Neutralization of Shallow Acceptor Levels in Silicon by Atomic Hydrogen

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Most of the shallow acceptor levels due to boron in single-crystal silicon can be neutralized by atomic hydrogen at temperatures between 65 and 300 °C. This treatment can result in a sixfold increase in resistivity.

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The possibility of hydrogenating Si dangling bonds has been clearly demonstrated in a variety of experiments involving amorphous, crystalline, and polycrystalline Si.[1-7] The evidence for passivation of dangling bonds includes the elimination of recombination-generation states at the free surface,[1] in the bulk,[2,3] and at grain boundaries.[4-6] These effects could be monitored as increased luminescence efficiency,[2,3] reduced leakage current in *p-n* junctions,[1] and lowered barrier height at grain boundaries.[4-6]

Here, we report a more subtle effect, namely the hydrogenation of a silicon dangling bond at the site of a substitutional acceptor.

The experiment consisted in measuring the change in resistivity of a B-doped Si single crystal after exposure to atomic hydrogen at various temperatures for about 1 h. The atomic hydrogen was produced by a rf glow discharge in 0.2 Torr of H_2. The sample was located outside the plasma in a heated region.

The spreading resistance was measured with use of a Solid State Measurement Inc. ASR 100 automatic spreading resistant probe on an angle-lapped surface. The resistivity was obtained from a calibration against samples of known resistivity. This is a technique widely used for determining resistivity profiles.[7,8] All the samples were annealed in vacuum at 550 °C for 1 h prior to the hydrogenation treatment.

Figure 1 shows the spreading resistance profile after a 1-h hydrogenation treatment at 122 °C for three B-doped samples having bulk resistivities of 2.0, 10, and 32 Ω cm, corresponding to a B-concentration in the range 4×10^{14} to 7×10^{15} cm^{-3}. The treatment causes an increase in resistivity near the surface by as much as a factor of 6. Prolonging the duration of the treatment does not change the maximum value of the surface resistance but rather increases the depth over which the spreading resistance has changed, i.e., the increased resistance forms a flat profile near the surface before decreasing to the bulk value. A flat resistance profile corresponding to the bulk resistivity value was obtained whenever a sample was heated in vacuum, thus eliminating the possibility that the observed effect could be attributable to heating alone (e.g., contamination).

Heating a treated sample at 500 °C for 1 h [to dehydrogenate it (Ref. 9 and 10)] resulted in the recovery of a flat resistivity profile at nearly the initial bulk value, thus confirming that the change in resistivity is due to the presence of hydrogen.

The above experiment was done to test the following model. A substitutional trivalent acceptor such as B is surrounded by four Si bonds of which only three can be satisfied at any given time, the fourth one providing the hole (a bond with an unpaired electron). If atomic hydrogen would bind at this site, supplying the pairing electron, the acceptor would be neutralized and the resistivity would increase. The observation that the resis-

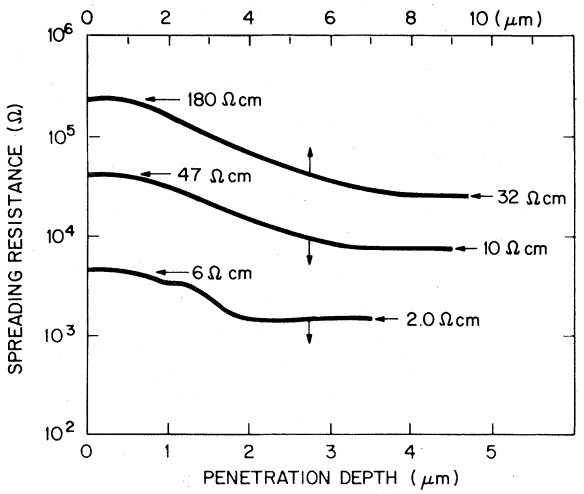

FIG. 1. Spreading resistance profile of three B-doped samples of (100) Si hydrogenated for 1 h at 122 °C. The resistivities were obtained from a calibration curve. Note the greater penetration depth of atomic hydrogen as the boron concentration decreases.

tivity increases only by a factor of ~ 6 suggests that ~ 15% of the shallow acceptors have not been neutralized by atomic hydrogen under present experimental conditions.

There are several experimental observations that agree with the present results. First, the doping efficiency of boron in hydrogenated amorphous silicon appears to be relatively small, with only about 0.1% of the boron contributing acceptor levels.[11] Moreover, Carlson *et al.*[12] found that the resistivity of heavily boron-doped amorphous silicon films tends to increase as the hydrogen content increases. Magarino *et al.*[13] have observed a similar result for boron-doped amorphous silicon grown by chemical vapor deposition. They found that the resistivity increased when the films were exposed to a hydrogen plasma. Many of the boron sites in amorphous silicon may be inactivated by a mechanism similar to that observed in the present work on crystalline silicon. Recently, Sah, Sun, and Tzau have proposed that B^-H^+ pairs are formed in crystalline silicon after avalanche hole injection or after irradiation by 5-keV electrons, the source hydrogen being posited as water-related species inside an adjacent SiO_2 film. Peartron and Tavendale[15] have recently observed the effect of hydrogen on deep levels of Au, Ni, Cu, Pt, and Pd in Si. Ours is the first definitive observation that shallow acceptors in crystalline Si can be neutralized by atomic hydrogen.

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