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Surface Science 601 (2007) 2189–2193

SURFACE SCIENCE

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Desorption of chlorine atoms on Si (1 1 1)-(7 × 7) surfaces induced by hole injection from scanning tunneling microscope tips

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Received 9 November 2006; accepted for publication 12 March 2007
Available online 19 March 2007

Abstract

We investigated desorption of chlorine atoms on Si (1 1 1)-(7 × 7) surfaces induced by hole injection from scanning tunneling microscope tips. The hole-induced desorption of chlorine atoms had a threshold bias voltage corresponding to the energy position of the S3 surface band originated in Si backbonds. The chlorine atom desorption rate was almost proportional to the square of the tunneling current. We have discussed possible mechanisms that two holes injected into Si surface states get localized at the backbonds of chlorinated Si adatoms, which induces the rupture of Cl–Si bonds to result in chlorine atom desorption.

Keywords: Desorption induced by electron stimulation; Scanning tunneling microscopy; Scanning tunneling spectroscopies; Chlorine; Silicon; Semiconducting surfaces

1. Introduction

Non-thermal atomic control by electronic excitations have been drawing much attention because of not only academic concerns but also opening opportunities for creating novel material structures with remarkable properties otherwise achieved [1,2]. A notable method of electronic excitation is tunnel injection of carriers from sharp probe tips of scanning tunneling microscopes (STM) [3–14]. In contrast to light illumination that generates electrons and holes in pairs, the tunnel injection of carriers enables us to generate excited carriers, either holes or electrons alone, in a specific electronic state of the samples by tuning the bias voltage applied between the sample surface and the STM tip. Also, STM allows us to observe directly the products or the results of the carrier injection with atomic resolution. Therefore, the use of carrier injection from STM tips as an excitation source is a very powerful method to investigate the mechanism of atomic or molecular reactions induced by electronic excitations.

Desorption of hydrogen atoms in Si (1 0 0)-(2 × 1) surfaces was found to be induced by hole and electron injection by multiple vibrational excitations of the Si–H through an inelastic tunneling or by Auger-type electronic excitations on relaxation of injected energetic electrons [3,5]. As for chlorinated Si surfaces, the present authors [7,9] found that both of the electron and hole injection from STM tips causes enhanced *diffusion* of chlorine (Cl) atoms on Si (1 1 1)-(7 × 7) surfaces with a linear current dependence and a characteristic bias dependence. We concluded that the mechanism was that injected electrons propagate in the spatially extended Si surface bands and get captured by Si–Cl antibonding states resulting in the Cl diffusion [7,9,10]. Similarly injected holes, after band propagation, are trapped by Si adatom backbonds to enhance Cl diffusion. For *desorption*, the present authors found the desorption of Cl atoms induced by electron injection from STM tips to the same Si (1 1 1)-(7 × 7) surfaces [7]. More recently, Sloan and Palmer [13] reported Cl atom desorption on dissociation of chlorobenzene molecules

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doi:10.1016/j.susc.2007.03.015

adsorbed on Si surfaces, and proposed a mechanism in which it is the attachment of two electrons injected from STM tips that causes C–Cl vibrational excitations leading to Cl dissociation or desorption.

In the present paper, we investigated *desorption* of Cl atoms on Si (1 1 1)-(7 × 7) surface induced by *hole* injection from STM tips. The sample bias voltage dependence of Cl desorption indicated that hole injection to the S3 surface band derived from Si backbonds is related to this phenomenon. Unlike the electron-induced Cl reactions (desorption and diffusion) and the hole-induced Cl diffusion, the desorption rate induced by hole injection was almost proportional to the square of the tunneling current. We consider a model in which two holes injected into surface states deeper than the edge of the S3 surface band get successively localized at a chlorinated Si adatom site to instabilize the Si–Cl bond ending up with the desorption of the Cl atom. For the detailed mechanism of bond rupture for desorption, we discuss two possible mechanisms, the multiple vibrational mechanism and the two-hole localization mechanism.

2. Experimental procedures

Samples cut from n-type Si (1 1 1) wafer (0.01–0.02 Ω cm) were introduced into an ultra-high vacuum STM chamber at a base pressure of $\sim 8 \times 10^{-9}$ Pa. Clean Si (7 × 7) surfaces were prepared by flashing at 1200 °C after outgassing at ∼500 °C for one night. The clean Si surfaces were chlorinated at room temperature up to a coverage of ∼0.3 by exposure to an atomic chlorine beam from a AgCl electrolytic cell [15]. STM experiments were conducted at room temperature with mechanically sharpened Pt–Ir tips prepared by outgassing at ∼600 °C for 15 min under a pressure of $\sim 1.3 \times 10^{-7}$ Pa. We performed STM imaging at a sample bias voltage V_S of +1.0 V with respect to the tip and a tunneling current I_T of 0.2 nA. We confirmed that the STM scanning under this condition does not cause any change in the surface structures [7]. The hole injection into the samples was conducted under various combinations of V_S and I_T.

3. Experimental results and discussion

Fig. 1a shows an STM image of a chlorinated Si surface with a Cl coverage of ∼0.3. It is known that in Si (1 1 1)-(7 × 7) surfaces at Cl coverages lower than one monolayer, chlorine atoms chemisorbed on top of adatom sites exhibit dark contrasts in STM images at $V_S \sim +1.0$ V [16], while non-chlorinated Si adatom sites are observed in bright contrasts. We checked that dark contrasts increased with prolonged Cl exposure. (The dark contrasts at some places exhibit reduced contrasts presumably due to a slight difference in the adsorption sate of the Cl atoms.) Fig. 1b and c shows a set of STM images before and after scanning at $V_S = -2.0$ V and $I_T = 80$ pA for hole injection to the sample area. Distinguished from Cl diffusion which is observed as the displacement of the dark contrast to the nearest adatom site, some of the dark contrast disappears as indicated by an arrow in Fig. 1b that changes to bright one as shown in Fig. 1c. One might consider that this is due to the Cl atom diffusing out of the image frame within a single scan time Δt. However, the probability of a Cl atom at the central position of an STM image diffusing out of the frame (30 nm × 30 nm) within $\Delta t = 35$ s is estimated to be extremely low from the previously measured rate of hole-induced diffusion (0.03 jumps for Δt) [7,11]. This means that it is quite improbable for all the events of dark-to-bright contrast changes to be due to out-diffusion of Cl atoms. Therefore, we could safely conclude that the dark-to-bright contrast changes indicate desorption of Cl atoms from the surface. A feature to be pointed out is that when we injected holes into the sample from the STM tip fixed at a set position, the Cl desorption were induced not only at the hole injection point but also in an extended range of ∼10 nm far from the tip position (not shown), just as in the Cl diffusion induced by electron injection [9,10].

Fig. 2 shows the sample bias voltage dependence of the desorption rates (solid circles) together with that of the diffusion rate (open circles) cited for comparison [9]. The reaction rates are defined by the number of the events that took place during a scan at $I_T = 80$ pA for 35 s over the area of 30 nm × 30 nm. The local density of states (LDOS) for the chlorinated sample measured by scanning tunneling

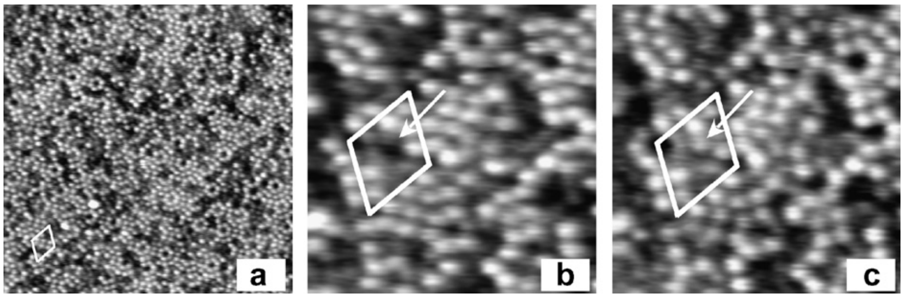

Fig. 1. (a) STM images of a chlorinated Si (1 1 1)-(7 × 7) surface with a coverage of 0.3. STM images before (b) and after (c) hole injection by scanning the area at $V_S = -2.0$ V, $I_T = 80$ pA. The dark contrasts represent Cl chemisorbed sites. Note the Cl pointed by an arrow in (b) changed to a bright contrast in (c). The imaging condition is $V_S = 1.0$ V, $I_T = 0.2$ nA.