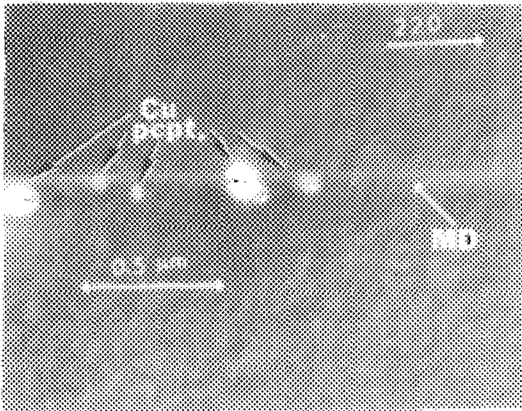

FIG. 4. Beveled TEM of Cu precipitates at a misfit dislocation MD.

misfit dislocations is clearly presented by the strain fields produced by the Cu precipitates as indicated on the micrograph in Fig. 4.

In summary, it has been demonstrated that interfacial misfit dislocations introduced during Ge-doped Si epitaxy can be used as extrinsic gettering sites. The dislocations, at densities from $10^6$ to $10^8$ $cm^{-2}$, have separations on the order of 1–10 $\mu$m and do not appear to interact such that threading dislocations result. Single, graded, and multistep layers have been grown to illustrate the defect density control possibilities and the flexibility of the procedure. Both Au and Cu diffusion from 200 to 300 Å thick evaporated surface films have been examined with SIMS and TEM. The relative gettering efficiency of high and low misfit dislocation density interfaces has been demonstrated for these metallic impurities to establish extrinsic gettering with interfacial dislocations as a viable alternative to conventional intrinsic and backside gettering.

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# Hydrogen localization near boron in silicon

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Several models of boron neutralized by atomic hydrogen in silicon were tested by secondary ion mass spectrometry and infrared spectrometry. The hydrogen concentration is comparable to that of boron. Boron neutralization appears as a drop in free-carrier absorption and as an increase in resistivity. A new infrared vibrational mode attributed to ⟨111⟩ vibrations of H tied to Si appears at 1875 $cm^{-1}$.

Shallow acceptors in crystalline silicon have been neutralized in several different experiments.[1–5] Although there is general agreement that after the treatment boron no longer acts as an acceptor, there has been no agreement on the specific model that describes the substitutional boron-hydrogen complex in silicon. Pankove *et al.*[1] introduced atomic hydrogen ($H_1$) into B-doped Si at ~125 °C and found a substantial increase in resistivity near the surface. Sah *et al.*[2,4] and Gale *et al.*[3] used avalanche breakdown or electron bombardment of a metal-oxide-semiconductor structure to drive $H_1$ from $SiO_2$ into the B-doped crystal and found a decrease in capacitance due to the widening of the depletion layer resulting

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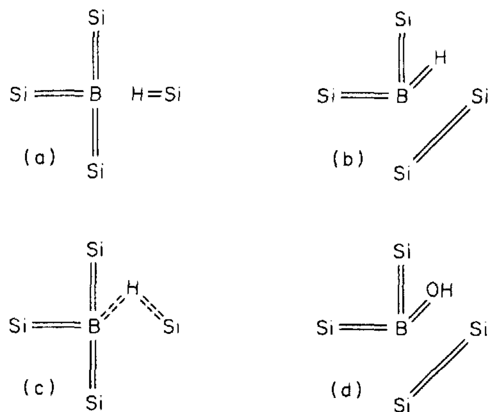


FIG. 1. Models of neutralized substitutional boron in silicon. Hydrogen bonded to (a) Si, (b) B, (c) "bridging bond", (d) OH bonded to B.

from the increased resistivity in the treated region. Hansen *et al.*[5] have tested Schottky diodes on *p*-type Si treated in a plasma of water vapor and found also a decreased capacitance for the same reason.

These various experiments have spawned four models that could explain the neutralization of boron. These four models are shown in Fig. 1. According to our model[1] [Fig. 1(a)] $H_1$ is tied to one of the four silicon atoms surrounding the substitutional boron atom, thus leaving all the valence bonds satisfied. Sah *et al.*[4] proposed that $H_1$ is tied to B thus requiring the reconstruction of dangling bonds between adjacent Si atoms [Fig. 1(b)]. An alternative model[6] is a bridging bond between B and Si [Fig. 1(c)]. The model that Hansen *et al.*[5] proposed has a hydroxyl group attached to boron [Fig. 1(d)].

In order to distinguish among these models we have made two types of measurements. In the first one, we examined the concentration profiles of boron, hydrogen, and oxygen in a B-implanted sample ($10^{16}$ B/cm$^2$ at 100 keV) that had been annealed at 1100 °C for 16 h and then hydrogenated at 125 °C for 156 h by exposure to $H_1$ generated by an rf glow discharge in 0.2 Torr of hydrogen. The purpose of this measurement was to check if oxygen might have either leaked into our system or been dislodged from the quartz walls in sufficient quantity to generate the hydroxyl of Fig. 1(d). The result of secondary ion mass spectrometry (SIMS) is shown in Fig. 2. It is evident that there is enough hydrogen to neutralize 80% of the boron to a depth of $\sim 2\,\mu$m, but the oxygen concentration is two orders of magnitude lower. Hence the hydroxyl-boron complex, if present, is not a significant component in our specimen. The inset of Fig. 2 shows the electrical neutralization of boron as an increase in spreading resistance near the surface.

The second measurement, the infrared absorption spectrum, was aimed at determining the nature of the H bonding, specifically whether the H atom was bonded to B or to Si or to both. The measurement was made by using a multiple internal reflection prism[7] of Si which initially was B doped on one surface by B ion implantation ($10^{15}$ ions/cm$^2$ at 100 keV) and then annealed at 1100 °C for 16 h. This surface was then hydrogenated for 65 h at 120 °C. The IR spectrum measured with a Fourier transform spectrometer is shown in Fig. 3. The spectrum exhibits two changes with respect to one measured after implantation and annealing, but prior to

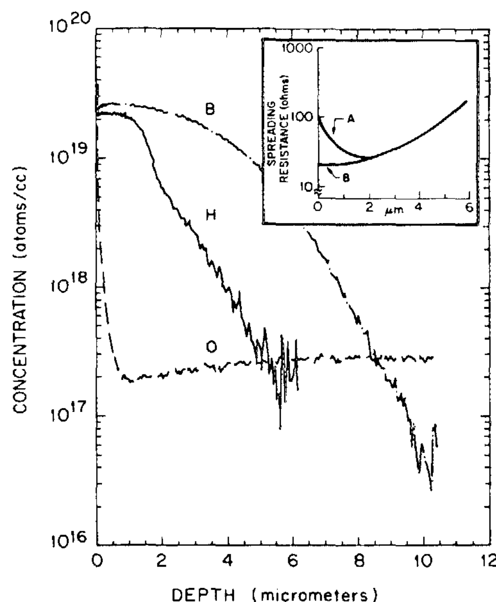


FIG. 2. SIMS concentration profiles of B, H, and O in silicon. The inset shows the spreading resistance of this sample before (B) and after (A) hydrogenation. The hole concentration at the surface is $2.0\times10^{19}$ cm$^{-3}$ before and $1.4\times10^{18}$ cm$^{-3}$ after hydrogenation.

hydrogenation not shown in Fig. 3. First there is a decrease in the free-carrier absorption that is consistent with the increase in electrical resistivity following hydrogenation. Second there is a relatively sharp absorption band at 1875 cm$^{-1}$. The frequency of this mode is in the range of H atom bond-stretching vibrations. In order to develop a structural model for the local bonding chemistry of the H atom, we first indicate the range of H atom bond-stretching frequencies so far measured for configurations involving B and Si atom neighbors.

The bonding of H atoms in amorphous Si has received considerable attention with two recent review articles summarizing the experimental results and their interpretation in terms of local bonding groups.[8,9] The result that is pertinent here concerns the frequency of monohydride or Si–H vibrations. Two modes have been identified, one at approximately 2000 cm$^{-1}$ and a second at about 2100 cm$^{-1}$. There have also been studies of H ion implantation into crystalline Si at low temperature with stretching frequencies ranging from 1885 to approximately 2200 cm$^{-1}$,[10,11] but the low-frequency vibration disappears at 200 K. Tsai[12] has studied the IR

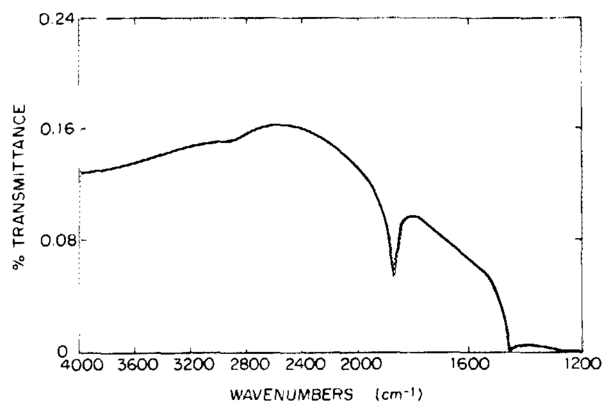


FIG. 3. IR transmission spectrum of H neutralized boron in silicon.



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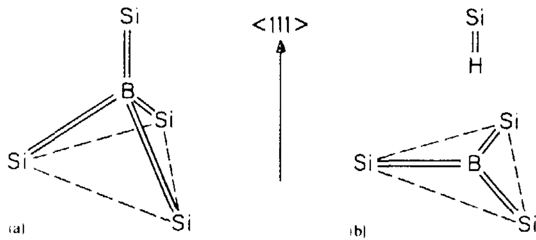


FIG. 4. Model of substitutional boron in silicon before (a) and after (b) H neutralization. In (a), a hole (not shown) in the vicinity of the boron provides charge neutrality.

spectra of *a*-Si:B:H alloys and has identified the vibrations associated with B–H bonding groups.

Terminal H bonding configurations (B–H) give a relatively sharp feature at 2560 $cm^{-1}$ whereas bridging H atoms (B–H–B) give a relatively broad feature centered at about 1985 $cm^{-1}$. These assignments are based on the interpretation of the IR spectra of diborane. There are no measurements to date that have identified other H atom bridging configurations with Si such as Si–H–Si or Si–H–B. Nevertheless, based on comparisons with the results in Ref. 12, we would expect these features to be relatively broad with linewidths greater than 100 $cm^{-1}$.

Based on the observations mentioned above, we conclude that the vibration at 1875 $cm^{-1}$ is a Si–H vibration. This follows from (1) the sharpness of the feature, linewidth less than 50 $cm^{-1}$, and (2) the frequency relative to the range of measured B–H and Si–H frequencies. Figure 4 presents a model for the local bonding configuration involving the H atom. This model accounts for the frequency of vibration as well as the change in electrical properties. The H atom is inserted between the B atom and one of its four Si atom neighbors and bonds to the Si atom generating a Si–H group. The B atom then relaxes toward the plane of its three Si neighbors. This particular type of "alloy atom" center satisfies all of the valence bonding requirements of the H atom, the B atom, and the four Si atoms. Neither the Si–H group nor the threefold-coordinated B atom is electronically active as a donor or acceptor, hence the drop in electrical conductivity and free-carrier absorption. The electronic configurations do not favor the formation of a three-center Si–H–B bond of the same general type as in the B–H–B bond in diborane. The stretching frequency of the Si–H vibration is at the low end of the reported range of Si–H bond-stretching frequencies. This can be explained in two ways: (1) the effective force constant of the Si–H vibration is reduced by a three-body force involving the Si–H–B triad of atoms; and (2) the frequency of vibration can be lowered due to local field effects associated with the dielectric cavity in the crystalline Si host material.[9] The first explanation involves a three-body force of the general form $k_{rR}$, where $r$ is the Si–H bond length and $R$ is the distance between the H and B atoms. For $k_{rR}$ positive, this type of force will always contribute a negative term to the potential energy; i.e., the contribution is given by $Ak_{rR}\Delta r\Delta R$, where $A$ is a constant and $\Delta r$ and $\Delta R$ are changes in the two interatomic distances. For the bond-stretching motion we are considering, $\Delta r$ and $\Delta R$ are always opposite in sign. This type of force is qualitatively similar to the force that couples intra- and interchain motions in trigonal Se and Te, and has a similar effect in reducing the frequency of a symmetric bond-stretching motion.[13]

The second model, based on local field effects, is discussed in Ref. 9. In either case, the magnitude of a frequency shift from about 2000 to 1875 $cm^{-1}$ is consistent with the model. For the force constant model the $k_{rR}$ force would have to be about 0.14 the size of the Si–H two-body force, and for the second case the size of the dielectric cavity would have to be about the size of a monovacancy.

Using Raman scattering, Steigmeier of RCA Zurich has found in one of our samples a weak structure at 1875 $cm^{-1}$. This finding, which implies a lack of inversion symmetry, is consistent with our Si–H model.

In summary, we have designed experiments to test the suitability of several models that might explain the neutralization of boron by hydrogen as evidenced by increased resistivity and decreased free-carrier absorption. We find that oxygen or OH is not a significant component, and the vibrational spectrum indicates that H is tied to one Si, and B to three Si.

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