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Growth and structural analysis of an ordered boron monolayer in Si(100)

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We have fabricated and characterized a novel structure: an ordered B monolayer deposited onto Si(100) and capped with epitaxial Si. X-ray structural data, compared to a first-principles model, suggests limited (<3 monolayers) segregation of the B during Si overgrowth, leaving over half of the B atoms in ordered sites. Ordering persists over length scales comparable to the clean-surface terrace width, as measured by grazing angle x-ray diffraction.

An ultimate limit in a semiconductor doping profile would be a spatially confined, periodic distribution. Such a structure would eliminate the ionized-impurity scattering limitations to the mobility,[1] and also preclude the statistical variations implicit in a randomly doped structure. Recent advances in the understanding of boron-silicon epitaxy have suggested the possibility of creating such a laterally ordered structure. These observations include the following: (1) boron forms an ordered reconstruction on the Si(100) surface;[2] (2) Si(100) epitaxy can be achieved at extraordinarily low temperature, reducing boron disordering during overlayer growth;[3] and (3) boron undergoes minimal surface segregation during Si epitaxy relative to other dopants.[4] In this paper, we report the growth and grazing angle x-ray diffraction analysis of an ordered B structure buried within epitaxial Si. We also describe a total-energy calculation to predict the atomic displacements of the silicon atoms near the interface. The essential conclusions of the study are the following: for the theory, the ordered boron configuration would induce significant vertical and horizontal displacements of Si atoms within the first three layers on either side of the interface; and for the experiment, deviations from the ideal structure are present in the form of boron occupation of up to three layers with an accompanying disorder in the two-dimensional structure. Nevertheless a large fraction of the boron resides in an ordered configuration and the x-ray analysis quantitatively confirms the predicted Si displacements.

Si(100) substrates were prepared using oxide desorption at 950 °C in an ultrahigh vacuum chamber at AT&T Bell Laboratories. Substrates were 10-Ω cm p-type B doped with a miscut of $<0.03°$. The cleaned substrate is held at 500 °C during deposition of B_2O_3 from a Knudsen cell, and a 30-sec 700 °C anneal removes the oxygen and orders the B. Boron at 0.5 monolayer (ML) coverage on the surface forms an ordered 2×1 structure which has a low-energy electron diffraction (LEED) pattern distinguished from the clean Si(2×1) pattern by virtue of its different LEED I-V characteristic.[2] Boron coverage is measured with the B(p,α) nuclear reaction. Silicon, deposited on this B-induced surface reconstruction at 180 °C with a growth rate of 0.1 Å/sec, forms a high-quality crystalline film, as determined by ion channeling, x-ray diffraction, and cross-sectional transmission electron microscopy.[3] This is in contrast to the Si(111)-$\sqrt{3}\times\sqrt{3}$B system where low-temperature cap layers contain a high density of stacking faults and dislocations.[5] Auger electron spectroscopy was performed as a function of film thickness to assess surface segregation of B. Diffraction measurements were performed at CHESS, and used monochromatic radiation at 1.1 Å wavelength from a Si(111) double-bounce monochromator and a conventional x-ray diffractometer diffracting in the vertical plane. In reporting this data, we use h, k, and l taken with respect to a ($3.84\times3.84\times5.43$ Å^3) unit cell.

A theoretical description of the local atomic structure, within the constraints of composition and symmetry, may be achieved by minimizing the total energy. The local-density-functional approach[6] is used to determine the total energy from first principles with the calculation carried out using modern steepest-descent techniques.[7] This theory has proven to be accurate for bulk, interface, and surface structural properties.[8] The atomic structure for the ideal 2×1 buried B layer is calculated using a supercell with 20 layers. Both the local atomic structure as well as the c-axis lattice parameter are determined. The plane-wave basis set is determined by a 20-Ry kinetic-energy cutoff. Further details are given in Ref. 9. In order to study structures of lower symmetry, a valence force field model was used with the B-Si bond-stretching and bond-bending parameters determined by fitting to the

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first-principles results.[10]

A model of the ideal B-Si structure is shown in Fig. 1 projected on the (110) plane with Si displacements predicted by first-principles total-energy calculations. The shaded circles have been registered so that atoms 1–10 exactly overlap the undistorted model. Because B has a covalent radius 0.29 Å smaller than that of Si, a sizable lattice contraction around the B layer is expected. This results in a rigid-body displacement of the Si layers in the [001] growth direction upon crossing the B layer. By symmetry, the displacements along [110] alternate in sign, moving toward the B atom introduced at position 15, while no displacements occur in the [1$\bar{1}$0] direction.

The decay of the B Auger signal, as the reconstructed layer is capped, is used to determine the surface segregation of the B. Figure 2 shows the B-Si Auger ratio as a function of Si capping layer thickness for different overlayer growth temperatures. The mean-free path for the 178-eV B Auger electron is 6.8 Å,[11] similar to the value of 6.5 Å from a fit to the exponentially decaying signal shown in Fig. 2. This indicates very little segregation of the B, less than 2–3 ML for 180 °C growth. Data at 240 °C show a slower decay of the B signal indicating some segregation. Figure 2 (inset) also shows integrated x-ray intensities plotted as a function of l for a sample with a 200-Å Si cap layer grown at 180 °C. Each point is obtained from an individual scan in the perpendicular direction to accurately subtract the background. Diffracted beams from the substrate and film interfere, leading to Pendellösung fringes, the position and amplitude of which are related to the magnitude and direction of the normal displacement of the film relative to the substrate. The sharp features of the interference are a clear indication of a high-quality crystalline overgrowth on an evenly distributed B layer. The dashed line is the result of a χ^2 fit involving a thin uniformly contracted buried layer with $\Delta z = -0.45 \pm 0.1$ Å. For comparison, the solid line is the result of a kinematical calculation of intensities for the exact detailed model shown in Fig. 1 as predicted by total-energy calculations. The predicted value of $\Delta z = -0.35 \pm 0.05$ Å agrees with the value derived from the best fit to the data.[12]

Figure 3 shows ($\frac{3}{2}$,0,0.1) x-ray diffraction intensity measurements from eight samples as a function of buried B coverage. Experimental errors are determined by averaging several different measurements on the same sample. The errors in the B coverage are statistical. A quadratic concentration dependence is shown and fits the intensity data better than a linear dependence. The intensity is largest at 0.5-ML B coverage,[2] confirming that the geometry under investigation is dependent on the presence of B.[13] The full width at half maximum (inset) of the reflection, after correcting for resolution effects, corre-

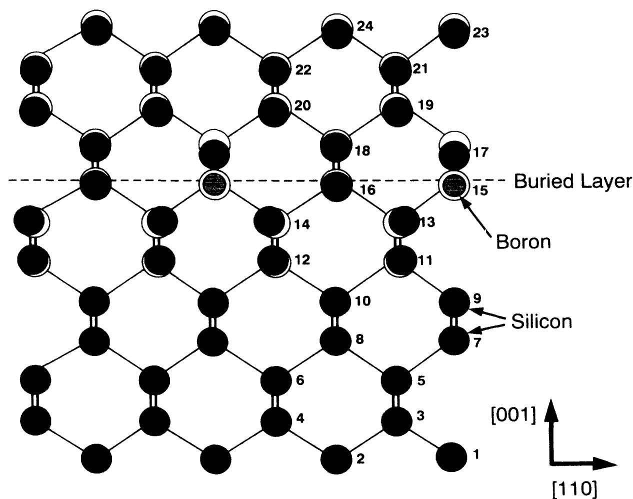

FIG. 1. Model of the ordered delta-doping layer with displacements obtained from total-energy calculations. The undistorted Si structure is represented by open circles and bonds, and displaced Si atoms are shaded. Atoms in one unit cell are numbered for reference.

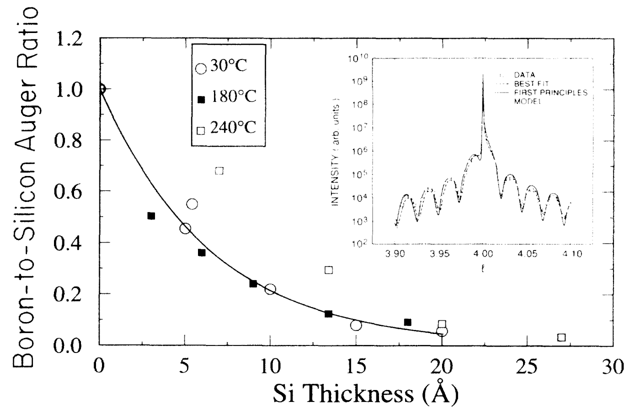

FIG. 2. Auger electron spectroscopy measurement of B-Si signal as a function of Si capping layer thickness. Three different Si overlayer growth temperatures are shown along with a fit to the 30 °C data giving a 6.5-Å extinction length (solid line) for the B Auger electron. Inset: the specular [004] x-ray reflection shows the rigid-body shift around the ordered layer as described in the text.

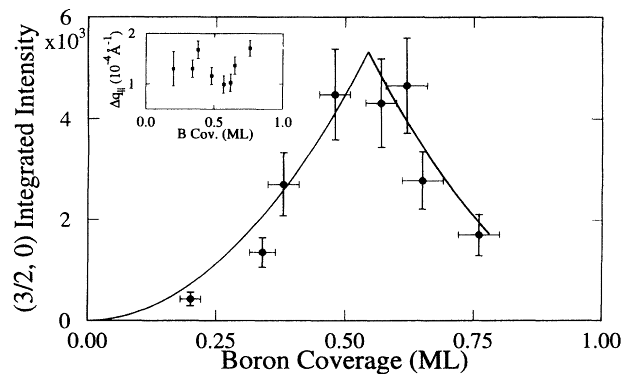

FIG. 3. Grazing angle x-ray diffraction intensity of the ($\frac{3}{2}$,0,0.1) peak as a function of buried B coverage. The solid line is for a quadratic coverage dependence. The inset shows the full width at half maximum of the ($\frac{3}{2}$,0,0.1) reflection also as a function of coverage.

sponds to a domain size of 1300–2500 Å with no obvious trend as a function of coverage. For comparison, a miscut of 0.03° on Si(100) corresponds to a terrace width of 2600 Å.

We analyze the quadratic dependence of Fig. 3 following the formalism described by Vlieg *et al.*[14] For half-order reflections, one component of intensity is proportional to the square of the B coverage, θ^2, and another proportional to $\theta(1-\theta)$ where by definition, $\theta=1$ at 0.5-ML coverage:

$$I_1 \propto |F_{hkl}|^2\theta^2 \int e^{i\Delta \mathbf{q}\cdot\mathbf{r}_\parallel} C_{2\times1}(r_\parallel)dr_\parallel \ ,$$

$$I_2 \propto |F_{hkl}|^2\theta(1-\theta) \int e^{i\Delta \mathbf{q}\cdot\mathbf{r}_\parallel} C_{\mathrm{boron}}(r_\parallel) C_{2\times1}(r_\parallel)dr_\parallel \ .$$

F_{hkl} is the structure factor and Δq is the deviation from the Bragg condition. Two length scales with which we associate correlation functions are the degree to which B forms two-dimensional islands $[C_{\mathrm{boron}}(r_\parallel)]$, and the terrace width of the surface on which B ordering took place $[C_{2\times1}(r_\parallel)]$. From the observation of the large domain size over a wide range of coverages, and the θ^2 dependence of the diffraction intensity, we conclude that, in our measurement, the second component is not distinguished from other sources of background.[15] This indicates that the B-B correlation function C_{boron} represents a very short length scale, giving a broad line shape as a function of q. The first component, which we measure, has a linewidth characteristic of the terrace distribution, represented by the correlation function $C_{2\times1}$. From these data, the following picture emerges for the formation of the B-ordered layer on the surface. At low B coverages, the (2×1)B reconstruction coexists with the clean Si(2×1) reconstruction, the B atoms occupying a preferred site[16] in the 2×1 unit cell, but *randomly* distributed over the 2×1 terrace. As B coverage increases, a larger fraction of the 2×1 unit cells contain a B atom, until finally at 0.5-ML B coverage, the surface is saturated and the (2×1)B structure is completely formed. At higher coverages, the order deteriorates, perhaps due to nonepitaxial B clusters on the surface. Growth of Si on the (2×1)B structure preserves the order to an extent discussed below.

The in-plane structure of the buried B layer was determined for a sample covered with 0.5 ML of B and capped with 50 Å of crystalline Si. The data set consisted of 60 measurements from which 25 inequivalent structure factors were obtained (Fig. 4). The data were averaged and error bars determined from statistical uncertainty and reproducibility. Shown in the inset is a typical angular scan. Figure 4(a) shows the diffracted intensities with error bars in comparison to intensities calculated for a (2×1)B-Si structure with no Si displacements. The calculated intensities decrease as a function of h and k due to the Debye-Waller factor and the atomic form factor. Obviously this simplified structure is in poor agreement with the data. Evidence for large Si displacements are apparent from the calculation (Fig. 1) and the Pendellösung fringes (Fig. 2 inset). Si displacements from the first-principles calculations are used to calculate the intensities in Fig. 4(b). A marked improvement between experiment

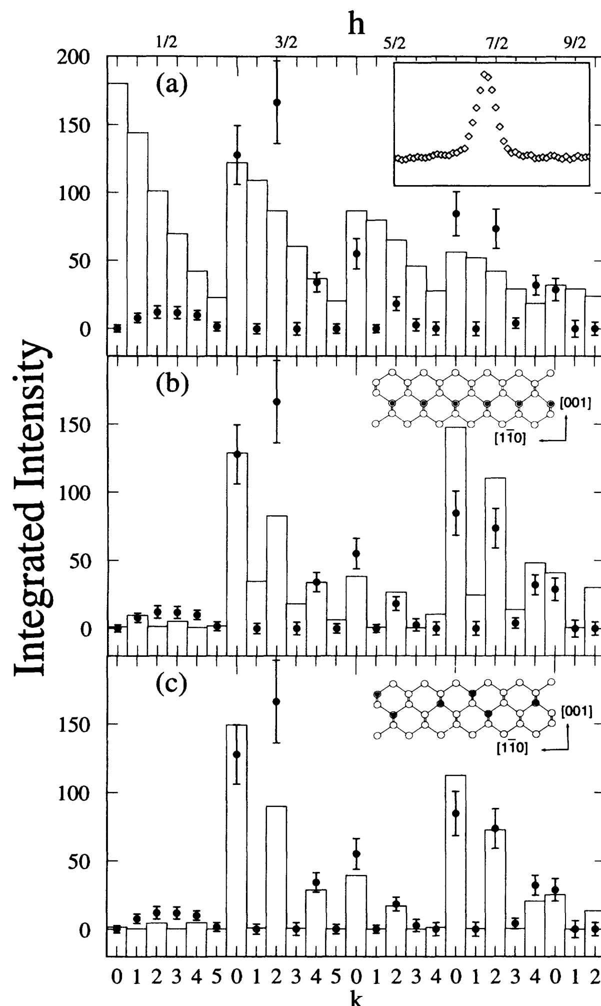

FIG. 4. Grazing angle x-ray diffraction data of 25 different half-order reflections are shown with three sets of calculated intensities. (a) B substituted in a 2×1 arrangement with no Si displacements toward the B. Inset: A typical angular scan. (b) 2×1 structure, shown (also Fig. 1) in inset with B in black, using Si displacements predicted from first-principles theory. (c) Structure shown in inset. The first two layers are ordered with B in positions 15 and 17, while in the third layer, B is distributed between 19 and 20. Positions 17, 19, and 20 are the nearest sites to which B initially at site 15 could segregate.

and theory is apparent ($\chi^2=4.9$). The main effect comes from two displacement terms included in the structure factor below:

$$F_{hkl} = -f_{\mathrm{B}} + f_{\mathrm{Si}}[1+(-1)^{h+1/2}\sin(2\pi h\delta_{13,14}) + (-1)^{h+k+1/2}\sin(2\pi h\delta_{19,20})] \ ,$$

where f_{B} and f_{Si} are the atomic form factors for B and Si and $\delta_{13,14}$ and $\delta_{19,20}$ are the in-plane Si displacements along [110] for atoms 13,14 and 19,20 respectively. Since the intensity is the square of the structure factor, the largest contribution comes from $k=$even, $h=\frac{3}{2},\frac{7}{2},\ldots,$ explaining the four largest intensities.

Possible spreading of the boron within the limits set by

our Auger data is studied by valence force field calculations of Si displacements for structures of lower symmetry with 0.5 ML of B in more than one layer. Improved models have an essential feature; they include two 2×1 structures offset by one-half the unit cell size in the $[1\bar{1}0]$ direction. As a result, the intensity is multiplied by $[1+\cos(k\pi)]^2$ coming from the sum, $e^{2\pi i(hx+ky)}+e^{2\pi i[hx+k(y+0.5)]}$, in the structure factor. Cancellation occurs when $k=$odd and constructive interference occurs when $k=$even. The data show negligible intensities for $k=$odd, in agreement with the population of two ordered layers with boron occupying sites 15 and 17. In addition, the detailed fit is improved by alternating neighboring B atoms between sites 15 and 17, rather than forming two separate domains. For example, the structure shown as an inset [Fig. 4(c)], with $\chi^2=1.8$, cancels $k=$odd reflections while not introducing B-B bonds by distributing $\frac{1}{3}$ of the B atoms in disordered sites (19,20).[17] This model is plausible in terms of growth since it can be formed by only two hops of the B atom. Site 17 is a nearest neighbor of site 15, and sites 19,20 are second-nearest neighbors of site 15. The limited mobility of B atoms during segregation thus produces a structure with 2×1 ordering over two layers.

In conclusion, we have investigated the growth and atomic structure of a dopant layer with 2×1 ordering embedded in crystalline Si. Ordering persists over length scales comparable to the clean-surface terrace width. Our calculations of the Si distortions around the B atoms explains the essential features of the x-ray diffraction data. The results support partial ordering of the B with limited segregation during growth. The potential for the achievement of more perfect order remains an interesting open problem.

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[15] The angular scan in Fig. 4(a) inset can be fit by a single Gaussian supporting the conclusion that we measure only one component of the intensity.

[16] The B surface site has not been experimentally determined as yet. Theoretical calculations point to site 15 with a site-17-terminated surface (Ref. 9) although the B-terminated surface has only a slightly higher energy (0.11 eV).

[17] We used a nonlinear least-squares-fitting routine and an l of 0.1. Disorder is included in the model [Fig. 4(c) inset—Si displacements are not shown] by doubling the effective vibration amplitudes in the Debye-Waller factor. The Si displacements obtained from the valence force-field model were increased by a factor of 1.4 to bring them close to the local displacements obtained from the total-energy calculations.