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計畫名稱	在四族半導體表面上的超薄離子固體自我組裝與其薄膜、介面性質（第 3 年）		
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目錄:

進度與結果簡要說明

今年，我們費了不少時間、精力、與經費資源用以搬遷實驗室到清華大學物理系，本計畫也隨之轉移，經過難免的許多磨練，現在已大致就序，我們的研究計劃工作已繼續開展。除此之外，我們也費了許多心思，對過去一段時間中的不能完全得到滿意分析方式與理解的好數據做了思考、與進一步的模擬計算，今年到目前為止有 6 篇成果已整理發表或正由期刊審查中，尚有數篇正整理與撰稿中，算是對去年的停滯有些補救。

我們對超薄離子固體累積更多更好瞭解，其中很值得在此一提的是，我們發現: 離子固體薄膜表面上的化學反應居然可以穿越數個原子層厚的薄膜，迫使薄膜與基版間的原子與電子結構產生具大的改變，也就是薄膜與基版間產生了電壓差為1.6-eV左右的電雙極層，這種由表面引發的介面電子組態的重整是史無前例的，我們相信對表面、介面、與薄膜研究社群會有不小的衝擊。這個結果”Electronic Reconstruction at a buried ionic-covalent interface driven by surface reactions”已投稿審查中。另外，我們也偶然地發現了一個表面上原子擴散運動的新機制，也就是熱運動中的原子藉由與相鄰的表面原子直接交換位置而移動，這種原子擴散運動雖是教科書上的典型說明，但卻從沒有在實驗上真正被觀察到，因此，我們相信這也是一篇很有價值的成果與科學發現。本篇報告“Possibility of direct exchange diffusion of hydrogen on the Cl/Si(100)-2×1 surface” 也已投稿審查中，稿件附於後。

在主計畫實驗硬體設施方面，我們已按原計劃構想，配合清華大學的經費挹注，提高原計劃中採購的一部份顯微鏡硬體規格至適合於液氦低溫的系統，這種低溫系統極有助於我們下一階段研究計劃的彈性與測量能力，也符合目前的研究趨勢，目前各種配件都採購完畢，預計暑假中我們可以自行組合各部份為一完全的實驗系統。

另一方面，我們一部既有 Omicron 真空電子穿隧顯微鏡系統(購於 1995 年)，最近其樣品夾(wobble stick)因使用過久而於數月前開始出現漏氣，現破洞已增大至真空系統無法抽至必須要的最小真空度，此真空電子穿隧顯微鏡系統設備為進行計畫所急須，而其離子幫浦中抽氣原件也急須更換，這是我們始料未及的新狀況，我們設備費已依原計劃用罄，後面兩年無新設備經費，因此我們在此請求增加此兩部份經費，讓該顯微鏡系統恢復運作。

Report on “Possibility of direct exchange diffusion of hydrogen on the Cl/Si(100)-2×1 surface”

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Abstract

The diffusion behavior of hydrogen substitutional sites on the chlorine-terminated Si(100) surface was investigated at elevated temperatures using time-lapse scanning tunneling microscopy (STM). STM movies show that each hydrogen atom undergoes Brownian motion within a monochloride dimer row. The position of a hydrogen substitutional site is exchanged directly with that of an immediate neighboring chlorine atom in either the same dimer (intra-dimer diffusion) or in one of the two adjacent dimers in the same row (intra-row diffusion). Accordingly, conceptual direct exchange diffusion (DED) in a two-dimensional lattice was experimentally observed. Analysis of STM movies at various temperatures yielded rather low attempt frequencies and energy barriers, leading to the suggestion that the diffusion mechanism involves an intermediate low-energy molecular state. Density functional theory (DFT) calculations were also performed and provided partial support for the proposed diffusion mechanism.

I. Introduction

The diffusion of atoms, molecules and small clusters is one of the fundamental processes that occur on surfaces.[1-4] A thorough comprehensive understanding of the surface diffusion mechanisms at an atomic level is extremely important to the technological development of surface catalysis and several nanofabrication processes such as thin film growth and etching. Most diffusion processes on surfaces discussed in the literature proceed by the exchange of an atom with a neighboring vacancy defect. The typical description of vacancy-driven surface diffusion is that an adatom hops among adsorption sites on a surface lattice via transition sites at a rate that increases with temperature. Although this conventional model of adatom diffusion via nearest-neighboring jumps generally requires a minimum of an activation energy of diffusion E_a, various pathways for surface diffusion have been identified both theoretically and experimentally.[2, 5-8] For example, adatom displacements to the adsorption site of a non-nearest-neighbor, known as long jumps, have been shown experimentally to proceed at temperatures as low as 0.1 T_m (melting temperature) and to dominate the diffusion process over single jumps at elevated temperatures in some cases.[2, 9]

Another particularly interesting example of an unconventional mechanism is vacancy-driven diffusion via atomic exchange.[2, 4] This process involves exchange between an adatom and an adjacent atom in the surface lattice. Atomic exchange processes have been demonstrated to take place in both hetero-diffusion and self-diffusion. Theoretically, an atom can diffuse by exchange of position with that of a neighbor, either directly or by rotation.[10] Such direct exchange diffusion (DED) does not involve defects and commonly requires high energy, so the probability of its occurrence is expected to be very low. DED has not been experimentally observed on surfaces. In the three dimensional case, a similar exchange diffusion mechanism without defects has been occasionally proposed to explain some new diffusion phenomena in solids.[11] This exchange diffusion is commonly referred to as concerted exchange (CE). However, CE does not seem to occur in practice since the associated transition state requires a high input of energy for the simultaneous and cooperative motion of more than one atom at a time.

This work describes a newly observed diffusion phenomenon on the Cl-terminated Si(100) surface. Scanning tunneling microscopic movies reveal that hydrogen substitutional defects migrate within the top chlorine layer and that this process is thermally activated. Hydrogen substitutional sites diffuse at moderate temperature without the participation of vacancies. In the simplest model — direct exchange diffusion, an H-site and a neighboring Cl-site in the surface lattice swap positions directly. This investigation proposes a model of this diffusion process and performs *ab initio* energy calculations. The success and discrepancy of this model and other alternative explanations are also discussed.

II. Experimental Details

The diffusion process was examined in real space and real time at atomic resolution by using a variable-temperature scanning tunneling microscope (STM) in a vacuum chamber with a base pressure of 1×10^{-10} torr. Samples of Si(100) were prepared from commercial wafers, outgassed in the vacuum chamber, and then heated by direct Joule heating to ~1400 K to generate clean and well-ordered surfaces with reconstructed dimers. After the clean Si(100) surface was cooled to almost room temperature, ultra-pure gaseous chlorine was introduced to the sample surface through a precision leak valve and a stainless-steel tube. The substrate was heated by passing a controlled dc current directly through the sample. The sample temperature that corresponds to each current was obtained using an infrared optical pyrometer and calibrated by gluing a tiny type-K thermocouple to the center of the sample following the final last STM run. The uncertainty in the temperature measurement was estimated to be approximately ±5 K. All STM images were captured in constant current mode. Various bias voltages were applied to support the positive identification of the various different surface species with negligible tip-induced diffusion. However, all of the images presented below were taken at a sample bias of -2.2 V and a tunneling current of ~0.1 nA.

Calculations of diffusion barriers were conducted using density-functional theory (DFT) calculations within the local-density approximation in the Vienna *ab-initio* Simulation Package (VASP).[12] Briefly, the Ceperley-Alder exchange-correlation function,[13] as parameterized by Perdew and Zunger,[14] was utilized. A repeated-slab supercell model was also applied. Each slab comprised eight atomic layers of Si and adlayers of Cl and H on the top surface. The bottom two silicon layers were constrained to remain in bulk-like positions. H atoms were attached to the bottom-layer Si atoms to saturate their dangling bonds. The heights of the supercell in the [100] direction were fixed at 20 Å, which was large enough to prevent coupling between the slabs, even when Cl and H were adsorbed on both Si surfaces. The wave functions were expanded using a plane-wave basis with an energy cutoff of 25.72 Ry (350 eV). The electron-ion interaction pseudopotentials that were supported by VASP were evaluated using the projector-augmented wave (PAW) method. A (4×4×1) *k* Monkhorst-Pack grid, equivalent to eight irreducible **k** points, was adopted to sample the surface Brillouin zone of a unit cell, which was two dimer rows wide with four dimers in each row. The structure was optimized until the residual force that acted on each atom was less than 0.01 eV/Å. Then, the nudged elastic band (NEB) method was used to determine minimum barrier energy diffusion paths between known initial and final geometries.[15]

III. Results and Discussion

The Si(100) surface has been well characterized because of its importance in fundamental science and technology. In a clean Si(100) surface, bulk truncated silicon surface atoms pair into dimers, eliminating one dangling bond per atom to reduce the surface free energy. Each surface Si atom has one dangling bond and the clean Si(100) surface.[16] The interactions of hydrogen and halogen with silicon surfaces have been extensively experimentally and theoretically examined because fundamental interest in their importance to etching and growth processes.[16-19] Many works have established that Cl atoms are singly bonded to dimer dangling bonds on Si(100) while the dimer structure is preserved without buckling, forming a (2×1) monochloride surface. A hydrogen atom also forms a similar single bond with a Si dangling bond and, therefore, readily replaces a Cl-terminated site without modifying the dimerized substrate structure, as displayed in Fig. 1(a).[20, 21]

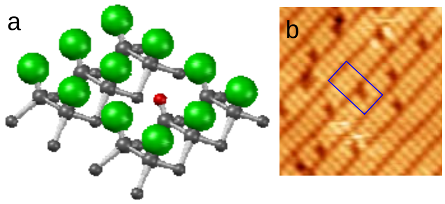

Fig. 1. (a) Ball and stick model of Cl-terminated Si(100) surface. The top-layer Cl atoms are green and a substitute H atom is red. Cl atoms each terminate a dangling bond on the Si surface with dimer reconstruction. (b) STM image of Cl-terminated Si(100) surface taken at room temperature. The dark defects are H substitution sites. The blue rectangle delineates the area that is schematically presented in (a). V_s = -2.2 V; I_t = 0.22 nA. Image size ~52×52 Å^2.

A. STM results

Figure 1(b) shows that the initial Cl/Si(100)-2×1 surface is well ordered following saturated exposure to Cl_2 at room temperature, with a few randomly located "dark" sites that are substituted for a single Cl site. Most of these defects are isolated and have a typical density of < 2%. Similar dark-looking sites can also been formed by exposure to a beam of light H atoms on the Cl/Si(100)-2×1 surface.[20] The "dark" sites generated either by an atomic H beam or by Cl_2 exposure show the same characteristics, as revealed by STM images obtained under various conditions and scanning tunneling spectra,[16] suggesting that all these "dark" sites are hydrogen substitution sites, or H-sites. These H-sites formed during the Cl_2 exposure are perhaps due in part to chemisorption during sample flash at high temperature.

Cl/Si(100)-2×1 surfaces with various amounts of H substitutional defects remain clean and stable for days under UHV cond itions at room temperature. H-sites are static at room temperature and are observed to become mobile in STM images acquired at sample temperatures of above ~500 K. Figure 2 presents four representative and consecutive STM images from an STM movie of a (2×1)

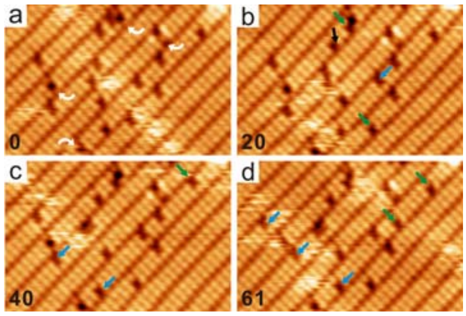

Fig. 2. (a-d) Four consecutive STM images from movie (~20 s/frame). The relative recording time of each image in seconds is indicated at the bottom left corner. The curved, white arrows point to unidentified, fixed surface species. The arrows indicate intra-row (blue) and intra-dimer (green) diffusion of an H site. The black arrow in (b) indicates an apparent double jump that results from two single jumps between the two frames. In the 60 consecutive images taken over a period of 1248 s, 51 intra-row jumps, 32 intra-dimer jumps and 6 apparent double jumps were observed. Image size ~74×49 Å^2.

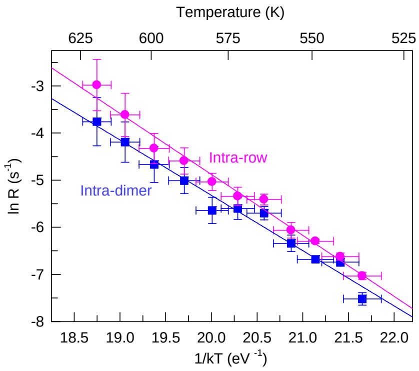

Fig. 3. .Arrhenius plots for intra-dimer and intra-row H-Cl exchange diffusion. The solid lines are fits. These lines yield an activation barrier E_a of 1.29 ± 0.05 eV and a pre-exponential factor ν_0 of $10^{9.1 \pm 0.5}$ s^{-1} for intra-row diffusion in the dimer row direction and $E_a = 1.17 \pm 0.06$ eV; $\nu_0 = 10^{7.8 \pm 0.5}$ s^{-1} for intra-dimer diffusion.

chlorine terminated Si(100) surface that was maintained at 560 K. In the images, H-sites usually move one atomic step a time to occupy a Cl-site either on the opposite side of the same dimer (intra-dimer diffusion) or on the neighboring dimers in the same dimer row (intra-row diffusion). After hydrogen has been displaced, the H-site does not become an isolated dangling bond, but appears as a Cl-site. A dangling bond is apparently higher than a Cl-site in the STM images, and so they can be easily distinguished.[22] Restated, an H-site appears to diffuse by the exchange of its position directly with that of a neighboring Cl-site. A displacement of two atomic steps can occasionally be observed between two consecutive images. The non-nearest-neighbor jumps occurred less frequently as the interval between two STM images were shorted, suggesting that most of them involved two single-jumps (two consecutive intra-row diffusion steps or a combination of an intra-row step and an intra-dimer step). The number of inter-row diffusion events is less than 0.2% of total diffusion events in our measurements, indicating a larger energy barrier.

Many STM movies were obtained and diffusion rates were calculated between 530 and 615 K. As the sample temperature increased, the H-sites diffused more frequently, suggesting that this process was thermally activated. Figure 3 plots the diffusion rates obtained from STM movies are plotted as a function of inverse temperature. The plots follow closely the Arrhenius law and yield an energy barrier of 1.29 eV and a prefactor of $10^{9.1 \pm 0.5}$ s^{-1} for intra-row diffusion. Intra-dimer diffusion has a prefactor $10^{7.8 \pm 0.5}$ s^{-1} and a slightly smaller energy barrier, of only around 1.17 eV. The values of the prefactors are orders of magnitude lower than the universal prefactor of $10^{13 \pm 1}$ s^{-1}, suggesting a more complex process than that of a vacancy-driven diffusion and/or considerable perturbation of the substrate during diffusion.[2, 3, 23] The activation energies obtained here are considerably lower than those of intra-row H atomic diffusion (1.7 eV),[24, 25] but higher than that (1.0 eV) of H intra-dimer diffusion and that (1.1 eV) of Cl diffusion on a clean Si(100) surface.[26, 27]

B. Model of DED mechanism and NEB calculations

As described above, the diffusion of hydrogen substitutional sites involves the concerted motion of H and nearest Cl atoms. Si-Cl and Si-H bonds have large bond energies of 3.956 eV and 3.301 eV, respectively. If the concerted motion of the H and Cl atoms involve the simultaneous breaking of Si-Cl and Si-H bonds, then much energy will be clearly required. However, the diffusion barrier is similar to those of simple H-adatom diffusion. Accordingly, a key question that is raised by the DED model is as follows: if two surface atoms with strong chemical bonds with a substrate are responsible for H diffusion, then how do they organize themselves into a low-energy state during the process? Notably H-Cl has a large bond energy of 4.444 eV. Hence, a natural conjecture is that two nearby intra-dimer or intra-row H and Cl atoms form an HCl-like molecular configuration as an intermediate product, and then switch positions during rebonding.

In an effort to confirm the existence of an HCl molecule as an intermediate state, the NEB method built in the VASP code was employed; the NEB technique has also been applied to determine activation energies of hopping and exchange-diffusion on surfaces. In this calculation, a "band" of intermediate states is produced by simple interpolation along an assumed reaction path that connects the initial state (with H and Cl on a single dimer or on a single side of two adjacent dimers in the same dimer row) with the final state (in which the positions of H and Cl are exchanged). Then, the atomic configurations in the different geometries are iteratively optimized using only ionic-force components that are perpendicular to the hypertangent.

Atomic configurations after NEB minimization, as presented partially in Fig. 4, show that H and Cl atoms move toward their final state positions approximately in the plane defined by <100> and along the line that connects initial H and Cl positions. During the transition, the relevant dimer bonds remain intact; no bridge-bonded state, such as that associated with Cl adatom diffusion, is obtained. In the image chain, the Cl atom appears to move along the outer circle, while H remains closer to the surface. The length of the bond between the H and Cl atoms is 1.32 Å, which is close to that (1.27 Å) in an HCl molecule.

The heights of the activation energy barriers obtained by comparing the initial and transition states are large (~2.86 eV) for both intra-dimer and intra-row DED, as presented in Fig. 4. This value is close to the energy (2.7 eV) required to remove the Cl and H atoms away from the surface and to form a H-Cl bond, suggesting that both Si-Cl and Si-H bonds are completely broken and HCl molecules are present. Although the experimental value may be imprecise, the heights of the energy barriers (~2.8 eV) in the LDA-DFT calculations fall outside the range of experimental uncertainty. Other modeling approaches, such as generalized gradient approximation (GGA) with spin and tight binding, have been demonstrated to yield values of

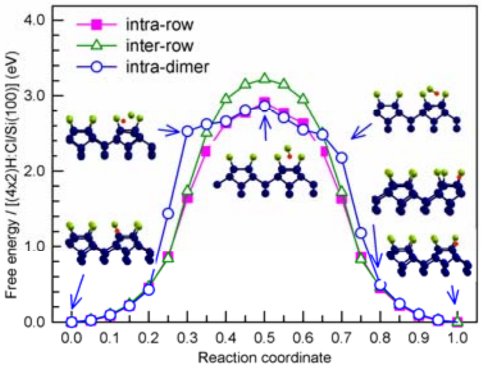

Fig. 4. Calculated barriers of three direct exchange diffusion channels as labeled. Selective atomic geometries for intra-dimer diffusion show that the transition-state atomic configuration involves an HCl molecule. Silicon atoms are shown in navy blue; hydrogen atoms are shown in red; chlorine atoms are shown in green.direction and $E_a = 1.17 \pm 0.06$ eV; $\nu_0 = 10^{7.8 \pm 0.5}$ s^{-1} for intra-dimer diffusion.

energy barriers that are closer to the experimental results. The interaction between atoms, molecules or surfaces at large separations is well known commonly to be incorrectly described in LDA or GGA, which exclude long-range interactions, such as van der Waals (vdW) forces.[28] Consider, for example, the physisorption of HCl on ice; the physisorption energy is around 0.3 – 0.5 eV.[29] These additional corrections and perhaps the use of more realistic image chains that include alternative intermediate states in NEB minimization can yield calculated values that are closer to experimental values.[30]

Notably, sharp STM tips can yield electric fields that are sufficiently strong to break chemical bonds.[31] Additionally, as noted by Boland, at positive sample bias, the interaction of the Si-Cl dipole on Cl/Si(100) with the field effectively reduces the depth of the potential energy well at a dangling bond site, effectively reducing the barrier to Cl adatom diffusion on a clean Si(100) surface.[32] This decrease should be particularly important for sharper tips, which generate stronger fields and field gradients. Even though negative sample bias was applied during observation and small tunneling currents were used to eliminate the aforementioned complications, the possibility that a sharp STM tip may have a partial role in hydrogen diffusion cannot be excluded completely. In view of this possibility, an alternative explanation of the STM observations that is based on the assumption that the electric field (and current) is *not* strong enough to break the Si-H or Si-Cl bond, but is strong enough to lower the energy barriers of DED through intra- or inter-dimer channels should be considered.

IV. Conclusions

Although the concept of DED is known, DED has not experimentally observed to the best of the authors' knowledge. Herein, a detailed atomic view of the diffusion of hydrogen substitution sites within the top chlorine layer on a Cl/Si(100)-2×1 surface was presented. Atomic-resolution STM images show that hydrogen diffusion occurs via direct positional exchange of an H-site and a neighboring Cl-site in the same row. Analysis of time-lapsed movies indicates a thermally activated process with a barrier of $E_a = 1.29$ eV and an apparent prefactor ν_0 of $10^{9.1 \pm 0.5}$ s^{-1} for intra-row diffusion and $E_a = 1.17$ eV; $\nu_0 = 10^{7.8 \pm 0.5}$ s^{-1} for intra-dimer diffusion. The energy barriers are substantially lower than expected, perhaps because the DED process involves an intermediate HCl molecular state. Energy calculations based on density functional theory verify the existence of this transition state molecule, but yield higher barriers of around 2.86 eV. The discrepancy in activation energy suggests that corrections such as dispersive forces are required in the calculation. Alternatively, a multiple-step process or the electric field under an STM tip may be involved in the exchange of positions. Our findings suggest the need for further study of the apparent DED process and open the way to further experimental investigations and theoretical calculations of the diffusion processes.

Acknowledgements

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