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Temperature programmed desorption studies of deuterium passivated silicon nanocrystals

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ABSTRACT

As grown silicon (Si) surfaces are known to reconstruct in order to reduce the number of dangling bonds. Surface reconstructions of hydride-terminated Si(100) and Si(111) surfaces have already been extensively studied using temperature programmed desorption (TPD). The surfaces of nanocrystals, are yet to be probed using TPD. Si nanocrystals less than 8 nm and ranging from 50 to 200 nm in diameter are grown on SiO₂ surfaces in an ultra high vacuum chamber and the as grown surfaces are exposed to atomic deuterium. Desorption spectra are interpreted using analogies to Si(100). TPD spectra show that that the nanocrystals surfaces are covered by a mix of monodeuteride, dideuteride and trideuteride species. Monodeuteride species can be isolated by selectively annealing away the dideuteride and trideuteride, monodeuteride and dideuteride species can be isolated by annealing away the trideuteride. The relative populations of the deuterides depend on particle size, and their manner of filling on nanoparticles differs from that for extended surfaces. Etching of the nanocrystal surface is observed during TPD, which is a confirmation of the presence of trideuteride species on the nanocrystal surface.

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1. Introduction

Bulk Si being an indirect semiconductor is a poor emitter of light. However, systems containing nanometer sized features of Si such as porous silicon [1], silicon/silicon dioxide superlattices [2], silicon nanoparticles [3,4] and silicon nanowires [5] have been known to emit light in the visible region of the spectrum with the wavelength being dependent on the size of the Si nanostructure. The ratio of surface atoms to the total number of atoms can be quite large in nanoscale systems. A Si atom in the bulk is bonded to four other Si atoms. At the interface however, there are unsatisfied (dangling) bonds. These uncompensated bonds establish localized defect states within the forbidden gap of Si nanocrystals, providing sites for non-radiative recombination of excitons [6]. Earlier studies with extended Si surfaces show that the unpassivated surface tends to minimize its energy by reducing the number of dangling bonds through relaxation and surface reconstructions [7,8]. Theoretical studies of similar reconstructions on nanocrystal surfaces show that such reconstructions result in severe distortion of the surface bonds [9]. Defect states associated with bond distortions are expected to appear in the band gap [10]. Puzder et al. [11] have predicted that surface step reconstructions unique to the highly curved surfaces of nanoparticles reduce the optical gap substantially. Relaxation will not eliminate all dangling bonds and

hence there will be some defect states due to the remaining dangling bonds. Another way of terminating the dangling bonds is by capping them with hydrogen.

Hydrogen-terminated extended Si(100) and Si(111) surfaces have been studied using TPD [7,12,13]. A monohydride-terminated Si(100) surface (one H atom per Si atom) can be obtained even with saturation doses of atomic hydrogen at elevated temperatures (~650 K). If H-dosing is done around 400 K, the surface first saturates with monohydride species after which dihydride species (two H atoms per Si atom) begin to form [14,15]. If dosing is done at low temperatures (~210 K), a trihydride species is formed. In TPD spectra, hydrogen desorption from the hydride species occurs at different temperatures [13]: the monohydride (β_1) desorbs around 780 K, the dihydride (β_2) desorbs around 680 K and the trihydride (β_3) appears as a broad feature <600 K. Trihydride species can abstract an H atom from a neighboring hydride and form SiH₄, which desorbs around 600 K. This results in etching of the Si surface.

The various hydride species on porous silicon surfaces and their desorption kinetics have been investigated using FTIR by Gupta et al. [16] and using TPD by Martin et al. [17]. They conclude that the as-prepared surfaces are covered by a mixture of mono-, diand trihydride species. FTIR studies conducted on aerosolized Si nanocrystals have shown that nanocrystal surfaces predominately contain trihydride and dihydride species [18].

We use TPD to probe the nature of the hydride termination on nanocrystal surfaces. Si nanocrystals are grown on SiO₂ surfaces at





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875 K. Large particles (50–200 nm) were grown using chemical vapor deposition (CVD) to see how they mimic the desorption features from extended Si surfaces. Nanoparticles (<8 nm) were grown using a mixed process of hot wire chemical vapor deposition (HWCVD) and CVD. Similar to extended surfaces, we find nanocrystal surfaces are terminated by a combination of deuteride species; however, in contrast to extended surfaces dideuteride and trideuteride species start forming before the monodeuteride state saturates.

2. Experimental

The experimental apparatus consists of a growth chamber, a heating furnace and an analytical chamber, all connected to each other via an intermediate transfer chamber. The base pressure of the growth and analytical chambers is $5\times 10^{-9}\,\text{Torr.}$ The transfer chamber and furnace have a base pressure of 3×10^{-8} Torr. More details of the system are available elsewhere [19,20]. Si particles were grown in the growth chamber with disilane (Voltaix; 4% in He). A hot tungsten filament situated 3 cm away from the substrate is used in HWCVD; a constant filament current of 4 A was used that led to an estimated filament temperature of 1500 °C [21]. Disilane partial pressures during CVD and HWCVD were 10⁻⁴ Torr and 8×10^{-8} Torr, respectively. The samples were transferred in situ to the analytical chamber where a differentially pumped Thermo Electron Smart IQ+ mass spectrometer covered by a nose cone with a 0.5 cm opening was used for TPD. Mass alignment of the mass spectrometer was done using He⁺ (mass/charge 4 [m/e 4]), Ar⁺ (m/e 40), and Xe^{+'} (m/e 129). All TPD spectra were collected using an ionizing energy of 57 eV and a constant dwell time. Particle size was determined using scanning electron microscopy (SEM) [Zeiss Supra 40VP] under an accelerating voltage of 15 kV after coating the sample with 1 nm of Ir. Secondary electrons are detected and the smallest particles that can be resolved are \sim 4 nm in diameter.

Si(100) wafers with 10 nm of thermal oxide were supplied by Freescale, Inc. These wafers were cut into squares of 1.6 cm \times 1.6 cm. Each piece was sequentially rinsed with acetone, ethanol and deionized (DI) water and then dipped in piranha solution (60% DI water, 10% H₂O₂ and 20% H₂SO₄) for 15 min. Subsequently, the samples were dipped in 2% HF for 4 s removing \sim 1 nm of the oxide, thoroughly rinsed in DI water and then dried using high purity helium. The cleaned samples were mounted on a 1 in. diameter molybdenum ring and inserted into an ultrahigh vacuum system using a load lock.

The samples were then annealed in the furnace at 975 K for 15 min and allowed to cool to \sim 375 K and baseline spectra were taken for various m/e signals in the analytical chamber. Baseline spectra were taken by heating the sample at 3 K/s from 375 K to 1000 K while monitoring signals D_2^+ , SiD_2^+ , SiD_2^+ , SiD_3^+ and SiD_4^+ corresponding to m/e ratios of 4, 30, 32, 34 and 36, respectively. The sample was then transferred to the growth chamber and heated to the growth temperature of 875 K and allowed to equilibrate thermally for 15 min. A 17 min CVD time was used to grow 50-200 nm sized Si islands (Fig. 1). Small particles <8 nm were grown using a two step process: HWCVD for 5 min followed by CVD for 4.5 min (Fig. 2). At a growth temperature of 875 K, Si nanoparticles are expected to be crystalline [22,23]. The inset of Fig. 2 presents a transmission electron microscopy image (JOEL 2010F operated at 200 keV) of a 5 nm nanocrystal that was grown by the two step process of HWCVD seeding and CVD on a 50 nm silicon dioxide membrane obtained from Structure Probe, Inc.

After growth was complete, the sample was allowed to cool to \sim 375 K. It was then transferred to the analytical chamber where a 3 K/s ramp was employed to flash the sample at 975 K to remove



Fig. 1. SEM image of silicon nanoparticles after 17 min CVD.



Fig. 2. SEM image of silicon nanoparticles after 5 min HWCVD seeding and 4.5 min CVD. Inset-TEM image of crystalline particle.

any disilane fragments that may have readsorbed on the nanocrystal surface while the growth chamber was being evacuated to base pressure. The sample was transferred back to the growth chamber after it cooled to ~375 K and the cracking filament, which was ~3 cm away from the sample was turned on under a D₂ pressure of 2×10^{-6} Torr. During dosing, the sample temperature rose by no more than 15–20 K. The sample temperature during dosing was estimated to be around 375–395 K. After dosing is complete, the sample was transferred to the analytical chamber and another TPD spectrum was collected. Sample temperature was determined using a type-K reference thermocouple that was fixed between the heating bulb and the sample. In separate experiments this reference thermocouple was calibrated against an instrumented sample that had a type-K thermocouple attached to the sample surface.

3. Results and discussion

Over Si(100) the monohydride and dihydride are denoted by β_1 and β_2 , which desorb around 800 and 680 K respectively; the trihydride denoted by β_3 appears as a broad feature below 600 K [13]. We use similar nomenclature as that used for the hydride states of Si(100), namely: β_1 for monohydride species, β_2 for dihydride species, and β_3 for trihydride species. D₂ exposures are reported in Langmuir (1 L = 10⁻⁶ Torr s); the efficiency of D₂ cracking and the absolute D atom flux are unknown.

3.1. Experiments with large particles

Large Si particles were grown using a 17 min CVD procedure and subjected to various doses of atomic deuterium. In between each dose, the samples were annealed at 975 K for 15 min. Fig. 3 shows D_2^+ (*m*/*e* 4) TPD spectra for various exposures starting from 120 L. Two peaks stand out clearly, one around 800 K and the other around 680 K and given similarities to TPD from Si(100), we associate these with monodeuteride and dideuteride species, respectively. Unlike extended surfaces [14,15], the dideuteride state starts filling in before the monodeuteride saturates. With increasing exposures, the intensities of both features increase indicating that both monodeuteride and dideuteride species form simultaneously on the nanocrystal surface. The intensity of the dideuteride is always lower than the monodeuteride. With increasing exposure, the leading edge of the β_2 feature shifts to a lower temperature raising the possibility of a new species, such as trideuteride (β_3) , which can form at higher exposures.

Cheng et al. [13] have demonstrated with Si(100) that trihydride species can desorb as silane by extraction of an H-atom from a neighboring Si-hydride thus etching the Si surface. If trideuteride species (SiD₃) formed on the nanocrystal surface, SiD₄ evolution should be detected during TPD. SiD^+ (*m*/*e* 30), SiD_2^+ (*m*/*e* 32) and SiD_3^+ (*m*/*e* 34) and SiD_4^+ signals were monitored during TPD. The SiD_4^+ signal has a very low intensity, so other fragments are used as an indication of trideuteride formation on the nanocrystal surface. Fig. 4 shows the D₂ TPD spectrum along with the corresponding etching products from an experiment in which the particles were subjected to 1800 L D₂. The β_3 feature is more apparent than in Fig. 3. The presence of β_3 and etching products confirms the presence of trideuteride species over the nanoparticles.

With extended Si surfaces, trihydride formation is not observed except at low temperature (T = 210 K) H-dosing [13]. On the contrary, there is substantial trideuteride formation on nanocrystal surfaces when subjected to atomic deuterium doses at 375 K. The Mo ring can introduce desorption features [24]. In order to ensure that none of these signals originated from the Mo ring, control experiments were conducted in which the Mo sample support ring was subjected to 17 min exposures to disilane at 875 K followed by atomic D doses. TPD spectra did not show the presence of any etching products, confirming that nanoparticles were solely responsible for the etching products.

The nanoparticles were also repeatedly subjected to a constant exposure of 1800 L D₂ with intermittent annealing at 975 K for 15 min to check if the intermediate annealing had any effect on

3600 L

18001



Fig. 3. D₂ desorption from large Si particles.



Fig. 4. D₂ desorption spectrum along with the corresponding etching products observed from large particles. The lines below each spectrum indicate the baseline signal intensity, which has been truncated for the sake of clarity.

the nature of the deuteride termination. The results are displayed in Fig. 5. The TPD spectra are identical and there is no change in the intensities or locations of the peaks. Additionally there were no differences in the SEM images before and after the experiments, indicating that the intermediate annealing does not substantially affect the size of big particles.

3.2. Experiments with small particles

A mixed process involving HWCVD seeding for 5 min followed by CVD for 4.5 min was employed to grow small Si particles <8 nm in diameter. After each TPD, the sample was flashed at 975 K using a 3 K/s ramp instead of the 15 min anneal in order to minimize agglomeration of the particles. The TPD spectra from repeated 1800 L doses are shown in Fig. 6. Unlike with large particles, there is an increase in β_3 with each dose, and β_1 and β_2 decrease in intensity. The total area decreases with each TPD such that after TPD 5 the area is 84% of the area associated with TPD 1.

The decrease in TPD area, primarily of the β_1 and β_2 features, likely results from a loss of Si nanocrystal surface area caused by both etching and agglomeration. Similar to the large Si particles,



Fig. 5. D2 desorption spectra from large Si particles subjected to repeated doses of 1800 L



Fig. 6. D_2 desorption spectra from small Si particles subjected to repeated doses of 1800 L. The thin line corresponds to a control experiment in which nanocrystals were not grown on the SiO₂/Si(100) substrate.

etching products are observed as shown in Fig. 7, and the β_3 feature in Fig. 6 is associated with etching. SEM images of the sample after the experiments (not shown) indicate some coalescence of particles; however, the resolution of the SEM does not reveal an average smaller size as a consequence of etching in those particles that have not coalesced. While the β_1 and β_2 area decrease can reasonably be connected to agglomeration, the exact cause for an increase in the β_3 feature with repeated TPD cycles remains unresolved. One possibility could be a progressive roughening of nanocrystal surfaces with TPD cycles that acts to increase the surface concentration of sites where trihydride species form.

The thin line in Fig. 6 is from a control experiment in which the Mo ring and silicon wafer were subjected to $1800 \text{ L} \text{ D}_2$. Winkenwerder et al. [24] have shown that the desorption feature at 800 K is due to D₂ desorption from silicon dioxide. Using control experiments (not shown), we conclude that the feature around 450–600 K is from the Mo ring. The intensities of the features from the Mo ring and silicon dioxide are much lower than those from the particles.



Fig. 7. D_2 desorption spectrum along with the corresponding etching products observed from the small particles subjected to the first cycle of D_2 exposure. The lines below each spectrum indicate the baseline signal intensity, which has been truncated for sake of clarity.



Fig. 8. D_2 desorption spectra from small particles. Inset: D_2 desorption from small particles subjected to 15 L exposure.

From experiments with large particles, we know that the different deuteride species form simultaneously unlike with extended Si surfaces; the same was observed with small particles. TPD spectra from smaller doses are displayed in Fig. 8. The 15 L dose is shown in the inset for clarity. The β_2 feature is present even at low exposures of 15 L and at higher exposures, both β_1 and β_2 increase in intensity illustrating that the monodeuteride does not saturate before the dideuteride fills in. Since no etching products are observed at such low exposures, we conclude that the feature at 450 K is from the Mo ring on which the sample is mounted.

With extended Si surfaces, it is possible to selectively desorb a particular hydride species, isolating the hydrides that desorb at higher temperatures. This technique may be useful in isolating a specific deuteride species on the nanocrystal surface. A 1800 L dose was employed, which was shown to create a surface covered by a mix of deuteride species (Fig. 7). The sample was then annealed at different temperatures for 15 min and allowed to cool to around 375 K following which a TPD spectrum was recorded. The "no anneal" spectrum in Fig. 9 is the initial TPD spectrum from the 1800 L dose. By annealing at 650 K, it is possible to completely isolate the monodeuteride. Annealing at 500 K results in a surface ter-



Fig. 9. D_2 desorption spectra from large Si particles subjected to repeated doses of 1800 L and subsequently annealed at 650, 550, 500, 450 and 700 K for 15 min.

mination devoid of trideuteride species. A slightly lower anneal temperature of 450 K results in the retention of the trideuteride species and a 700 K anneal desorbs all the deuteride species leaving behind a small feature that is due to deuterium desorption from the SiO₂ surface [24].

4. Summary

TPD experiments reveal that Si nanocrystals both big and small behave very differently from extended Si surfaces. Formation of the dideuteride and trideuteride species seems to be facilitated by the curvature of the nanocrystal. The presence of SiD_4 fragments in the TPD spectra is confirmation of the presence of trideuteride species. Interestingly, we find that unlike extended surfaces, trideuteride species are prevalent on the nanocrystal surface even when the dosing temperature is around 375 K. Tsai et al. [25] have shown with FTIR that porous silicon gives only a weak luminescence when SiH species are present on the surface; the luminescence starts to increase only when SiH_2 species are present. Our results indicate that it is possible to control the type of hydride termination on nanocrystal surfaces.

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