H Coverage Dependence of Si(001) Homoepitaxy

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We have investigated the role of surface H in Si(001) homoepitaxy using *in situ* medium energy ion scattering and time-of-flight H recoil detection. The addition of submonolayer coverages of atomic H produce relatively modest effects on epitaxy for $T_g \leq 200\,^\circ$C. But at surface H concentrations surpassing 1 monolayer, we find a disruption of epitaxy, which is delayed to higher temperatures than on bare Si(001). The degradation of epitaxy correlates with the presence of surface dihydrides, which break the dimer configuration of Si(001).

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It is commonly held that at low growth temperatures (T_g), epitaxy proceeds up to a certain film thickness, $h_{\rm epi}$, before amorphous material begins to grow [1,2]. Furthermore, $h_{\rm epi}$ depends on T_g with an Arrhenius relation, suggesting an activated process [2]. But it is not understood whether the breakdown in epitaxy is an intrinsic property of crystal growth, or an extrinsic phenomenon. Various investigators have suggested intrinsic origins of $h_{\rm epi}$, including surface roughening [2,3] or surface disorder [4,5]. Alternatively, extrinsic sources might determine $h_{\rm epi}$. Segregated adsorbates could potentially influence surface mobility and adversely affect the growth dynamics. In particular, for growth below 450 °C, H can accumulate on the growth front. To clarify the role of adsorbates in determining $h_{\rm epi}$, we have examined Si growth in the presence of *controlled* quantities of surface H, with *in situ* determination of both Si crystallinity and H depth distribution with medium energy ion scattering (MEIS). For H coverages between 0.2 and 1 monolayer (ML), we find almost no effect on epitaxy (1 ML $= 6.78\times10^{14}/\text{cm}^2$). But at higher coverages, there is a sharp breakdown in crystal growth, requiring a higher T_g to obtain epitaxy. Thus, we find that $h_{\rm epi}$ is an intrinsic property of Si(001) homoepitaxy, but one that can be influenced by adsorbates.

We have chosen H/Si(001) as a case study for several reasons. First, adventitious H adsorption is quite common, yet hard to detect by conventional surface science techniques. Second, H is commonly used to assist in Si epitaxy. When Si is grown by chemical vapor deposition (CVD) from gas-phase precursors (e.g., SiH_4) at low temperatures, H passivates the surface, rendering it inert to contaminants that would prevent epitaxy [6,7]. Furthermore, it is believed that H may actually be beneficial for epitaxy, contributing to interface abruptness for heterolayers by reducing surface segregation and diffusion during growth [8]. Analogous behavior has also been found when a variety of dopants are adsorbed on the growth front [9].

The experimental approach in this Letter differs from many previous studies [2,10] in several key respects: Previous work used molecular H, which has a negligible sticking coefficient on Si(001), making surface contamination nearly unavoidable. Also, the present study includes a means of monitoring H coverage during growth. As a result, we can confidently distinguish the effects of surface H from spurious effects.

The measurements reported below relied on two experimental probes: MEIS [11] and time-of-flight elastic recoil detection (ERD) [12,13]. Both experiments used the same electrostatic detector and ultrahigh vacuum system and used the same specimens, grown *in situ.* For MEIS, the sample was probed with a 220 keV Li^+ beam. Li^+ ions that undergo Rutherford-like core collisions with heavy substrate atoms (Si) are detected. The "backscattered" Li^+ ions lose energy quasicontinuously to the sample's valence electrons. Tabulated stopping powers are commonly available to convert the ion energy loss to a depth scale. In addition, channeling was used to determine film crystallinity. Complementary information on the depth distribution of light elements was obtained by ERD. When an incident ion beam encounters a light species, the probe ion undergoes a small angle scattering event, imparting a substantial recoil energy to the target nucleus. The recoiling proton is detected directly. For ERD, we also used an incident 220 keV Li^+ beam, but the beam was chopped, so a timing-coincidence circuit could distinguish recoiled H^+ ions from backscattered Li^+ ions. For both techniques, the ion energies are sufficiently great to allow the use of well known screened Rutherford cross sections to interpret results. All the spectra shown were taken with the sample aligned to the $[11\bar{1}]$ channeling direction. Backscatter Si spectra are shown at a scattering angle of 50°, which is 14.74° from the surface. H recoil spectra were taken at a scattering angle of 44.3°. All of the data were obtained with ion beam doses less than 4×10^{14} ions/cm^2, which is sufficiently low to prevent significant H desorption or Si lattice damage.

Si(001) samples were prepared by outgassing at 600 °C, followed by a brief flash to 1200 °C. For H terminated surfaces, the samples were exposed to a flux of atomic H from a glass flask, 99.999% purity, with an auxiliary liquid nitrogen trap. The gas was introduced through a molybdenum tube with a concentric W filament. A 100 L

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(1 langmuir= 10^{-6} Torr sec) dose (background pressure) gave a surface coverage of 1.2 ± 0.1 ML, measured by ERD. The samples were allowed to thermally equilibrate a total of 90 min prior to growth, to 35 °C. Similar results were obtained with 45 min equilibration. Temperatures were estimated by extrapolating the power required to achieve 400 °C, as measured by infrared pyrometry. H coverages were measured before growth. Identical results were obtained on samples that did not undergo H coverage determination. Sample cleanliness was checked with x-ray photoemission, which showed only trace quantities of oxygen on H dosed samples. To eliminate the possibility of oxygen influencing the results, a sample was dosed with H, then immediately annealed to 600 °C, to desorb H, but not oxygen. Growth on the H desorbed sample was identical to growth on a bare surface, so any contaminants have insignificant effect. More detailed desorption experiments will be described below. Si was evaporated from an electron beam heated crucible, at a rate of 1 ML/min. After deposition, no impurities save H were detectable by either ion scattering or x-ray photoemission, suggesting that any gases present during deposition either do not stick to the sample, or fail to segregate during growth.

First, let us compare the crystallinity of films grown on bare and H terminated Si(001). A series of 50 ML films were grown at various temperatures, and analyzed by MEIS (Fig. 1). For $T_g = 200\,°C$, a backscatter peak is seen near the surface of samples grown with or without H. If H is present, the surface peak is noticeably larger. For comparison, the yield from a room temperature (RT) sample is also plotted, showing the result from an amorphous overlayer. For an epitaxial overlayer, the ions would channel through all but the very surface of the sample, and the spectrum would show only a surface peak. The yields from the 200 °C samples are much lower than the RT sample, indicating that the films are indeed epitaxial. If we compare the results at lower T_g, we see that the H terminated sample grown at 175 °C is largely amorphous. But growth on the bare surface shows a substantial degree of epitaxy down to 125 °C.

Clearly, the onset of epitaxy happens at a much higher T_g in the presence of H. But how does the H behave during growth? To address this, we have studied the H depth distribution as a function of T_g. A series of 20 ML films were grown on H terminated substrates for RT $\leq T_g \leq 120\,°C$. All of the films grown in this temperature regime were fully amorphous, yet substantial differences were found in the H depth distribution (Fig. 2). At RT, the H is evenly distributed throughout the deposited Si layer. As soon as T_g is increased, the H begins to segregate from the film. At $T_g = 120\,°C$, the H depth distribution is essentially identical to the original H terminated substrate, which is shown at the top of Fig. 2.

The efficiency of H segregation during growth is striking; the level of incorporation is less than the background level in Fig. 2. We can place an upper limit on the rate of

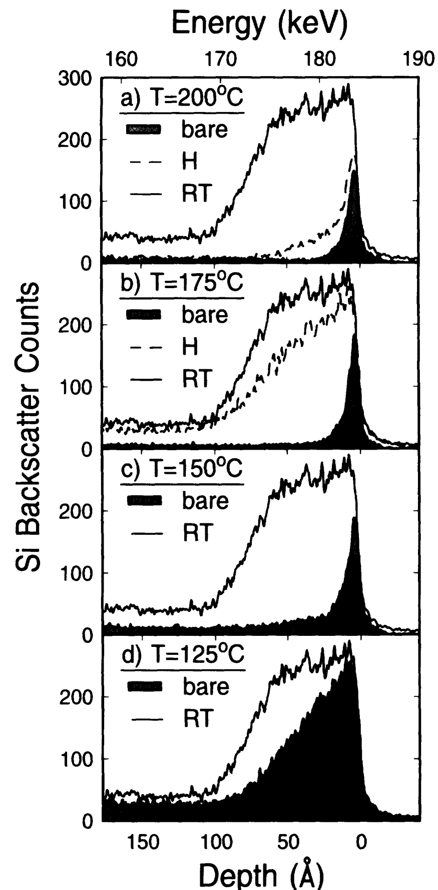

FIG. 1. Structure of Si films grown on Si(001) at varying temperatures. For RT growth (solid line) an amorphous overlayer forms. At higher T_g, an epitaxial layer grows, and ions channel through the epilayer. Films grown on H/Si(001) (dashed line) are amorphous at higher T_g than films on bare Si(001) (filled).

H incorporation by observing the decrease in surface concentration with film thickness. From the attenuation of the H surface peak, we estimate a H concentration in the film of less than 1% for $T_g \geq 120\,°C$. Furthermore, H is able to uniformly redistribute throughout the amorphous layer during growth at RT. Evidently, the H depth distribution is determined by the density of dangling bonds, or trap sites, rather than the mobility during growth. Growth at $T_g \geq 120\,°C$ results in an amorphous network with relatively few dangling bonds, and therefore little subsurface H. The high H mobility suggests that trapping of subsurface H is not an important effect for $T_g \geq 120\,°C$, but that H must play some role in altering the Si(001) surface.

We can gain further insight on the effect of H on Si(001) homoepitaxy by examining the coverage dependence of epitaxy. We adopted the following strategy: samples were treated with varying H doses prior to growth. Both the H coverage (before growth) and Si backscatter yield (after growth) were measured. The procedure was iter-

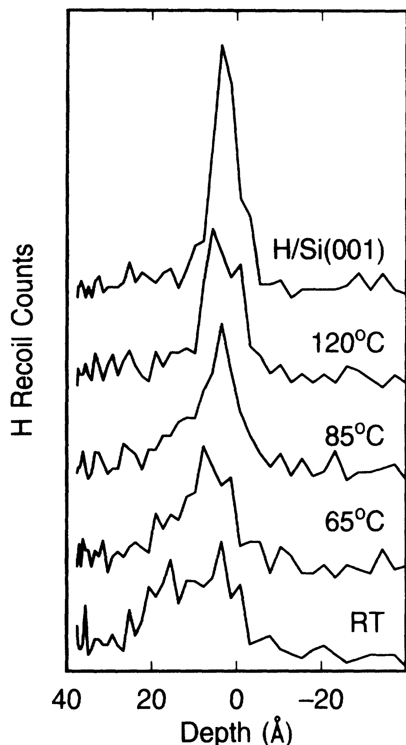

FIG. 2. H depth distribution for a-Si films grown on H/Si(001). At RT, a uniform depth distribution is observed. At elevated T_g, H is segregated from the film. All of the films showed nearly identical thicknesses of a-Si.

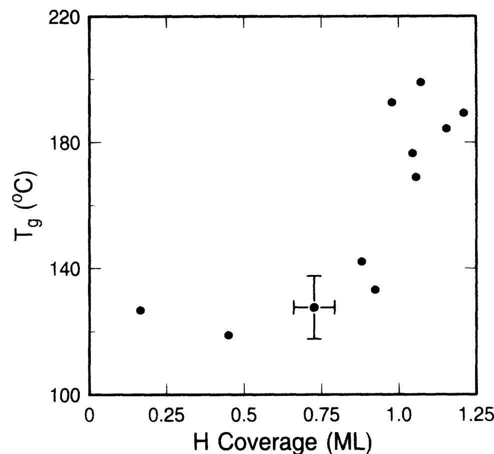

FIG. 3. H coverage dependence of Si homoepitaxy. T_g is defined as the minimum temperature required to grow 20 ML of epitaxial Si. A steep increase in T_g is observed at 1 ML.

ated, for different T_g, until 10–30 ML grew epitaxially. To present the data in a coherent fashion, we have adjusted T_g assuming an Arrhenius behavior as found in Ref. [2]. (The effect of the extrapolation is quite small, since the largest correction is 20 °C.) For H coverages $\leq$ 0.8 ML, there is almost no effect on the temperature required for epitaxy of 20 ML (Fig. 3). But as the coverage exceeds 1 ML, we observe a sharp increase in T_g. (Unfortunately, there is not a sufficient range of film thicknesses accessible to confirm Arrhenius behavior, but this should have no effect on our conclusions.)

From the coverage dependence observed in Fig. 3, we can speculate on the origin of the higher T_g required for epitaxy at high H coverages. It is well known that H can bond to Si(001) in a dihydride configuration, which is unstable for $T \geq 350\,°\mathrm{C}$ [14,15]. It is plausible that this configuration has a substantial effect on Si(001) epitaxy, since it breaks the dimer configuration present on both the monohydride and bare surfaces. If the dihydride site acts as a nucleation site or, alternatively, prevents nucleation of succeeding layers, substantial surface roughening may follow. Alternatively, formation of a hydrogen-passivated bulk defect may be thermodynamically favored over segregation of the dihydride. The critical role of higher order hydrides was tested by selectively desorbing dihydrides before growth. Converting the sample to a monohydride termination resulted in behavior similar to the bare surface. Samples were prepared with 1.2 ML of H (100 L exposure), which normally causes amorphous growth at 125 °C. Samples annealed for 5 min at 300 °C before Si deposition at 125 °C showed no change in H coverage, and resulted in an amorphous overlayer. But samples annealed to 350 °C before growth showed a reduction in surface H to 0.8 ML, and resulted in an epitaxial overlayer, confirming that the change in h_{epi} correlates with the presence of higher order hydrides.

Now let us return to examining the effect of adventitious H adsorption on h_{epi}. It is unlikely that H accumulation during growth has had a significant effect on previous studies [2]. Without deliberately introducing H, a well-defined h_{epi} can be seen in Fig. 1(d). Examination with ERD showed 0.2–0.3 ML of H after growth, the result of vacuum contamination. But the same degree of disruption of epitaxy was observed with much more H, so h_{epi} is not a sensitive function of H coverage in this regime. It would be valuable to examine growth at lower H concentrations, but it is not experimentally feasible.

To conclude, we have investigated the role of H in the growth of amorphous and epitaxial Si on Si(001). As the H coverage passes a full monolayer, there is a sharp increase in the temperature required for epitaxy. This increase is tentatively attributed to the presence of surface dihydrides, which can potentially disrupt the dimer structure of Si(001). The effects of H incorporation are negligible, since segregation starts at T_g much lower than the onset of epitaxy. If, in fact, higher order hydrides play a role in disrupting epitaxy at low temperatures, this effect would not be observed in Si CVD, which uses the monohydride surface [6,7,16]. However, our results are pertinent to molecular beam epitaxy in a H rich environment, as found in growth on HF cleaned Si(001) or chemical beam epitaxy.

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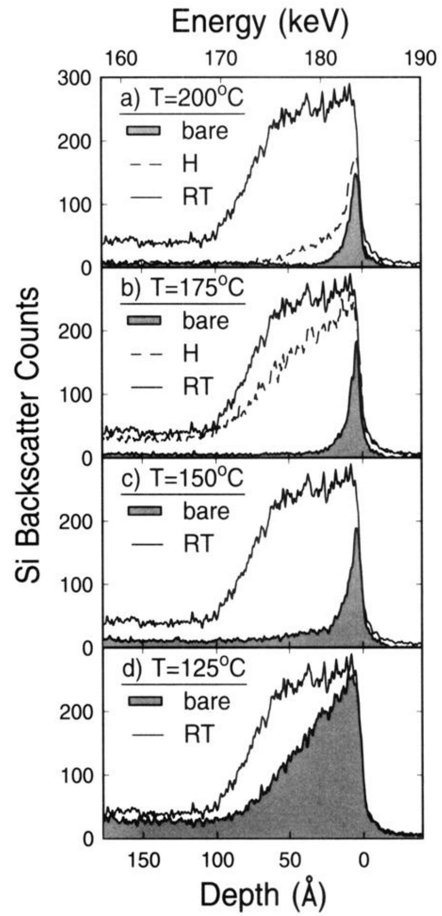

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