright spots that

each occupies a dimer site. Figure 1(c) shows that the surface after annealing at 1000K is formed by rows of buckled dimers, very much similar to the 0.4-ML-Ge/Si(100) surface before Cl termination.

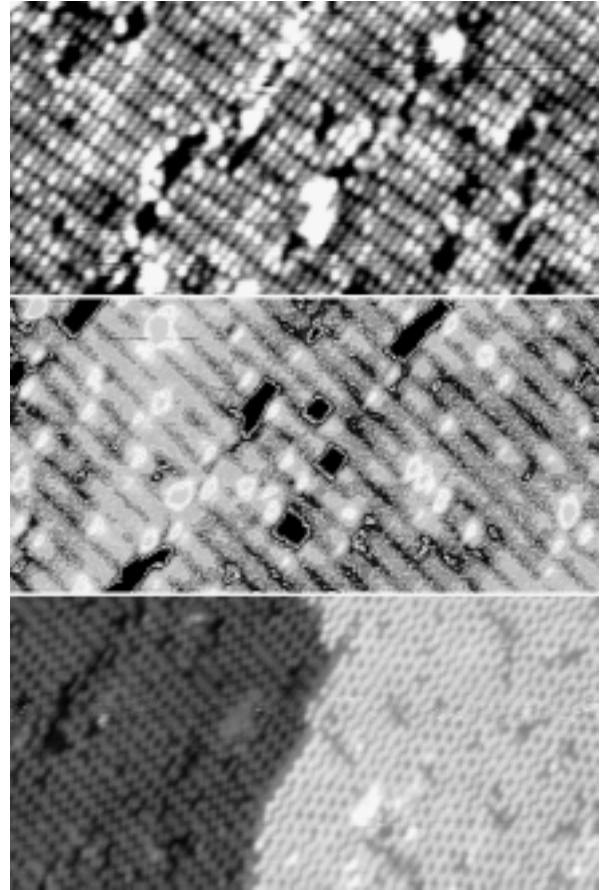


Fig. 1

B. Photoemission Results for the 0.4-ML-Ge/Si(100)-2x1 Surface

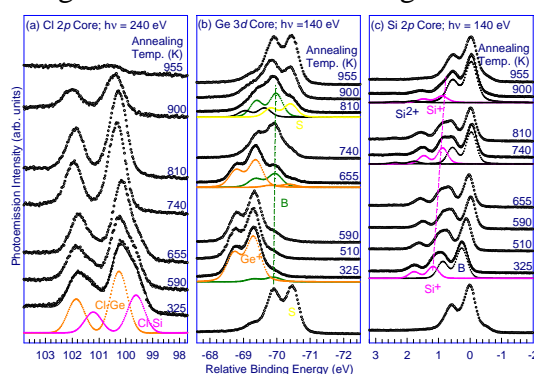
High-resolution core-level photoemission spectroscopy distinguishes atoms at nonequivalent sites and in different chemical bonding configurations, according to their binding energy shifts [11]. Figures 2(a), 2(b), and 2(c) show the surface-sensitive Cl 2p, Ge 3d, and Si 2p core-level spectra (circles), respectively, and their decomposition into constituent components from the 0.4-ML-Ge/Si(100)-2x1 surface and from the same surface after chlorine

termination at 325K and successive annealing to higher temperatures, as indicated. All fitting was least-squares fitting. Each component that consists of a pair of spin-orbit split doublets is assumed to have the same Voigt line shape in the analysis []. Figure 3 plots the intensities that are associated with the relevant components.

Before annealing to higher temperature, the Cl 2p core level (bottom spectrum in Fig. 2(a)) has two components that correspond to emission from Cl attached to Si and Ge (labeled Cl-Si, and Cl-Ge), respectively []. The difference between the binding energy of Cl-Si and that of Cl-Ge, 0.64 eV, is rather large in consideration of the similar electronic structure of Si and Ge. Without performing detailed corrections for the effects of the defects, the coverage of chlorine is nominally 1 ML since each surface atom (Si or Ge) has a dangling bond. The intensity ratio (38:62) of the Cl-Ge and Cl-Si components directly indicates that the Ge and Si coverage on the topmost surface layer is 0.38 and 0.62 ML, respectively, after one cycle of Ge ALE. The corresponding Si 2p spectrum (second to bottom spectrum in Fig. 2(c)) displays two spin-orbit-doublets (labeled Si⁺ and B). The chemical shift of Si⁺ relative to B, approximately 0.91 eV, is consistent with a nominal charge state of +1 for the Si directly bonded to Cl []. Consequently, the Si⁺ component originates in Si directly bonded to Cl, while the B component from bulk Si. Similarly, the corresponding Ge 3d line shape in Fig. 2(b) includes a dominating Ge⁺ component and another small, but discernible B component. The deposited Ge atoms which reside on the

dimer layer contribute to the Ge⁺ component upon Cl termination and therefore, account for the coverage of the Cl-Ge component (0.38 ML). The intensity the B component is about one ninth of that of Ge⁺. Accordingly, the amount of Ge atoms that are present under the surface layer during the growth is ~0.04 ML neglecting the effect of layer attenuation.

Figure 3 shows that annealing the



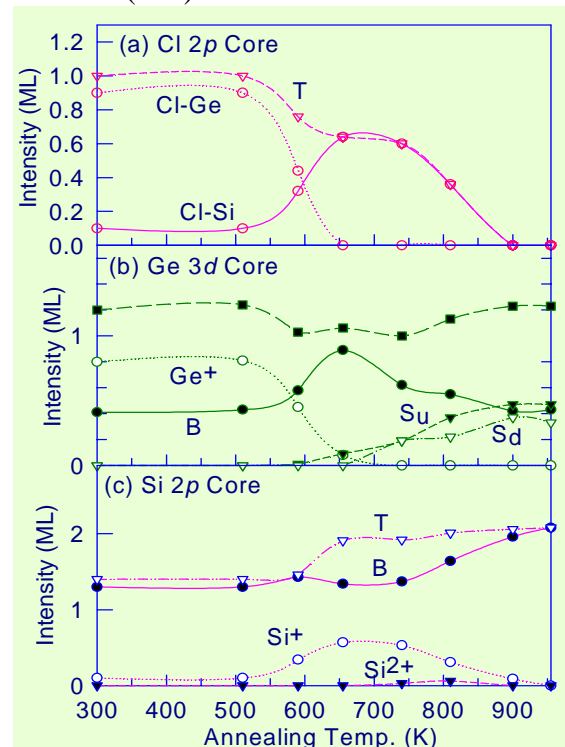
chlorine-terminated 0.4-ML-Ge/Si(100) surface substantially changes the relative intensity of many of the components, or the population of the corresponding atoms in different layers of the thin films. Below 810K, the total intensity of the Cl 2p spectra (curve T in Fig. 3(a)) remains fairly constant, implying that most surface chlorine atoms remain on the surface. However, the intensity of the Cl-Si component increases at the expense of that of Cl-Ge between 590K and 740K. When the surface is annealed above 740K, the intensity of the Cl-Ge component vanishes; the corresponding Cl 2p spectrum in Fig. 2(a) includes only the Cl-Si component, suggesting that all surface chlorine atoms bond 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 Ge 3d and Si 2p spectra in Figs. 3(b) and 3(c). The intensity

of the Si⁺ component increases, while the Ge⁺ component vanishes gradually between 600 and 740K. Upon annealing at 740K, the Ge 3d spectrum consists mainly the B component and two smaller doublets, labeled Su and Sd. The Su and Sd are commonly attributed to emission from the up- and down-atoms, respectively, in the Ge-Ge or Ge-Si dimers with no Cl-termination. The presence of the Ge-Ge or Ge-Si dimers is evident in Fig. 1(b) as bright protrusions because their paired dangling bond states typically allow more efficient electron transfer between the tip and the surface, leading to a larger apparent height in STM images [1]. The Si 2p spectra in Fig. 2(c) show that the intensity of Si⁺ increases during the consecutive annealing to 810K and a new component (labeled Si²⁺) emerges. The chemical shift of Si²⁺ relative to B, of around 1.82 eV, is consistent with a nominal charge state of +2 for the Si directly bonded to two Cl atoms [1].

A theoretic study found that after 1-ML Si is deposited on the Ge(100) surface the energy associated with a segregated structure, in which Si occupies the second layer while Ge-Ge dimers float to the surface, is 0.38 eV/dimer less than that of the nonsegregated Si-Si dimer-terminated surface. The same study also determined that chlorine passivation on the Si/Ge(100) surface 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. Experimental work verified that the thermodynamic driving force behind the energy differences is sufficiently large to

drive the exchange of the Cl-Ge bonds for Cl-Si bonds upon thermal activation. Interestingly, the same theoretical approach found that the 1-ML-Ge film on the Si(100) surface remains thermodynamically stable upon chlorine termination since the Cl-Ge-Ge-Ge terminated surface is 0.23 eV/dimer energetically favored over the segregated (Cl-Si-Si-Cl terminated) structure. The Cl induced instability, i.e. the Si segregation, of the ultra thin Ge films on the Si(100) surface found herein suggests that more hetero-Ge-Si bonds formed by the incorporation of Ge into the bulk Si environment raises the chemical and strain energies less than was determined by the aforementioned calculation. Instead, the energy difference between the Cl-Ge and Cl-Si bonds is likely to be the dominant factor that drives the reactions occurred on the Cl-terminated Ge film as in the case of Cl:Si/Ge(100).



C. Selective Etch of Si

The etch product GeCl_2 desorbs from the $\text{Ge}(100)$ surface at ~ 620 K, much lower than that (~ 900 K) of SiCl_2 from the $\text{Si}(100)$ []. In Fig. 2, the Cl 2p signals decline above 810 K and disappear at 1000 K. The STM image (Fig. 1(c)) shows that the surface, consisting of rows of dimers, is basically identical to that it was exposed to Cl_2 . The Ge 3d and Si 2p spectra (top of Fig. 2(b) and 2(c)) after complete chlorine desorption have line shapes that are very similar to those (bottom of Figs. 2(b) and 2(c)) before Cl_2 exposure at near RT. Furthermore, the integrated intensities of the Ge 3d spectra before and after the Cl_2 adsorption and desorption are approximately equal.

In the case of 2-ML coverage, Fig. 5(a) indicates that the integrated Cl 2p intensity falls significantly at ~ 600 K and fades away at ~ 850 K. However, the line shapes and intensity of the Ge 3d and Si 2p spectra after complete chlorine desorption (top spectra in Figs. 4(b) and 4(c)), again, resemble those before Cl_2 exposure (bottom spectra in Figs. 4(b) and 4(c)). These findings suggest that the initial thin Ge layers (up to 2 ML) on the $\text{Si}(100)$ surface are essentially the same before and after all reactions, i.e. chlorine adsorption, Si segregation, exchange of Cl-Ge and Cl-Si and chlorine desorption occurred. Since the amount of Ge on the $\text{Ge}/\text{Si}(100)$ surfaces remains the same, so adsorbed chlorine atoms leave the surface predominantly in the form of SiCl_2 (and maybe some Cl_2), but not GeCl_2 during annealing processes. Restated, Si is preferentially consumed during the etching of ultra thin Ge films on Si with Cl_2 molecules. Similar observations of selective etching

have also been reported for the Si/Ge system []. These highly asymmetric etching rates for Si and Ge on the Ge/Si surfaces is unsurprising given that no Cl-Ge bonds are present on the surface above 740K, even though the grown Ge layers float on top on the relatively sharp Ge/Si interfaces.

D. Summary

This study utilizes core-level photoemission spectroscopy and scanning tunneling microscopy to elucidate the Cl-terminated ultra thin Ge films on the $\text{Si}(100)$ surface during annealing at various temperatures. The two techniques form a powerful combination of surface probes. STM yields a direct view of the surface atomic structure; photoemission analysis of the Cl 2p, Ge 3d, and Si 2p core levels provide a strong spectroscopic contrast between atoms in different chemical environments. STM images show that a dimer-reconstructed structure remains as the basic atomic building blocks throughout chlorine termination and annealing of the thin Ge films on the $\text{Si}(100)$ surface. The increase of Cl-Si related core-level peaks, the vanishing of the core-level components due to Cl-Ge species, and the loss of the STM contrast between Cl-Si and Cl-Ge atomic features clearly demonstrate that Si in the subsurface layers segregates to the surface to form Cl-Si bonds that replace Cl-Ge bonds at around 700 K. Above ~ 810 K, chlorine desorbs in the form of SiCl_2 , although the top layer of the starting 2-ML- $\text{Ge}/\text{Si}(100)$ surface is composed primarily of Ge-Ge dimers.