行政院國家科學委員會專題研究計畫　期中進度報告

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(2/3)

計畫類別：個別型計畫
計畫編號：NSC93-2112-M-009-019-
執行期間：93 年 08 月 01 日至 94 年 07 月 31 日
執行單位：國立交通大學物理研究所

計畫主持人：林登松

計畫參與人員：楊鎧民、謝明峰、馮世鑫、鄭人夤、張君黛、邱祺雄

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 94 年 5 月 9 日

行政院國家科學委員會補助專題研究計畫 □ 成 果 報 告 V 期中進度報告

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成果報告類型(依經費核定清單規定繳交)：v 精簡報告

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執行單位： 交通大學物理研究所

中　華　民　國 94 年 5 月 10 日

行政院國家科學委員會專題研究計畫期中報告

計畫編號：NSC　93－2112－M－009－019
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一、進度與結果簡要說明

本年度我們主要研究重點在以穿隧效應顯微鏡 STM 之實空間影像來研究 H 在 H/Si(100)-3x1 樣品上的熱脫附引起的結構相變化現象。我們得到是很好的數據，也已分析完畢，其中一些結果"Atomistic View of the Recombinative Desorption of H_2 from H/Si(100)" 已被 Physical Review Letter 接受刊出，這部分結果我們報導如下。在這個子題方向，下一年度我們仍將研究 1x1 結構轉為 2x1 結構的過程。

其他新領域的嘗試性工作如 UHV non-contact AFM 對 SiO_2 薄膜之研究也結束實驗部分工作，目前正整理數據，準備發表，我們認為這部分工作成果價值也非常高。我們也已開始研究著手製作下一階段的樣品，也就是以 ion implant 改變局部表面區域的功函數，以研究接觸電位差對非接觸式原子力顯微鏡測量的影響。

我們也繼續檢視 STM 之 Cl_2, HCl, HBr/Si(100)-2x1 表面在吸附過程的實空間影像，探討各種反應模型，我們得到不少很有趣的資料，但解釋上遇到一些瓶頸，我們接下來將改弦易轍，換另外的實驗方式逼近問題，待得到有更好的了解後，再完整報導發表。

二、一些數據與分析: " Atomistic View of the Recombinative Desorption of H_2 from H/Si(100)"

A. Introduction

Recombinative molecular desorption from a surface generally requires the assembly and organization of constituent atoms or molecular fragments on the surface into favorable precursor or pre-desorption configurations that are compatible with the free molecular shape. Geometric constraints can play an important role in the pathway leading to a pre-desorption configuration, and this subject matter is of fundamental interest to surface physics and chemistry. In this paper, we report a study with scanning tunneling microscopy (STM) of the relevant atomistic issues associated with the desorption of H_2 from hydrogenated Si(100) surfaces. Being a simple model system, H/Si(100) has attracted intense interest, both experimentally and theoretically.

B. Results and Discussion

The key question is how two H atoms on H/Si(100) can organize themselves into a state conducive to recombination and desorption. The underlying principles are quite simple, as we shall demonstrate: the two H atoms must move sufficiently close to each other, and subsequent desorption must not leave behind a highly unstable surface configuration. The relevant geometries are indicated schematically in Fig. 1.

Figure 2 shows representative STM images for a (3x1) surface after annealing for 0, 0.5, 4.5 and 33 h, respectively, at 570 K, which is barely above the threshold for desorption. The initial (3x1) surface is fairly well ordered, with some randomly located antiphase domain boundaries. Figure 2(d) shows that after 33 h anneal the surface is essentially completely converted to a monohydride (2x1) surface. In the process, H in the amount equivalent to 1/3 of a Si monolayer is desorbed. Since the dimer rows for the initial (3x1) reconstruction and the final (2x1) reconstruction are organized with different periodicity, the conversion must involve dimer row reorganization. A detailed examination of the STM images at

intermediate stages of desorption reveals two kinds of reactions are happening as described below.

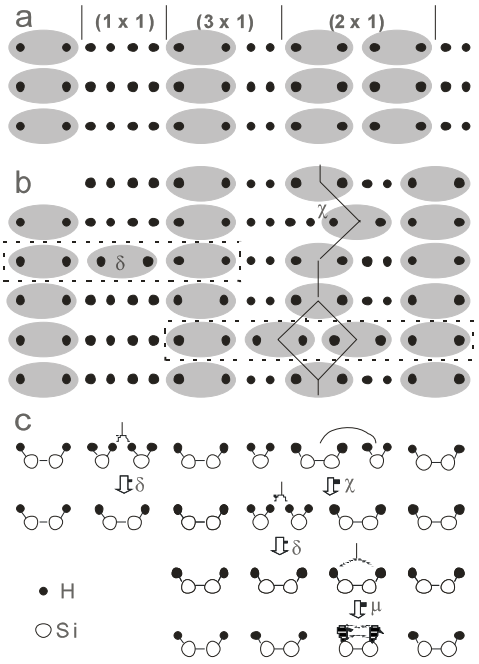

Fig. 1. Schematic diagrams showing (a) top view of (1x1) dihydride, (2x1) monohydride, and (3x1) mixed monohydride-dihydride phases, (b) top and (c) side views of atomic configurations involved in χ, δ, and μ reactions as discussed in the text. Dashed rectangles indicate (6x1) and (8x1) units. Dashed-dot lines outline the V- and diamond-shaped structures.

First, let us focus on a domain boundary involving a local (1x1) patch consisting of two adjacent dihydride rows, as shown in Fig. 3(a), which is an image obtained after annealing for 0.5 h. Here, one can see two cases of recombinative desorption. In each case, two adjacent dihydrides donate one H each to form a desorbing H_2 molecule, leaving behind a monohydride dimer. The process is schematically illustrated in Fig. 1(x). The resulting surface structure consists of three adjacent monohydride dimers stringed along the dimer bond direction. For simplicity, we shall refer to this as a (6x1) unit. Desorption from a single dihydride is never observed, despite a favorable H-H distance. The reason is that the end product would be a Si surface atom with two dangling bonds, which is energetically unfavorable. Likewise, desorption does not occur for two adjacent dihydrides lined up perpendicular to the dimer bond direction. This dihydride pair desorption mechanism accounts for the conversion of (1x1) patches into monohydrides, but is incompatible with the (3x1) geometry because the dihydrides are separated by monohydride dimers.

The second kind of reaction occurs in ordered (3x1) areas. An example is shown in the image in Fig. 3(b), taken after 0.5 h of annealing. Here, a monohydride dimer is seen to switch its position with its neighboring dihydride, resulting in a kink in an otherwise straight row. As theory indicates, the barrier involved in this switch is actually quite low. The resulting configuration can be considered as a combination of two antiphase domain boundaries, one atomic row wide. This antiphase defect pair (ADP) contains two adjacent dihydrides, and can therefore desorb via the same process as discussed above. Indeed, STM images taken at intermediate annealing times show a number of such reaction products. An example is shown in Fig. 3(c) taken after 0.5 h or annealing. The local surface geometry consists of four monohydride dimers stringed along the dimer bond direction. This is referred to as an (8x1) unit in the following. This desorption process is schematically indicated in Fig. 1(c).

As the annealing progresses, further desorption appears to favor sites next to where desorption has already occurred. Thus, (8x1) and (6x1) units tend to expand into (8xn) and (6xn) patches. Since the initial (3x1) surface also contains (4x1) units in antiphase domain boundaries, the overall surface structure can become fairly complicated as domains form, grow, and collide. Some examples of (8xn), (6xn), and (4xn) patches are highlighted in Fig. 2(c). The complicated domain patterns eventually give way to a simple monohydride surface with an overall (2x1) reconstruction as seen in Fig. 2(d). However, cases are found where a single row of dihydrides gets trapped in large patches of (2x1) monohydrides. This can be considered as a kind of (2x1) antiphase (or twin) domain boundary, and an example is shown in Fig. 3(d). These features

are relatively rare, but are robust as desorption can no longer proceed via the same mechanism. It is interesting to note that antiphase domain boundaries do not normally occur on clean (2x1) surfaces, as the bare Si atoms with double dangling bonds at the boundary are highly unstable. For the present system, such boundaries exist because of stabilization by the adsorbed hydrogen.

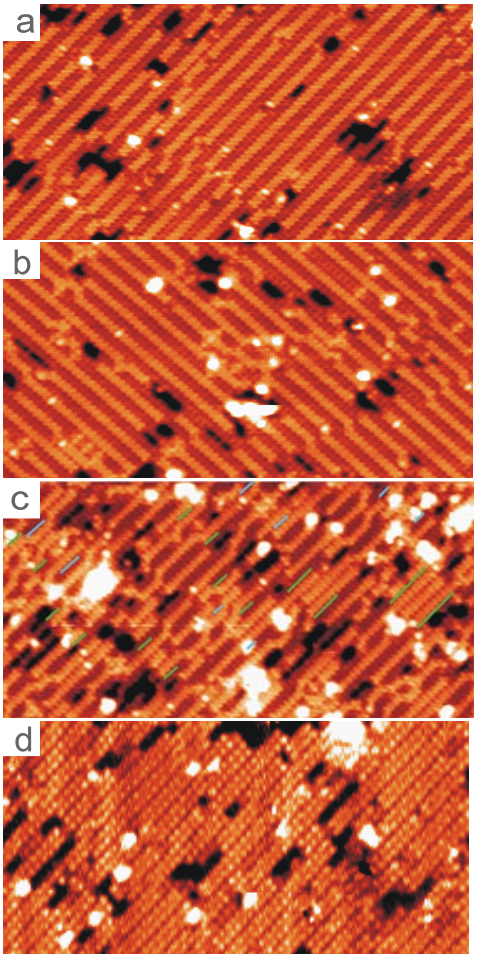

Fig. 2: STM images taken at room temperature after a (3x1) sample has been annealed at 570 K for (a) 0, (b) 0.5, (c) 4.5, and (d) 33 h. The dark pits are single or double vacancies. In (a)-(c), the brighter rows are monohydrides and the dimmer rows are dihydrides.

D. Summary

Our results illustrate two basic principles relevant to recombinative desorption: the constituent atoms must be organized first on the surface into favorable pre-desorption states that are compatible with the free molecular geometry, and the resulting surface structure must be energetically favorable.

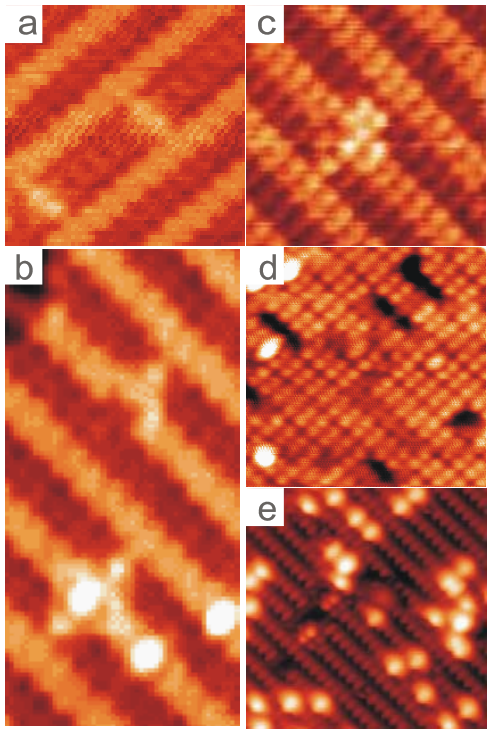

Fig. 3 Close-up images showing (a) two (6x1) units formed as a result of the δ desorption process in a two-row-wide (1$\times$1) dihydride domain, (b) a V-shaped kink (ADP) resulting from a position-switching χ process and (c) a diamond-shaped (8x1) unit resulting from a combined χ and δ processes, (d) an ADP neighboring an (8x1) unit, (e) a dihydride row trapped in a 2x1 domain, and (f) desorption μ events from a monohydride (2x1) phase. Figure 3(f) was taken at a sample bias of -2.1 V, while all of the others were taken with +2.3 V. Images (a)-(d) were taken after annealing a (3x1) sample at 570 K for 0.5 h, while image (e) was taken after a 33 h anneal. Image (f) was taken after annealing a (2x1) monohydride surface for 1 min at 725 K.