Effects of B doping on hydrogen desorption from Si(001) during gas-source molecular-beam epitaxy from Si_2H_6 and B_2H_6

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Boron doping concentrations $\gtrsim 6\times10^{19}$ cm^{-3} were found to increase Si(001) growth rates R_{Si} at low temperatures while decreasing R_{Si} at higher temperatures during gas-source molecular beam epitaxy (GS-MBE) from Si_2H_6 and B_2H_6. In order to probe the mechanisms governing these effects, Si(001) samples with *B* coverages θ_B ranging from <0.05 to $\simeq 0.5$ ML were prepared by exposing clean Si(001)2×1 wafers to B_2H_6 doses between 2×10^{17} and 4×10^{20} cm^{-2} at 200–400 °C. The samples were then heated to 700 °C to desorb the hydrogen, cooled to 200 °C, and exposed to atomic deuterium until saturation coverage. D_2 temperature programmed desorption spectra exhibit β_2 and β_1 peaks due to dideuteride and monodeuteride desorption at 405 and 515 °C as well as new *B*-induced peaks, β_2^* and β_1^*, at 330 and 470 °C. Increasing θ_B increases the area under β_2^* and β_1^* at the expense of β_2 and β_1. Moreover, the total *D* coverage continuously decreases from $\simeq 1.23$ ML in the absence of *B* to $\simeq 0.74$ ML at $\theta_B = 0.5$ ML. We propose that the observed *B*-induced decrease in the Si*-*D* bond strength, where Si* represents surface Si atoms bonded to second-layer *B* atoms, is due to charge transfer and increased Si* dimer strain. The Si* to *B* charge transfer also deactivates Si surface dangling bonds causing the decrease in θ_D. These results are used to explain the GS-MBE growth kinetics. © *1996 American Institute of Physics.* [S0003-6951(96)00951-5]

The incorporation probability of *B* from B_2H_6 in GS-MBE Si(001) has been shown to increase linearly with increasing B_2H_6/Si_2H_6 flux ratios and to decrease exponentially with inverse film growth temperature.[1] *B* is incorporated into substitutional electrically active sites at concentrations C_B up to the highest values investigated in Ref. 1, 2.5×10^{19} cm^{-3}, with no measurable effect on film growth rates R_{Si}. However, even higher *B* concentrations are of interest for the emitter regions of heterojunction bipolar transistors in order to reduce the reverse injection current.[2] Recently, we have found that the use of B_2H_6/Si_2H_6 flux ratios corresponding to $C_B \gtrsim 6\times10^{19}$ cm^{-3} leads to *B* surface segregation and an increase in R_{Si} by up to 50% in the low-temperature surface reaction limited regime while decreasing R_{Si} by a corresponding amount in the higher temperature flux-limited regime.[3]

In this letter, we present the initial results of experiments designed to provide insight into the mechanism by which extremely high *B* doping concentrations affect GS-MBE Si(001) growth rates in opposite directions at high and low growth temperatures. Specifically, temperature programmed desorption (TPD), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) were used to investigate the effects of increasing *B* coverage on Si surface dangling bond coverages and Si–H bond strengths. In order to suppress the background signal during TPD measurements on clean and *B*-doped Si surfaces, deuterium rather than hydrogen was used to probe dangling bond coverages.

The experiments were carried out in a four-chamber ultrahigh-vacuum system[1,4] with a base pressure of $\simeq 5\times10^{-11}$ Torr. The film growth chamber, which is equipped with reflection high energy electron diffraction (RHEED) and a quadrupole mass spectrometer (QMS), is connected through a transfer chamber to an analytical station containing provisions for AES and LEED. TPD measurements were performed in a separate chamber attached to the analytical station and containing a heavily differentially pumped Extrel QMS.

The Si(001) substrates used in these experiments were 1×3 cm^2 plates cleaved from 0.5-mm-thick *n*-type ($n = 1-2\times10^{14}$ cm^{-3}) wafers. The substrate cleaning procedure described in Ref. 1 yielded starting surfaces with 2×1 RHEED patterns and sharp Kikuchi lines. No residual C or O was detected by AES. The clean substrates were then exposed to controlled fluxes of B_2H_6 delivered through a tubular doser located 3 cm from the substrate at an angle of 45°.[1] Hydrogen desorption, sample annealing, and deuterium exposures were carried out in the analytical chamber. D_2 was delivered through a doser identical to that described above and a hot *W* filament in the gas stream was used to crack the gas. For TPD experiments, the sample was placed 2 mm from the 5-mm-diam hole in the skimmer cone between the mass spectrometer and analytical chambers. Samples were heated at a linear rate, typically $2\,°C\ s^{-1}$, by direct current while the temperature was determined by a thermocouple calibrated using an optical pyrometer.

B_2H_6 exposures, typically at a flux of 2.2×10^{16} $cm^{-2}\,s^{-1}$, were carried out at temperatures between 200 and 400 °C for times ranging from 5 to 30 min. The B/Si(001) samples were then heated to 700 °C for 5 min to desorb the hydrogen. LEED patterns in all cases were 2×1. However, the amount of diffuse scattering increased with increasing B_2H_6 exposure temperatures and times. This is consistent with previous scanning tunneling microscopy

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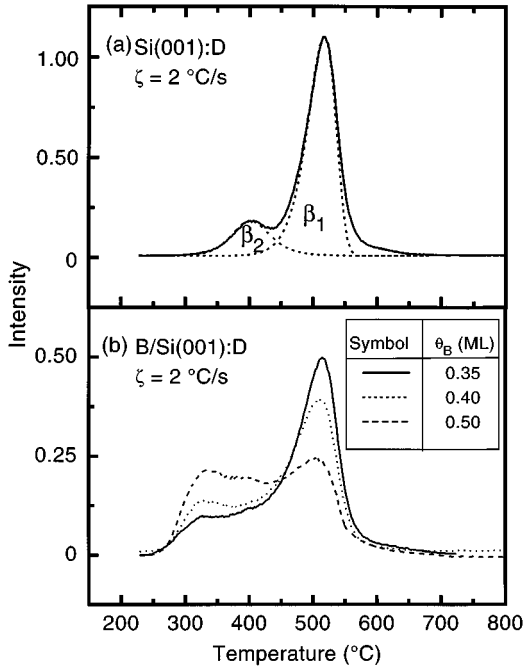

FIG. 1. D_2 TPD spectra from deuterium-saturated (a) Si(001) and (b) Si(001) with preadsorbed B coverages θ_B. The same intensity scale is used in (a) and (b).

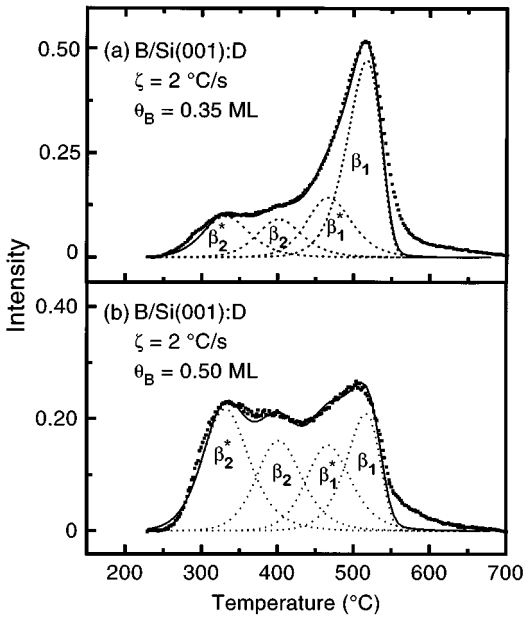

FIG. 2. Fitted D_2 TPD spectra from deuterium-saturated Si(001) with preadsorbed B coverages (a) $\theta_B=0.35$ ML and (b) $\theta_B=0.50$ ML. The intensity scales are the same as in Fig. 1(a).

(STM) results by Wang *et al.*[5] showing that B on Si(001) moves to second-layer positions and induces local ordering with $c4\times4$ symmetry. The ordered domains are, however, much smaller than the LEED electron-beam coherence length so diffraction patterns remain 2×1. B coverages θ_B were estimated based upon AES measurements of B KLL (178 eV) and Si LMM (92 eV) peak intensity ratios. Sensitivity factors and electron escape lengths were taken from Ref. 6 and calibration was provided using a Si(111)$\sqrt{3}\times\sqrt{3}$ test sample which was known to have 0.33 ML of B in the third layer.[7] θ_B in the B/Si(001) samples ranged from less than the AES detection limit, $\simeq$0.05 to 0.5 ML, increasing with exposure temperature in agreement with B_2H_6 reactive sticking probability results in Ref. 1.

Typical D_2 TPD results from a Si(001)2×1 wafer exposed to saturation deuterium coverage, but with no B_2H_6 exposure, are shown in Fig. 1(a). The spectrum consists of two peaks, labeled β_2 and β_1, due to desorption from the 1×1 dideuteride phase and the 2×1 monodeuteride phase, respectively. The peaks are centered at 405 and 515 °C. While β_2 desorption is second order, β_1 follows first order kinetics, except at very low deuterium coverages $\theta_D<0.1$ ML,[8] due to π-bonding-induced pairing of dangling bonds on single dimers.[9] The data can be fit using a standard Polanyi–Wigner analysis in which the desorption rate $d\theta_D/dT$ is expressed as[10]

$$\frac{d\theta_D}{dT}=-\left(\frac{\nu\theta_D^n}{\zeta}\right)\exp(-E_a/kT), \tag{1}$$

where ν is the attempt frequency, θ_D is the instantaneous D coverage, n is the order of the desorption reaction, ζ is the sample heating rate, E_a is the desorption activation energy, and k is Boltzmann's constant. At high pumping speeds,[11]

$$\ln\left(\frac{\theta_D(T)}{\theta_0}\right)=-\frac{\nu}{\zeta}I(T) \tag{2}$$

for first-order desorption and

$$\theta_D(T)=\frac{\theta_0}{1+\left(\frac{\nu}{\zeta}\right)\theta_0 I(T)} \tag{3}$$

for second-order desorption. θ_0 in Eqs. (2) and (3) is the initial coverage and $I(T)$ is given by

$$I(T)=\frac{E_a}{R}\left|\frac{e^{-\epsilon}}{\epsilon^2}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}n!}{\epsilon^{n-1}}\right|_{T_0}^{T} \tag{4}$$

in which $\epsilon=E_a/kT$. The fitted results in Fig. 1(a) were obtained with E_a and ν equal to 1.88 eV and 1×10^{13} s^{-1} for β_2 and 2.52 eV and 1×10^{15} s^{-1} for β_1 in reasonable agreement with Refs. 8 and 12. The relatively poor fit at the highest temperatures is also observed for Si(001):H TPD[13] and due, as noted above, to the fact that β_1 desorption deviates from first-order kinetics at low D (or H) coverages.

Typical D_2 spectra from B-doped Si(001) surfaces are shown in Fig. 1(b). Compared to the pure Si TPD spectra in Fig. 1(a) the adsorption of B has clearly reduced the onset temperature for D_2 desorption while the features have broadened indicating the presence of new peaks. In addition, the total saturated D_2 coverage decreases with increasing B concentration from 1.23 ML with no B exposure to 0.84, 0.82, and 0.74 ML with $\theta_B=0.35$, 0.40, and 0.50, respectively. This stems primarily from the rapid decrease in $\beta_1(\theta_B)$.

All D_2 TPD spectra from B preadsorbed samples were found to be well fit with four peaks: the initial β_2 and β_1 peaks together with the two lower-temperature B-induced β_2^* and β_1^* peaks at 330 and 470 °C. Examples of fitted spectra are shown in Figs. 2(a) and 2(b) for samples with

$\theta_B = 0.35$ and 0.50 ML. Best fit values for E_a and ν are 1.56 eV and 1×10^{12} s^{-1} for β_2^* and 2.29 eV and 3×10^{14} s^{-1} for β_1^*.

Previous STM results,[5] have show that *B*-induced Si(001) surface reconstructions consist of two primary $c4\times4$ structural subunits containing four second-layer *B* atoms and two first-layer Si dimers with *B* backbonds. In one subunit, there is also a dimer vacancy while in the other there is an additional Si dimer which is unmodified and bonded only to second-layer Si atoms. Thus, the β_1 and β_2 peaks should be observed even for $\theta_B = 0.5$ ML, in agreement with the results in Figs. 1(b) and 2(b), since undisturbed Si dimers still exist.

The Si–B bond length, 2.0–2.1 Å,[14] is considerably shorter than Si–Si, 2.35 Å, and *B* has both a higher electronegativity than Si and an empty sp^3 orbital. Thus, we propose that the decrease observed in θ_D with increasing θ_B is, in addition to the increased concentration of Si dimer vacancies, due to the partial deactivation of Si dangling bonds resulting from charge transfer from Si adatoms to subsurface *B* similar to the case for B/Si(111)$\sqrt{3}\times\sqrt{3}$ in which charge transfer was deduced from tunneling spectra.[15] The deactivation of Si dangling bonds also reduces the tendency for *D* atoms to pair up on single dimers and thus leads to second order β_1^* desorption kinetics. The lower activation energies measured for deuterium desorption from Si*-*D* and Si*-D_2 (where Si* signifies a *B*-bonded Si adatom) results from the combination of Si*-*B* backbond charge transfer and the additional strain in Si* dimers.

The β_2/β_1 integrated area ratio in Fig. 1(a) for non-*B*-exposed Si(001) is 0.23, far less than the value of unity which would be expected for complete dideuteride coverage. This has been explained previously for Si(001) with saturated H coverage as being due to steric hindrance resulting from electronic repulsion between adsorbed H nearest neighbors.[16] However, the results in Fig. 2 show that the β_2/β_1 ratio increases with *B* coverage ($\beta_2/\beta_1 = 0.30$ and 0.81 at $\theta_B = 0.35$ and 0.50 ML). This is because the steric hindrance is partially removed since unmodified Si dimers have no nearest neighbors in adjacent 110 dimer rows. At $\theta_B = 0.5$ ML, the fraction of unmodified Si dimers is approximately 0.25 in rough agreement with the reduction in the β_1 peak area from that measured for pure Si(001):*D*. A similar scaling is observed at lower *B* coverages.

The deposition rate during GS-MBE Si(001) from Si_2H_6 is given by $R_{Si} = 2J_{Si_2H_6}S_{Si_2H_6}\theta_{db}^2/N$ where $J_{Si_2H_6}$ and $S_{Si_2H_6}$ are the incident Si_2H_6 flux and reactive sticking probability, θ_{db} is the dangling bond coverage, and N is the bulk Si atom density.[17] At low film growth temperatures, R_{Si} is very strongly dependent upon θ_{db} which is a complex function of $S_{Si_2H_6}$, $J_{Si_2H_6}$, T_s, and the hydrogen desorption rate. Our TPD results clearly show that high subsurface *B* coverages result in a weakening of Si*–H bonds, thus increasing the hydrogen desorption rate which, in turn, increases θ_{db} in the surface reaction limited regime and, hence, increases R_{Si}. At high film growth temperatures in the absence of *B*, θ_{db} approaches unity, $S_{Si_2H_6}$ is essentially independent of T_s, and $R_{Si} \propto J_{Si_2H_6}$.[17] Thus, in the impingement flux limited regime, the primary effect of high *B* coverages is to deactive a fraction of the Si dangling bonds leading to a decrease in θ_{db} and the observed decrease in R_{Si} at constant $J_{Si_2H_6}$. We have performed TPD measurements on very highly doped GS-MBE Si:B films. The spectra are similar to those shown in Figs. 1(b) and 2 and can thus be used to estimate *B* surface coverages.

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