Effect of H on Si molecular-beam epitaxy

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In Si crystal growth by molecular-beam epitaxy (MBE) at low temperatures there is known to be an epitaxial thickness: an initially crystalline regime before the deposited film becomes amorphous. The predominant impurity in MBE is hydrogen, but the role of background H in low-temperature MBE has not previously been assessed. Here the effect of deliberate dosing of the Si surface with atomic H during low-T growth is studied. The epitaxial thickness is shown to be sensitive to very small additional H fluxes ($\approx 10^{-9}$ Torr, i.e., an increase in H only marginally above ambient). With further increases in dose rate, the epitaxial thickness decreases as $h_{\mathrm{epi}}=h_0-k(\ln P_{\mathrm{H}})$. Using secondary-ion-mass spectrometry data on the segregated H at the interface, we argue that breakdown in epitaxy is not caused directly by the surface concentration of adsorbed impurities. It is deduced that very small concentrations of H may influence the Si surface diffusion rate. The possible effect of background H adsorption on previous experiments on Si steps and surface diffusion is discussed.

I. INTRODUCTION

The low-temperature limit to epitaxy is of interest in both understanding the fundamental mechanisms of crystal growth and applying low-temperature epitaxy to the fabrication of abrupt junctions. In molecular-beam epitaxy (MBE), considerable interest has been aroused by the discovery that there is a limited thickness h_{epi} for epitaxy at low temperatures.[1] Understanding the cause for this thickness limit is the key to overcoming the so-called "doping problem" in Si MBE,[2] and this low-temperature limit has been intensively investigated in Si, Ge,[3] and GaAs.[4,5] The surprise of limited-thickness epitaxy was that crystalline growth was followed by amorphous deposition at fixed substrate temperature. This implied that the surface changed in either structure or composition during epitaxy so as to cause the subsequent formation of the amorphous phase. Possible limits on epitaxy are thus focused on gradual changes in either structure (step densities, etc.) or composition (e.g., from impurity segregation). H is a particularly important candidate, since H is the dominant background gas in almost all ultrahigh-vacuum (UHV) chambers and, most significantly, H is difficult to observe or detect using most analytical techniques. In a previous study[6] Wolf *et al.* had shown that at high temperatures ($\simeq 500\,°\mathrm{C}$), high pressures of H_2 ($\approx 10^{-5}$ Torr) can influence the crystallinity of the deposited Si MBE film. (This preliminary study had attributed this phenomenon to the segregation of H to a critical level.) Here we describe the effect on low-temperature Si MBE of deliberate dosing with atomic deuterium, as a function of pressure. The low-temperature and -pressure experiments allow us to bridge the gap between Wolf *et al.*'s measurements[6] and the epitaxial thickness results.[1] Hydrogen is shown to exert a very strong effect, apparently through its influence on Si surface diffusion. We deduce that although the breakdown of epitaxy is triggered by surface roughness and increased step density, H plays a pivotal role in limiting Si surface diffusion in UHV experiments below 500 °C.

The immediate impetus for our study of the role of H in limited-thickness epitaxy was provided by our attempts to monitor background impurities during MBE experiments. Residual gas analysis (RGA) shows that while most impurities are fairly well behaved (outgassing slightly during growth and substrate heating, and being suppressed by cool cryoshrouds), H_2 levels changed in surprising ways. In particular, H_2 appeared to come predominantly out of the Si gun itself: H_2 remained at ambient during substrate heating, rose sharply when Si evaporation began, and dropped below ambient as the Si gun was turned off. This last observation suggests that the Si gun may getter pump the whole chamber during cooldown, and that controlling the H level will depend on controlled source outgassing prior to the growth experiment. Finally, growth with prior outgassing modified one important conclusion of the early work,[1] that the activation energy for the epitaxial thickness increased with increasing deposition rate. More recent results show a fixed activation energy (0.5 eV) at rates from 0.1 to 50 Å/s. There was thus good reason to suppose that residual H in the chamber is playing at least some role in the effect.

II. EXPERIMENT

The experiments were carried out in a standard Si MBE chamber with a base pressure of $\approx 10^{-10}$ Torr, and a pressure during deposition of $\approx 10^{-9}$ Torr, predominantly molecular hydrogen. Si deposition was carried out using an *e*-gun at rates between 0.1 and 10 Å/s. Clean (100) substrates were prepared using a HF dip,[7,8] followed by H desorption and deposition of a 300–800 Å buffer at high temperature. The substrates were then cooled to a growth

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temperature in the limited-thickness epitaxy regime (i.e., 0–400 °C) and allowed to equilibrate prior to deposition. The atomic deuterium source used an UHV leak valve to generate a rapid leak of D_2 through a narrow-bore (0.1 mm) Ta tube. The Ta tube extended well into the chamber, terminating ≈ 2 cm from a W filament held at 2000 °C about 6 cm beneath the Si substrate holder. By comparison with a large number of previous studies using atomic H sources in surface science[9–11] we expect the W filament to generate a significant flux of H. The source was calibrated by dosing clean Si surfaces with small fluxes at low temperature, burying the resulting partially H-terminated surface with amorphous Si, and then measuring the integrated coverage of H(D) in this film with secondary-ion-mass spectrometry (SIMS). The calibration was repeated at three different flux rates for ≈ 0.1 monolayer (ML) coverages in order to check that the source was linear in measured chamber pressure. Given the H coverage resulting from a known chamber pressure/time exposure, we can now calibrate the dose rate for a given chamber pressure reading. After Si growth, cooling, and removal of the wafer from the chamber, the epitaxial thickness was measured using transmission electron microscopy (TEM) of cross-section samples. In order to improve the accuracy of these measurements a Ge marker layer 1 ML thick was usually deposited just prior to the low-temperature Si MBE. (Control experiments without the Ge demonstrate that the marker layer exerts no influence on the epitaxial thickness.) The cross-section TEM images look essentially identical to those obtained from hydrogen-free growth,[1] showing a rough amorphous-crystal interface at the transition from epitaxy to amorphous deposition, with a few stacking faults in the vicinity of this interface, and a transition width of $\approx \frac{1}{3} h_{epi}$. The epitaxial thickness measured here is defined to the midpoint of this transition (i.e., the average height of the fluctuating amorphous-crystal interface). The similarity of samples grown in the presence and absence of hydrogen suggests that the same phenomenon is occurring under both hydrogen dosing and ambient conditions.

The effect of atomic H on the epitaxial thickness was determined for three different substrate temperatures. Previous studies[1] had shown that the epitaxial thickness increases rapidly with temperature (an Arrhenius with an activation energy 0.5 eV) so extreme care was taken to equilibrate the substrate under identical conditions for each deposition. Because of the difficulty in measuring absolute temperatures in MBE the temperatures given here are accurate only to ± 50 °C; however, given the extreme care used to reproduce conditions from run to run, the temperature variation within a given set of (fixed temperature) data is probably $\approx \pm 5$ °C. Between deposition runs the chamber was pumped to its base pressure using Ti sublimitation pumping; during deposition the chamber was pumped only with a cryopump (with a very slow rate of pumping H_2). With these precautions, the only run-to-run variation should be the H_2 ambient in the chamber and the resulting H flux seen by the substrate.

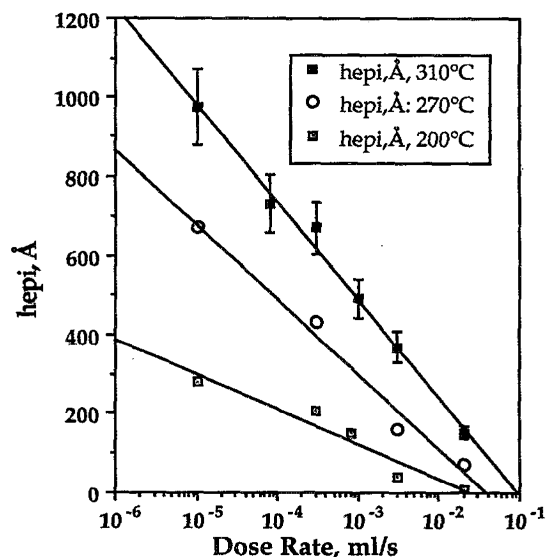

FIG. 1. Dependence of epitaxial thickness on H dosing. H flux shown as both measured chamber pressure (mainly H_2), and calibrated H dose rate (calibrated at three pressures by measuring deuterium coverages in SIMS after controlled exposure at known pressure). Note very slow (logarithmic) pressure dependence of h_{epi}. [Data can also be fitted as power-law behavior for small powers ($h_{epi} \alpha P_H^{0.2}$)]. Effect is probably due to change in Si surface diffusion due to adsorbed hydrogen.

III. RESULTS

Figure 1 shows the variation in epitaxial thickness with increasing dose rate of atomic hydrogen, at three different substrate temperatures. Each point on Fig. 1 corresponds to a separate deposition run and TEM sample to measure the epitaxial thickness. In addition to the hydrogen dosage experiments, each temperature curve also shows an "ambient" point for a nominally zero H_2 leak rate (leak valve closed, filament off) but with a dose rate calculated for the observed ambient pressure (10^{-9} Torr). There are several points to be noted regarding this plot. First, hydrogen does appear to exert a strong influence on the epitaxial thickness. There are two possible explanations at this stage: Either the epitaxial thickness is caused by hydrogen segregating to some critical concentration and causing a breakdown in epitaxy, or hydrogen affects some important process at the Si surface (such as the surface diffusion coefficient). Second, the dependence of h_{epi} on the dose rate P_H is slow and, within experimental error, logarithmic: $h_{epi} = h_0 - k \ln(P_H)$. Plots of a power law form of Fig. 2 also show a linear fit (within experimental error) for a very weak power-law dependence: $h_{epi} = h_0 - k P_H^{0.2}$ (or $h_{epi} \alpha P_H^{-0.2}$, etc.). As we shall see, this weak dependence is not consistent with a breakdown in epitaxy directly caused by buildup of hydrogen, and will lead us to suggest that H affects the rate of surface diffusion of Si. Finally, we also note that in Fig. 1 the "ambient" points appear to lie on the pressure-dependent curve extrapolated from higher pressures. Although the pressure dependence is only approximately determined at this stage, this observation would

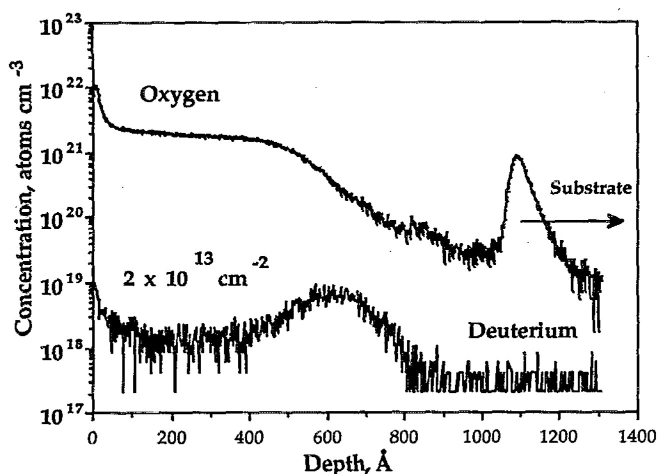

FIG. 2. Measured segregation of hydrogen in SIMS depth profiling. Note peak in D at amorphous-crystalline interface and high incorporation level in *a*-Si. Total D coverage trapped at *a*-Si/*c*-Si interface here is ≈0.11 ML. Hydrogen surface coverages down to 0.01 ML also appear to influence the epitaxial thickness and Si surface diffusion.

appear to suggest that the epitaxial thickness observed under ambient conditions is influenced by the ambient H in the UHV chamber.

Dosing with deuterium during low-temperature growth also allows us to study the segregation of H during deposition. A number of samples grown for the pressure-dependence studies of Fig. 1 were subsequently depth profiled using SIMS. Figure 2 shows a typical deuterium depth distribution in SIMS. All SIMS profiles showed a very low background count in the substrate (as expected), a low (background) level in the crystalline Si deposited at low temperature, a peak in the H(D) concentration at the interface where the Si becomes amorphous, and a subsequent high level of deuterium. The H concentration in the amorphous film corresponded (within ±10%) to the calculated ratio of Si-to-H flux rates, i.e., the incorporation of H in an *a*-Si film is very close to 100%. The peak in the H at the interface arises from segregation of H arriving at the surface during crystalline deposition, and its subsequent trapping at the amorphous-crystalline interface (since incorporation in *a*-Si is ≈100%). The negligible incorporation of H in *c*-Si would suggest that the height of the interface peak should correspond to the total H dose during low-temperature crystal growth. In fact, the H peak is frequently substantially lower than the total dose to breakdown (in Fig. 2 the H peak is 0.1 ML for a dose of ≈1.0 ML): This may arise from diffusion of H into the bulk *c*-Si, nonunity sticking coefficient at the clean Si surface, or desorption of H during the crystal-growth process. The sticking coefficient is, as usual, taken to be near unity for temperatures below ≈350 °C:[11] The solubility of H in *c*-Si is $<10^{10}$ cm^{-3} at this temperature,[12] so that (despite fast diffusion) loss of H into the bulk should also be negligible. Extrapolation of higher-temperature data on desorption at low coverages[11] suggests that the total desorption (and in-diffusion) rate is $\approx 10^{-5}\ \theta$ ML/s at ≈360 °C, so that times $\approx 10^4$ s (3 h) are required for detectable adsorption/in-diffusion. We deduce that the most likely explanation for the reduced coverage of H is that the crystal-growth process itself enhances desorption of hydrogen. Precedent for such a process may be found in the "Si-beam clean" of Si where SiO is desorbed during Si deposition onto SiO_2 at temperatures far below where SiO_2 itself desorbs. We note that desorption of the dihydride phase of H on Si(100) is though to occur at these temperatures despite the stability of the monohydride.[11,13]

IV. DISCUSSION

Our new picture for the behavior of surface H during the growth of Si is thus that all H arriving at the surface sticks and then segregates, but with significant desorption due to the Si deposition process. We have considered the possibility that the complicated adsorption isotherm arising from this effect may be responsible for the pressure dependence in growth seen in Fig. 1. We note that, under certain circumstances, an adsorption isotherm with a desorption term depending on deposition rate may produce a logarithmic pressure dependence of the time (or thickness) required to build up a given coverage. This might appear to support a model for limited-thickness epitaxy in which hydrogen segregates to a critical concentration, and the surface accumulation of H is solely responsible for the breakdown of epitaxy.

However, the SIMS data offers a direct check of the possibility that hydrogen adsorption may be solely responsible for the breakdown of epitaxy. Using SIMS to monitor the trapped D at the *a*-Si/*c*-Si interface gives a direct measure of the surface concentration at which epitaxy is lost. (Here is the critical advantage of deuterium over the earlier studies[6] involving hydrogen SIMS, where levels much below a monolayer segregating to the interface were difficult to detect.) Although a picture in which H alone disrupts crystal growth requires this trapped coverage to be constant, the "critical" coverage of deuterium for different pressures (at fixed temperature) actually shows variations by up to an order of magnitude. The model for a breakdown of epitaxy at a threshold coverage of hydrogen can therefore be discarded on the basis of the pressure dependence in Fig. 1, and the measured coverage from SIMS. The more likely explanation for limited-thickness epitaxy is therefore that the phenomenon is intrinsic to low-temperature growth of Si, loss of epitaxy being due to the buildup of surface roughness during growth with limited diffusion (i.e., at low temperatures). Other experiments[14] have also suggested a direct link between local roughness and the breakdown of epitaxy.

Given that roughness causes the breakdown of epitaxy, the probable explanation for the strong effect on crystal growth seen in Fig. 1 is that H suppresses Si surface diffusion. We have no direct evidence to support this, but such an effect is clearly plausible. First, if surface hydrogen reduces diffusion then we expect to see the epitaxial thickness affected in a way analogous to the effect of Si deposition rate. Either hydrogen or Si deposition rate would now be responsible for the production of diffusion sinks (Si steps, kinks, etc., or hydrogen-passivated dangling

bonds). Previous results[15] have shown that the epitaxial thickness is only very weakly dependent on Si deposition rate, decreasing as $h=h_0-h_R \ln(R)$. The fact that hydrogen closely mimics the effect of an increased Si arrival rate is consistent with a surface diffusion rate that is affected by the surface concentration of adsorbed hydrogen. Second, Si diffusion is thought[16] to occur along channels in the dimerized (100) surface, maintaining bonds to two dimer dangling bonds at each successive minimum. The presence of adsorbed H would be expected to block the diffusion by saturating the dangling bonds at a given dimer, reducing the effective surface diffusion length to the H-H spacing. If H influences diffusion across a step then we expect an even stronger effect even at very low coverages (as observed). Monte Carlo simulations of growth suggest that step crossing is likely to dominate roughening.[14]

We should emphasize that, if our conclusions are correct, then hydrogen has an almost ubiquitous influence on the behavior of Si growth and Si surface diffusion characteristics. Surface science studies of surface diffusion and step distributions during growth (e.g., Ref. 17) have generally been performed in the low-temperature regime ($T < 500\,°C$) where the sticking coefficient for atomic H is large. Although these experiments were all carried out in UHV, with a base pressure $\approx 10^{-10}$–10^{-9} Torr, this will not guarantee a surface that is clean of H. If remote pressure gauges and other filaments lead to an atomic H flux only 10^{-2} of the chamber H_2 pressure, then the H dose rate in typical UHV is close to 10^{-5} ML/s. Accepting 0.01 ML as the upper limit before H blocking dominates the surface diffusion would suggest a time limit of 10^3 s (15 min) at a temperature below 500 °C. Very few experiments to date would satisfy this rigorous criterion, so that it is conceivable that (for example) the measured diffusion behavior[17] is at least partly limited by adsorbed hydrogen. Although the conclusions from our study remain tentative, the results seem to merit some reexamination of the earlier data.

V. SUMMARY

In summary, we have investigated the role of hydrogen, the most significant background impurity, in Si MBE at low temperatures. Hydrogen is shown to exert a strong influence on the crystallinity of deposited films, the epitaxial thickness h_{epi} decreasing rapidly with H dosing only marginally above ambient. The epitaxial thickness then decreases logarithmically with increasing dose rate of hydrogen. However, both the logarithmic pressure dependence and SIMS data on deuterium segregation are inconsistent with a breakdown in Si epitaxy caused by hydrogen alone. The transition from epitaxial to amorphous deposition appears to be caused by buildup of roughness: The role of background hydrogen is to accelerate the roughening rate. We suggest that H may have an influence on crystal growth through its effect on the Si surface diffusion coefficient.

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