Chemical Physics Letters 610–611 (2014) 223–227

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Hydrogen-induced healing of cluster-damaged silicon surfaces

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ARTICLE INFO

Article history:
Received 26 April 2014
In final form 16 July 2014
Available online 23 July 2014

ABSTRACT

A silicon surface which was partly damaged by the violent impact of hydrogenated silicon clusters has been treated by atomic hydrogen. After the exposure with hydrogen atoms, we observe that the ill-defined silicon surface is rearranged to its initial crystalline structure and that the silicon atoms of the deposited cluster are now incorporated in the crystalline structure of the repaired substrate surface.

1. Introduction

Recently, hydrogenated silicon nanoparticles synthesized in a plasma enhanced chemical vapor deposition (PECVD) reactor have been shown to be ideal precursors for the deposition of high quality silicon thin films, such as polymorphous [1], microcrystalline [2], and epitaxial silicon thin films [3,4] with relatively high deposition rates. Deposition mechanisms of hydrogenated silicon clusters on crystalline silicon substrates under realistic plasma conditions have been investigated by Ning et al. by means of molecular dynamics (MD) simulations with a special emphasis on the experimental parameters governing the various deposition processes from soft-landing to destructive deposition [5,6]. Among other impact parameters, cluster impact energy has the most significant influence on the deposition mechanisms. Low impact energies lead to the soft-landing of the clusters on the substrate. In the intermediate impact energy range, the clusters partially dissociate. Complete cluster dissociation followed by fragment migration onto the surface and cluster atom penetration into the lattice is found for high impact energies.

During the growth of thin silicon films by PECVD, there is always a continuous flux of atomic hydrogen to the surface. This is the result of the dissociation of silane and hydrogen molecules in the plasma reactor. Atomic hydrogen plays a crucial role in PECVD. For instance, it is known to heat up plasma-born hydrogenated silicon clusters [7], to trigger the auto-assembly of silicon nanocrystals [8–14], and to cause silicon surface etching [15,16]. Fontcuberta et al. have studied the role of atomic hydrogen on the growth of thin silicon films based on *in situ* spectroscopic ellipsometry measurements. In their experimental investigation, hydrogenated amorphous silicon (a-Si:H) and hydrogenated polymorphous silicon (pm-Si:H) films were exposed to hydrogen plasmas. For both materials, they observed the formation of a hydrogen-rich subsurface layer during the first minute of the hydrogen exposure. Thereafter, the hydrogen-rich subsurface layer thickness remained relatively constant while the total film thickness decreased. The hydrogen diffusion coefficient and etching rate were found to be higher in a-Si:H films than in pm-Si:H ones. Since a possible transition to the microcrystalline phase is in general induced by H-atoms, the authors conclude that microcrystalline materials can be obtained from amorphous silicon films, but not from polymorphous ones even for relatively similar large atomic hydrogen flow conditions in the plasma reactor [15,16]. The work of Sriraman et al. [17] demonstrated hydrogen-induced relaxation of partially strained silicon thin films by both MD simulations and infrared spectroscopy. The authors [17–19] have illustrated one possible mechanism: hydrogen atoms diffusing through the amorphous silicon films can insert temporarily into strained Si—Si bonds leading to the formation of intermediate bridging and bond-centered Si—H—Si configurations. When the H-atoms move away, the strained Si—Si bonds relax resulting in crystalline configurations because the silicon atoms are now able to move into lower energy states.

In the present work, we will employ atomic hydrogen to treat the silicon surface which was locally damaged by the violent impact of a hydrogenated silicon cluster to see if there is a transition to an ordered structure as the one of the initial silicon surface before the cluster-induced damage.

2. Simulation details

We have employed the general chemical dynamics computer program VENUS [20] with the empirical interatomic Ohira-Tersoff

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http://dx.doi.org/10.1016/j.cplett.2014.07.034
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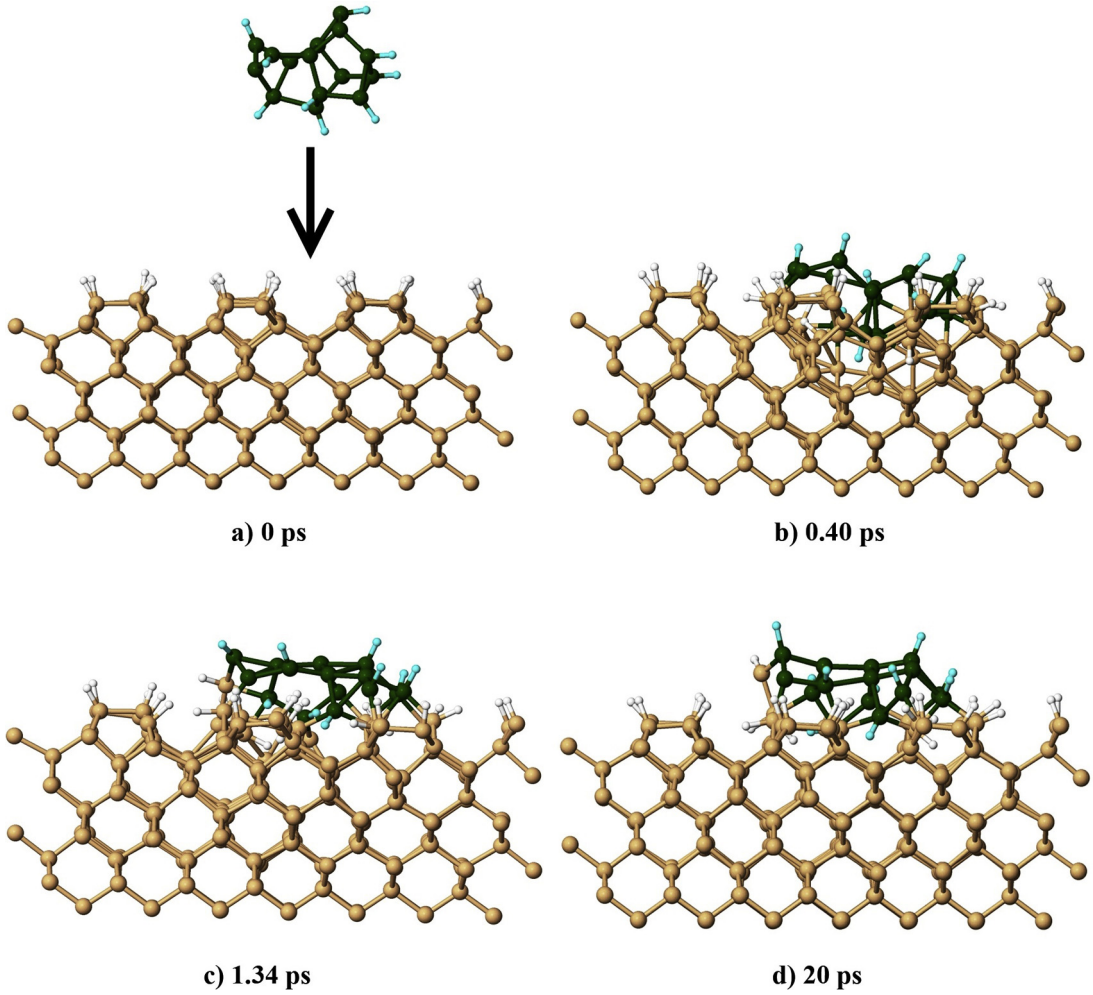

Figure 1. Snapshots of the atomic configurations at various times during the deposition of the $Si_{15}H_{10}$ cluster onto the substrate at 573 K with an impact energy of 3.70 eV/atom. The large brown spheres represent surface silicon atoms while the green ones represent silicon atoms of the $Si_{15}H_{10}$ cluster. The small white spheres represent surface hydrogen atoms while the cyan ones represent hydrogen atoms of the $Si_{15}H_{10}$ cluster. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

potential [21–23] to simulate the deposition of plasma-born hydrogenated silicon clusters on crystalline silicon substrates and the H-treatment of cluster-damaged silicon surfaces. The time step used in our MD simulations was chosen to be 0.1 fs to follow trajectories of up to 400 ps.

2.1. Deposition of plasma-born hydrogenated silicon clusters on H-terminated Si(1 0 0)-(2 × 1) surfaces

We have chosen plasma-born $Si_{15}H_{10}$ clusters to deposit on H-terminated Si(1 0 0)-(2 × 1) surfaces. The $Si_{15}H_{10}$ cluster was previously generated in a growth process under realistic plasma conditions presented in Refs. [8,24]. This cluster was optimized to its minimum energy structure and heated up to 300 K to reproduce our experimental plasma conditions.

The H-terminated Si(1 0 0)-(2 × 1) substrate has the dimensions of 21.72 Å × 21.72 Å × 10.86 Å and consists of 288 silicon atoms terminated by 32 hydrogen atoms. Periodic boundary conditions are applied in the two directions parallel to the surface plane. The top silicon layer is a (2 × 1) reconstructed layer including silicon dimers. The bottom two silicon layers are kept rigid in their equilibrium positions to avoid the translation and bending of the entire substrate in space. To control the substrate temperature, we apply a Berendsen thermostat [25] to the three silicon layers above the two rigid layers. The H-terminated Si(1 0 0)-(2 × 1) substrate was heated to 573 K corresponding to the low temperature requirement in silicon thin film production in industry.

The $Si_{15}H_{10}$ clusters were initially placed at positions sufficiently far from the substrate so that their interaction with the surface can be neglected. The clusters were then deposited onto the surfaces with impact energies between 0.42 and 6.21 eV/atom corresponding to soft-landing and destructive deposition, respectively. More in detail, at impact energies from 0.42 to 1.84 eV/atom, the $Si_{15}H_{10}$ cluster lands on the surface forming new Si—Si bonds between the cluster and the substrate. No cluster atoms penetrate into the substrate during these deposition processes. Clusters deposited with impact energies from 2.39 to 5.30 eV/atom; however, partly or completely penetrate into the substrate. Some of those cluster silicon atoms then move to the surface and settle there by forming bonds with surface silicon atoms. High impact energies above 6.21 eV/atom cause serious and irreversible damage to the crystalline substrate structure. To investigate the hydrogen treatment of silicon surfaces after they became damaged by the cluster impact, we start from a trajectory in which the cluster with an impact energy of 3.70 eV/atom approached the silicon substrate at 573 K leading to a 'rough' surface with a locally disordered structure (see Figure 1d).