行政院國家科學委員會專題研究計畫　成果報告

以創新的方法研究矽鍺晶面上氫分子脫附的物理(3/3)

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行政院國家科學委員會專題研究計畫期末報告

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計畫類別：個別型計畫

計畫編號：NSC　91－2112－M－009－039

執行期間：　91 年 8 月 1 日至 92 年 7 月 31 日

計畫主持人：林登松　教授　　交通大學物理研究所

本成果報告包括以下應繳交之附件：

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中　華　民　國　　92 年　09 月　10 日

行政院國家科學委員會專題研究計畫期末報告

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執行期間：　91 年 8 月 1 日至 92 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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一、摘要

Chlorine termination of mixed Ge/Si(100) surfaces substantially enhances the contrast between Ge and Si sites in scanning tunneling microscopy observations. This finding enables a detailed investigation of the spatial distribution of Ge atoms deposited on Si(100) by atomic layer epitaxy. The results are corroborated by photoemission measurements aided by an unusually large chemical shift between Cl adsorbed on Si and Ge. Adsorbate-substrate atomic exchange during growth is shown to be important. The resulting interface is thus graded, but characterized by a very short length scale of about one monolayer.

二、數據與分析

A detailed understanding of the atomic processes of deposition is essential for the synthesis and manufacturing of nanoscale materials and devices. A system that has attracted much attention in the past decade is the growth of Ge on Si(100).[i,ii,iii,iv] It is of technological interest because of its potential for optoelectronics, wireless and broadband communication, and computing applications.[v] There is also much scientific interest because it is a simple model system suitable for fundamental investigations, both experimental and theoretical.[vi, vii] Indeed, this system has been examined in detail by numerous methods, including scanning tunneling microscopy (STM) and photoemission spectroscopy.[1,2,4,viii,ix] These two techniques form a powerful combination of surface probes, and are the methods chosen for the present study. STM provides a direct view of the surface atomic structure, and past investigations have already yielded a wealth of information. However, it has been proven very difficult to distinguish Si and Ge atoms on the surface due to their similarity in electronic structure, and the problem is compounded by non-uniform apparent buckling of dimers for both the clean and mixed surfaces.[9] Thus, critical growth issues in regard to atomic spatial distribution, atomic exchange, and intermixing remain largely unexplored or unanswered. Photoemission studies of the core levels, likewise, are hampered by a lack of strong spectroscopic contrast between atoms in different environments. The intrinsic surface shifts of core levels can be useful indications of surface chemistry and composition, but for Ge/Si, the shifts are mostly quite small and not fully resolved, and the assignments of some of the components remain uncertain.[2,4,x]

In the present work, we report a new approach that overcomes these difficulties and is based on an idea analogous to the chemical staining method widely employed in optical microscopy of biological samples.

Trials of various "staining agents" have indicated Cl as a suitable choice. Terminating the Ge/Si surface with Cl leads to a large STM contrast between Si and Ge surface sties, thus permitting a detailed counting and characterization of the spatial distributions of the different surface atoms. Photoemission measurements also reveal an unusually large chemical shift between Cl adsorbed on Si and Ge,[xi,xii] thus permitting an independent determination of the surface composition. Measurements of the Si and Ge chemically-shifted core levels provide additional information regarding the surface and subsurface composition. This approach is applied to a study of the growth of Ge on Si(100) by atomic layer epitaxy (ALE) with digermane as the source gas. ALE offers an important advantage over the standard molecular beam epitaxy (MBE) method in that the amount of deposition is quantized (0.4 atomic layer per cycle for the present case).[8] Therefore, process control is easily achieved under wide ranges of experimental conditions. Because of the similarity between Ge and Si, one might expect the ALE growth mode at the initial stage to be similar to that of Si on Si(100) – layer buildup via step flow over an otherwise intact substrate. The lower surface free energy of Ge also favors an abrupt interface.[3] Our results show that, instead, the deposited Ge atoms replace Si atoms at random positions on the surface, resulting in a growing surface composed of a Si/Ge surface alloy. The interface is not abrupt, but the intermixed region is characterized by a very short length scale of a mere one monolayer.

Both Si(100) and Ge(100) form a (2x1) dimer reconstruction, as observed by STM. The same (2x1) dimer structure is also observed for the first few cycles of ALE growth of Ge on Si(100). All dimers appear to be about the same under a variety of biasing conditions,[1,8] making the distinction between Ge and Si highly uncertain. One could imagine that the simplest growth mode would be for the deposited Ge atoms to diffuse on the surface to nearby step edges, where they contribute to step flow as in the growth of Si on Si at similar temperatures. [xiii] A careful STM examination shows that the overall step structure after growth to be similar to that of the original surface. Therefore, step flow does occur for the first few cycles of deposition, but there is no evidence for bands or areas of different chemical compositions neighboring step edges.[8]

It is known that Cl adsorption on pure Si(100) and Ge(100) surfaces saturates the dimer dangling bonds while preserving the basic (2x1) dimer structure. Analyses of STM images are considerably simplified because the resulting dimers are symmetric with no buckling to cause confusion.[xiv,xv] Figure 1(a) shows a STM image of Si(100) after one cycle of ALE deposition (0.4 ML Ge) followed by Cl termination. The two atoms in a dimer are well resolved in this high-resolution image. Clearly, there are two kinds of surface atoms, with one kind being much brighter than the other. The bright atoms are associated with Ge, as the number of such atoms increases as more Ge is deposited. This contrast enhancement is most pronounced for STM images of the empty states with a sample bias ~2 V. An immediate conclusion, based on the spatial distribution of Ge, is that the simple picture of incorporation of diffusing Ge at step edges leading to step flow is incorrect. Rather, the deposited Ge atoms replace Si at random sites on the surface, resulting in both Ge-Ge and Ge-Si dimers with no apparent ordering or organization. Note that a pair of Ge atoms is deposited for each digermane molecule, and the conventional picture for Ge/Si growth involves diffusing dimers as the basic building block for growth.[1,xvi] Yet in the present case isolated Ge atomic sites are abundantly observed, suggesting that individual Ge adatoms are responsible for the growth.

Figure 1 (b) is a much larger-scale scan for a sample deposited with two ALE cycles. The population of the bright (Ge) atoms is now significantly higher. Direct counting of the Ge and Si surface atoms yields a relative measure of the surface Ge and Si coverages. The absolute coverages are obtained by normalizing the sum of Si and Ge coverages to 1 ML. The results are shown in Fig. 2 as diamonds after 0, 1, 2, and 3 cycles of ALE deposition.

Figure 3 displays the Cl 2p core level spectra for Cl-terminated surfaces of Si(100) and the same after 1, 3, and 5 cycles of Ge deposition for Ge coverages of 0.4, 1.2, and 2.0 ML, respectively. For Cl-terminated Si, the two peaks correspond to the spin-orbit splitting of Cl attached to Si (labeled Cl-Si in the figure). With increasing Ge coverages, a new chemically-shifted component, labeled Cl-Ge, emerges and becomes increasingly more intense. This component must correspond to Cl adsorbed on Ge. The difference in binding energy between Cl-Si and Cl-Ge, 0.64 eV, is surprisingly large in view of the similar electronic structure of Si and Ge. This large difference is, however, quite welcome in the present investigation, as the intensity evolution of the two components, obtained by a least-squares fitting of the line shapes, yields a direct measure of the surface Si and Ge coverages. The results, shown in Fig. 2 as circles, are in excellent agreement with the surface coverages obtained by STM counting (diamonds).

Figure 4 shows the Si 2p and Ge 3d core level spectra for the Cl-terminated surfaces with various amounts of Ge deposition. The Si 2p spectrum for the Cl-terminated Si(100) shows two components. The Si^+ component, at a higher binding energy, corresponds to Si directly bonded to Cl, while the B component corresponds to subsurface Si. The chemical shift of Si^+ relative to B, about 0.9 eV, is consistent with a nominal charge state of +1 for the Si directly bonded to Cl.[11] In the same figure, the intensity of Si^+ diminishes for increasing amounts of Ge deposited on the surface. AT a 2-ML Ge deposition (5 cycles of ALE), there is very little Si^+ left, because the sample surface is now nearly fully covered by Ge under the Cl layer. The measured intensity evolution of Si^+ reflects the Si coverage in the dimer layer. The results are shown in Fig. 2 using squares, and are in good accord with those obtained from STM counting and Cl core level intensity measurements.

Figure 4 shows that the Ge core level lineshape similarly consists of two components, Ge^+ and B, with the former being Ge in the surface dimer layer in direct bonding with Cl, and the latter being Ge in the subsurface region. At one cycle of ALE deposition, the spectrum is dominated by Ge^+ with a small, but noticeable, B component. This indicates that most of the Ge atoms reside in the dimer layer, but some are already covered by the growth. The intensities of both components increase for more cycles of ALE growth as expected. The increase in B simply means that more Ge atoms become buried under the surface as the deposition increases. The intensity of Ge^+ provides a measure of the Ge coverage in the dimer layer. Results from this analysis are shown in Fig. 2 using squares, which agree well with the results from the other measurements. The somewhat larger discrepancy at 3 and 5 cycles of deposition is not inconsistent with an experimental error of up to ~10% each for STM counting and core level intensity measurements.

The two curves in Fig. 2 represent the average of the three independent measurements, where available: STM counting, Cl core level analysis, and Si/Ge core level analysis. The good agreement among the three measurements confirms our interpretation and assignments. The shapes of these curves are an indication of the degree of intermixing at the interface. For an ideal layer growth and an abrupt interface, the curves should be straight lines going from 1 to 0 for Si and 0 to 1 for Ge at the completion the first ML deposition of Ge. As the STM results show, Ge atoms, upon deposition, replace Si at random surface sites, rather than coalescence and cover up the substrate surface. This growth behavior rules out an abrupt interface, and leads to a graded, intermixed region.[xvii] The range of this intermixing is, however, very limited.

Fitting the two curves in Fig. 2 to exponential decay functions, the decay length is about 1 ML. This is consistent with the surface-layer interchange mechanism mentioned above, and implies no appreciable interlayer or bulk diffusion otherwise to further broaden the intermixed region.

This study is made possible by a large STM contrast between Ge and Si using Cl as a contrast-enhancement agent. Also, the difference in Cl 2p chemical shift between Cl adsorbed on Ge and Si (0.64 eV) is unusually large, which facilitates a detailed analysis of the surface composition. The sign of the Cl 2p chemical shift difference suggests that Cl bonded to Ge (Cl-Ge) is more negatively charged, or more ionic, than Cl bonded to Si (Cl-Si), in agreement with a recent calculation.[15] This, in turn, implies that there is a sizeable difference in the electronic structure between Cl on Ge and Cl on Si, which is likely the reason for the enhanced STM contrast.

In summary, distinguishing Si and Ge atoms on mixed Si/Ge surfaces in atomic-resolution images has been a difficult issue for this important prototypical system. In our work, image contrast enhancement is facilitated by Cl termination, which additionally aids spectroscopic measurements of surface chemical composition. This approach enables three independent measurements: STM counting, Cl core level analysis, and Si/Ge core level analysis, which together provide a consistent and detailed picture of the atomic processes involved in the growth. ALE deposition of Ge on Si(100) is characterized by Ge replacement of individual Si surface atoms, resulting in a mixed alloy surface layer that enriches with Ge as it grows. The interface is thus graded, but the intermixing length scale is a mere one monolayer due to the surface nature of the intermixing process.

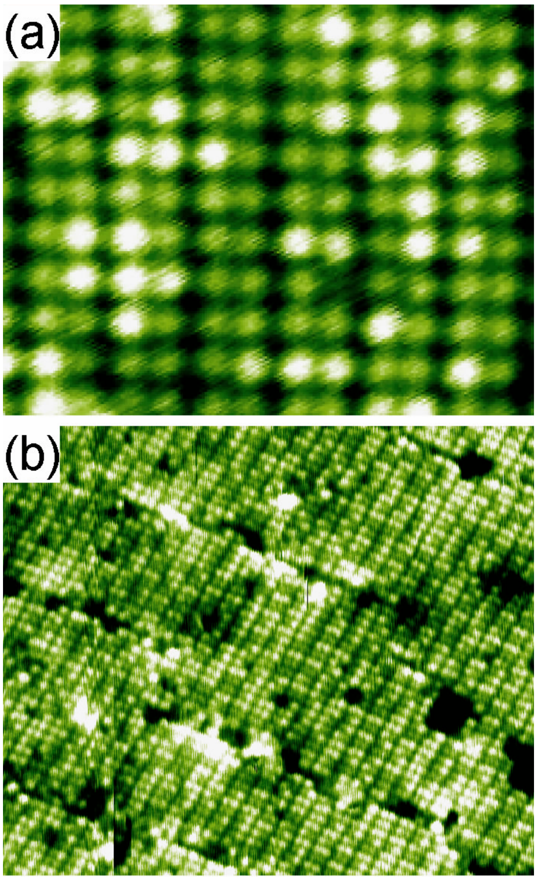

FIG. 1. Ge ALE growth and Cl termination, and covers an area of 48 x 36 Å^2. (b) is the same but for two cycles of Ge ALE growth

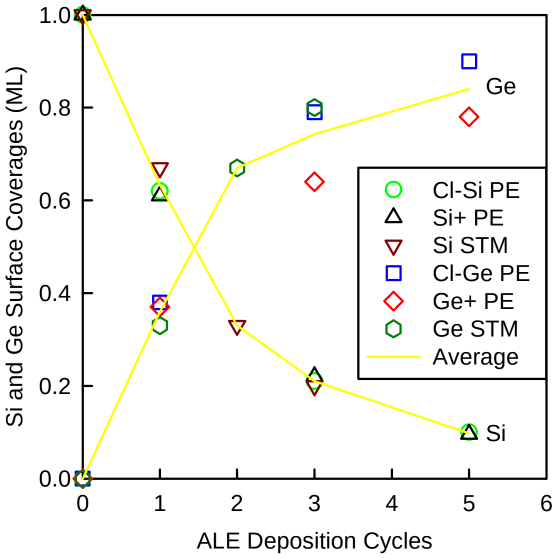

FIG. 2. Si and Ge surface coverages (within the dimer layer) deduced from three independent measurements: STM counting, Cl 2p core level analysis, and Si/Ge core level analysis. The curves represent averages of the results, where available, for both Si and Ge.

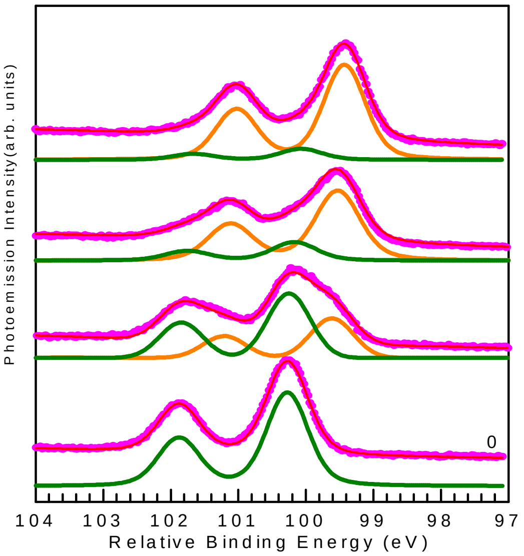

FIG. 3 Photoemission spectra for the Cl 2p core level. The samples are Cl-terminated Si deposited with 0, 1, 3, and 5 cycles of Ge ALE (corresponding to Ge deposition of 0, 0.4, 1.2, and 2.0 ML, respectively). The two components, Cl-Si and Cl-Ge, correspond to Cl bonded to Si and Ge, respectively.

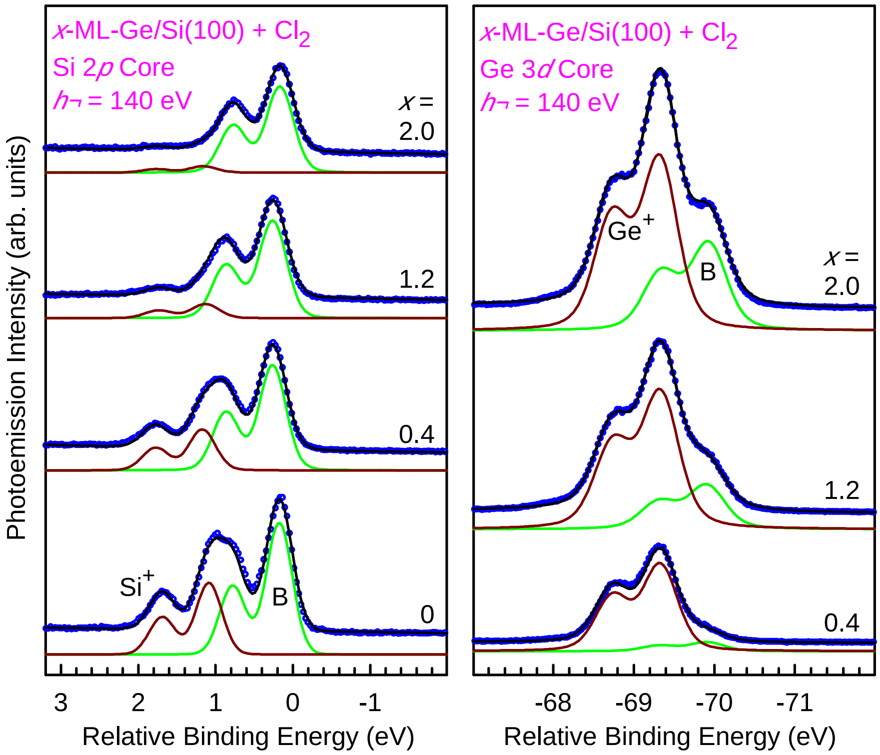

FIG. 4. Photoemission spectra for the Si 2p and Ge 3d core levels. The samples are Cl-terminated Si deposited with 0, 1, 3, and 5 cycles of Ge ALE (corresponding to Ge deposition of 0, 0.4, 1.2, and 2.0 ML, respectively). Two components are seen in each case. The components labeled Si$^+$ and Ge$^+$ correspond to Si and Ge dimer atoms directly bonded to Cl, respectively, while the B components correspond to Si and Ge in the subsurface region.

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