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VUV laser photodesorption of hydrogen from Si(100)(2×1): H surface assisted by scanning tunneling microscope

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Abstract. We report experiments of VUV laser photodesorption of hydrogen from Si(100)(2×1):H surfaces assisted by an UHV room temperature scanning tunneling microscope (STM). The variation of isolated dangling bonds created has been measured for several fluences by a statistical analysis of the STM observation as a function of the irradiation dose. Structural surface modifications are discussed as well as the signature of photochemical processes.

1. INTRODUCTION

Hydrogen passivated semiconductor surfaces are of major importance in microelectronics for techniques using chemical vapour deposition (CVDs) [1] and, more recently, in nanotechnology using self assembled monolayers (SAMs) [2]. The desorption of hydrogen from an Si(100) surface has been extensively studied, thermally [3], photo-dynamically [4] and electronically [5]. Initially motivated by material processing, laser induced effects on silicon surfaces were principally used to study structural changes [6]. Fundamental aspects emphasised by direct electronic processes during atom removal on silicon in the low fluence regime has lead to an interest in the photochemical phase of photodesorption [7]. Influenced by studies of hydrogen desorption from electron stimulated excitation using STM [8], photodesorption has been firstly studied using vacuum ultra violet (VUV) on Si(111) surfaces where the surface reconstructions form a array of single (1x1) Si – H bonds [9]. The photochemical aspect has been pointed out by showing a linear influence of H_2 time of flight detection as a function of the laser fluence while the desorption temperature is kept constant. Although these studies conclude that structural surface changes have a minor importance on the dynamic of hydrogen interaction with the silicon surface, other work [10] indicates interesting changes in the H desorption signal from Si(100)(2×1):H surfaces when the incident angle of the laser beam changes. The transition dipole moment has been measured to be $\sim 18^\circ$ indicating that photodesorption could occur along a silicon dimer row using a suitably chosen polarized and oriented laser beam. More recently T.F. Heinz et al. [11] showed that the STM and laser apparatus can be combined to monitor either diffusion or desorption of H from Si(100) surfaces as the laser allows a very rapid heating pathway in accordance with dynamic analysis timescale of the STM.

In this work we show for the first time the measurement of the number of hydrogen desorbed sites from Si(100)(2×1):H surface when irradiated with a 157 nm VUV beam realised with STM statistical analysis of the room temperature STM images. The measurement is performed by counting the number of dangling bonds created after irradiation over several portions of the surface which have been carefully observed and identified before the irradiation and just after hydrogenation. The number of dehydrogenated sites is measured for several irradiation doses and for several fluences below the heating threshold surface excitation. These results are discussed bellow and reveal new questions in the dynamic of hydrogen desorption from this surface. Furthermore we show STM topographies which relate structural surface changes that will be examine as well.

2. EXPERIMENT

2.1 The STM system

The experiment is a UHV room temperature STM working at a low pressure of $\sim 3 \times 10^{-11}$ torr and is mainly described in [12]. The samples used were n-type As doped Si(100) with a resistivity of $\rho \sim 0.004 - 0.006\,\Omega$.cm and a thickness of $e \sim 250$ µm. The preparation starts by degassing the sample holder with its mounted sample for a period of 24 hours. Then the silicon sample is resistively heated to 650 °C. We proceed then with three to five thermal flashes cycles consisting of a rapid increase of the temperature up to 1050 - 1080 °C during 3 - 5 seconds, followed by a slow decline in temperature from 950 °C to 800 °C. The clean sample is then cooled to $\sim$ 380 °C and prepared for hydrogenation. The method used to passivate the sample is described elsewhere [13]. The hydrogenated sample is then transferred in the STM chamber to be observed.

2.2 The Laser system

The laser used is an Existar M-100 (TUILaser) excimer laser at 157 nm working with a premix of F_2 in He. It delivers 15 mJ per pulse at 20 Hz with pulse duration of $\sim$ 8 ns FWHM. The setup to guide the VUV beam to the sample is described in figure 1.

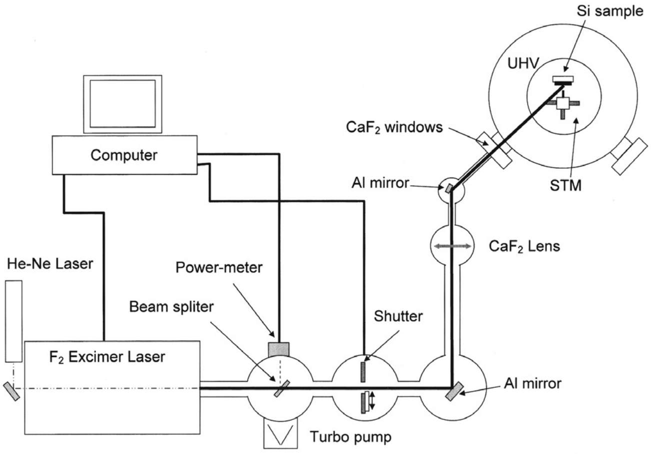

Figure 1. Experimental setup to combine UHV STM and 157 nm laser systems.

An He-Ne laser beam is passed through the excimer cavity and is aligned on the centre of the VUV rectangular shape beam. This allows a pre-alignment of the VUV beam through the optical components without having to pump the secondary vacuum system. Five vacuum cylinder vessels are connected together to insure a good vacuum ($\sim 1.0 \times 10^{-6}$ mbar) along the VUV path. Each of them is dedicated to receive an optical function such as a beam splitter (i.e. a thin CaF_2window that reflect only 5% of the incident VUV energy), a shutter synchronized with the external laser trigger (i.e. to allow a precise irradiation dose by pulse counting), mirror and CaF_2 lens that directs and focalizes the VUV beam onto the sample surface, respectively. The VUV beam is focused on the silicon surface to obtain a spot having an area of the order of several square millimetres, depending on the desired fluence. The connection between the UHV STM system and the secondary vacuum parts is obtained by a home made flange sealed externally with a Teflon gasket on a CaF_2 window. Due to this existing mechanical connection to the STM, the VUV laser beam has a fixed and arbitrary incident angle with the surface of 62°. Finally, the laser, the power meter and the shutter can be controlled via a computer. A precise measurement of the VUV transmission and reflection of all the optical components is performed before and after the irradiation processes to take into account any variation of their initial specification during laser use. Therefore, the energy per pulse, the fluence and the total irradiation dose, applied to the silicon surface is perfectly known. The laser spot size focused on the surface is measured by applying the laser beam to a quartz piece shaped like a silicon sample held in a sample holder and positioned like it inside the STM. The VUV laser beam is then positioned horizontally and vertically in order to coincide with the STM tip and to explore the irradiated zone where beam energy slowly varies in comparison with nanoscale areas observed with the STM.

3. RESULTS AND DISCUSSION

The observation of the surface with the STM is the result of the relaxed excited surface after irradiation. Because the number of dangling bonds (DBs) observed can vary from one STM topography to another after irradiation, the sample is scanned horizontally within the irradiated zone with images varying from 100×100 nm^2 to 20×20 nm^2 at selected places.

Figure 2.a shows a typical image of the Si(100)(2×1):H surface after hydrogenation and before irradiation. During the irradiation of the surface many processes can occur (i.e. new isolated DBs created, the creation of DBs near an existing DB, or the desorption and re-deposition of impurities from one area of the surface to another (cf Fig. 2.b), and of course the diffusion of hydrogen on the surface). Figure 2.b shows the result of an irradiation of the Si(100)(2×1):H surface after a 6 J dose at 2.8 mJ.cm^{-2}. It is very difficult to isolate on STM topograpies the DBs that have been created nearby a silicon dimer with an existing DB or nearby a defect. Therefore we have limited this study to the counting of only new isolated DBs observed on the surface. To measure the statistical variation of the number of new dehydrogenated sites created by the laser irradiation we have performed a precise counting of the dangling bond (DBs) existing after hydrogenation and just before irradiation. This involves the treatment of several tens of images especially when the irradiation dose and the fluence are low. We have voluntary limited our study to fluences lower than 5mJ.cm^{-2} to avoid any thermal contribution due to electronic desorption processes.

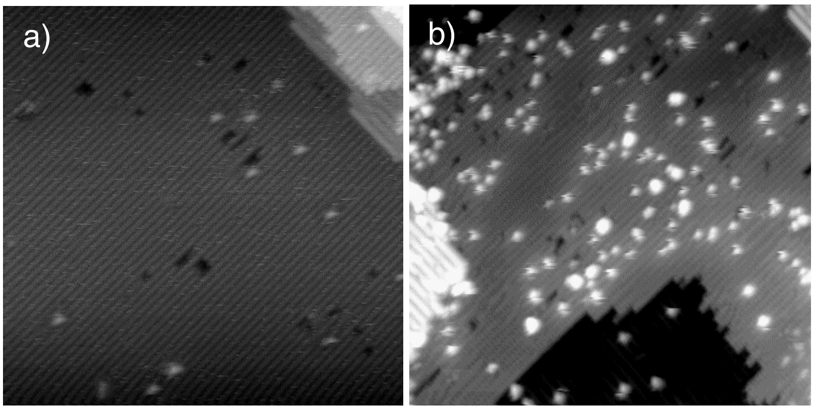

Figure 2. STM topographies of a) Si(100)(2×1):H at I = 0.2 nA, Vs = - 2.0 V, 40×40 nm^2 after hydrogenation. b) other area of Si(100)(2×1):H at I = 0.2 nA, Vs = - 2.0 V, 40×40 nm^2 after 157 nm irradiation, Dose = 6 J at 2.8 mJ.cm^{-2}.

3.1 Variation of new dehydrogenated sites vs Irradiation dose and fluence

We have measured the mean values of the of number of dehydrogenated bright sites created (i.e. the number of DBs counted after irradiation minus the number of DBs existing before irradiation) for irradiation doses varying from 0.87 J up to 23 J for 3 different pulse energy denities ~ 0.7 mJ.cm^{-2}, ~ 2.8 mJ.cm^{-2} and ~ 4.0 mJ.cm^{-2}.

The figure 3 shows that the variation of new DBs sites varies linearly with the irradiation dose applied to the surface. It indicates that the regime studied causes no particular damage on the surface structure. Furthermore, it shows a dispersion of the linear law around an average slope. These results indicate that the DBs observed with our method are created with a one photon process. Additionally, the DBs observed on the surface are isolated and does not appear as pairs like when the DBs are thermally created. The previous work performed on Si(100)(2×1):H [9] shows that photodesorbed H at 157 nm follows a first order kinetics. However the comparison between the present result and those from ref. 10 is made difficult by the fact that in the photodesorption experiment [10], hydrogen may originate from both the surface and sub-surface sites whereas here we observe with the STM exclusively surface sites. Furthermore, because of the lack of sensitivity, the photodesorption experiment [10] has been performed in a regime of high dose ($>$ 100 J.cm^{-2}) in comparison with our case (24 J.cm^{-2}). This emphasis the very high sensitivity of the STM for studying such laser photodesorption effects.

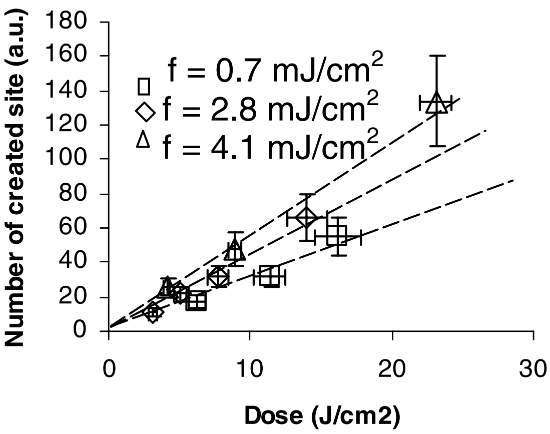

Figure 3. Variation of created DBs sites on Si(100)(2x1):H vs the irradiation dose for the 3 different fluences cited.

3.2 Surface structure observed with the STM

To understand the nonlinearity of the curve of figure 3.b it is important to observe thoroughly STM topographies of the surface after irradiation into more details.

The structure of the surface (2×1) is preserved as shown on figure 4.a or 4.b for long irradiations but it appears dark zones occasionally surrounded by dangling bonds. These dark areas look very similar, in addition of the previous mentioned dehydrogenated sites (bright spots) to missing dimers which would result has the desorption of Si-H species along silicon dimers as showed on figure 4.a. Furthermore, other dark areas with less well defined geometry (figure 4.b) are assigned to a local decreasing of the conductivity of the surface occupied states. This latest phenomenon may be due to dopant diffusion or hydrogen diffusion towards the surface trapped within dopant area as we use strongly doped samples.

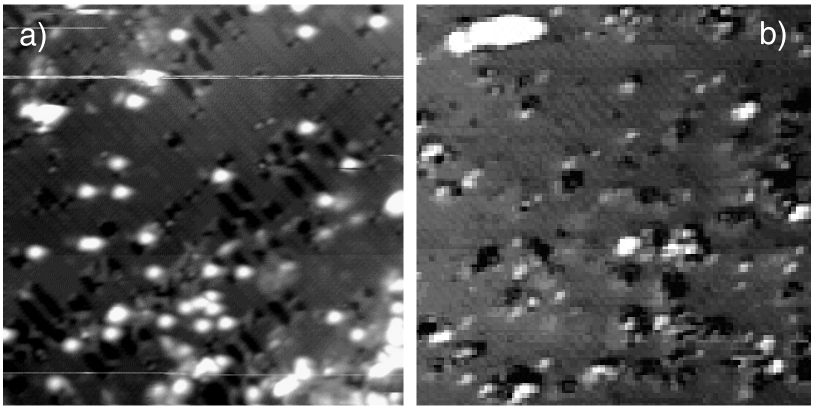

Figure 4. STM topographies of a Si(100)(2$\times$1):H surface at I = 0.2 nA, Vs = - 2.0 V, after 157 nm irradiation, dose $\sim$ 22 J at 4 mJ.cm^{-2}. a) 40 $\times$ 40 nm^2 and b) 80 $\times$ 80 nm^2.

4. CONCLUSION

We have performed the first analysis of a pure photochemical process at atomic scale using STM techniques and laser photo-desorption experiment. We have shown that the creation of DBs at the surface of the Si(100)(2$\times$1):H is rapidly coupled with other electronic processes inducing complex reactions within the surface and sub-surface.

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