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May 1992

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Selective area, synchrotron radiation induced, delta doping of silicon

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We have used broadband synchrotron radiation to induce selective area surface doping of boron into silicon. The source of the boron was *nido*-decaborane ($B_{10}H_{14}$) adsorbed on Si(111) at 100 K. Irradiation caused decomposition of the adsorbed molecule which lead to an enhanced concentration of free boron in the irradiated area. Using Si $2p$ core level photoelectron spectroscopy, the surface chemical composition and Fermi level position in both the irradiated and unirradiated regions were determined. The downward movement of the Fermi level was greater in the irradiated region than in the unirradiated region, and greater for *n*-type than for *p*-type Si.

I. INTRODUCTION

Selective area processing using electrons, ions, or photons to induce surface structural modifications, is a powerful technique for production of submicron devices. Recent years have seen synchrotron radiation (SR) emerge as a viable alternative for selective area deposition and etching. Recently, we have used SR for local deposition of contamination free boron films on Si using decaborane ($B_{10}H_{14}$) as a source compound.[1,2]

Boron is the most common dopant for *p*-type Si. It has been shown that atomically sharp doping layers (δ doping) may be created by annealing adsorbed decaborane or heavily (boron) doped silicon.[3-8] A $(\sqrt{3} \times \sqrt{3})R30°$ reconstructed surface results from this process, as determined by low-energy electron diffraction (LEED) measurements.[3] It is thought that the B atoms occupy a subsurface, substitutional site, with a Si adatom above it. High resolution, core-level, Si $2p$ photoelectron spectroscopy (PES) has been used to monitor the changes in surface chemical and electronic structure that occur following annealing of heavily doped Si.[4-6] These studies revealed the presence of an intense surface component, shifted in binding energy by 0.4–0.5 eV from the bulk component. The species associated with this shift have been identified as a Si atom bound to a second layer boron atom. Using scanning tunneling microscopy (STM), Avouris and co-workers have shown that both surface and subsurface boron may be formed following annealing of decaborane adsorbed on Si(111) at room temperature.[7,8]

The present work is concerned with examining the interface formation resulting from adsorption of decaborane on Si(111)(7×7) at 100 K, irradiation with broadband synchrotron radiation, and annealing to temperatures ≤1100 K. Through analysis of Si $2p$ core level PES data,

we have reached the following conclusions: (1) Reaction of adsorbed decaborane with clean Si(111) results in a downward movement of the Fermi level. The movement is greater for *n*-type than for *p*-type Si, and is also greater where the adsorbed decaborane has been irradiated with broadband SR. (2) The surface chemical composition of the irradiated region of the surface results in the formation of three distinct surface moieties, whose concentrations increase with annealing temperature, reaching a maximum following annealing to ~900 K. This behavior is not observed in the unirradiated region of the surface.

EXPERIMENT

These experiments were performed on the Mark V Grasshopper beamline at the Synchrotron Radiation Center, University of Wisconsin-Madison, in an ultrahigh vacuum chamber at a pressure of 1×10^{-10} Torr. Electron energy analysis was done using a spherical-sector, electron energy analyzer. All spectra were taken with a photon energy of 130 eV. Moderately doped *n*-type ($7 \times 10^{14}/cm^3$) and *p*-type ($2 \times 10^{15}/cm^3$) Si(111) wafers were used as samples for these measurements. The $5 \times 15 \times 0.4$ mm samples were cleaned by cycles of argon ion bombardment (500 eV) and annealing to 900 °C until characteristic surface state emission was observed by photoelectron spectroscopy (PES), thereby indicating a well-ordered 7×7 surface. Gas dosing was done using a calibrated, microchannelplate doser with the sample maintained at a temperature of 100 ± 10 K using liquid nitrogen as a refrigerant. Temperatures were measured with a chromel-alumel thermocouple ($T < 300$ K) or an infrared pyrometer ($T > 550$ K). During gas dosing the chamber pressure was less than 5×10^{-10} Torr. The *nido*-decaborane(14) (hereafter denoted as DB) was obtained from the U.S. Army at Redstone Arsenal, vacuum sublimed and stored *in vacuo* prior to use. Purity was confirmed by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR),

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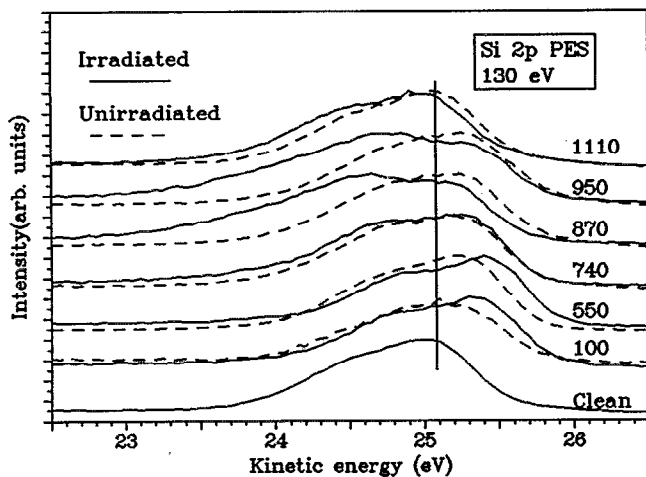[a]Present address: Advanced Photon Source, Argonne National Laboratory, 9700 Cass Ave., Argonne, IL 60439.

FIG. 1. Series of Si 2p core level PES spectra taken under various conditions. The bottom spectrum is from a clean Si(111)(7×7) surface. Above it are spectra following dosing of the surface with 2×10^{15}/cm² of decaborane. The succeeding spectra result from annealing the surface to the indicated temperature (K) for 1 min. Solid curves are from the irradiated region and dashed curves are from the unirradiated region of the surface. The vertical line shows the energy of the bulk Si $2p_{3/2}$ peak of the clean surface.
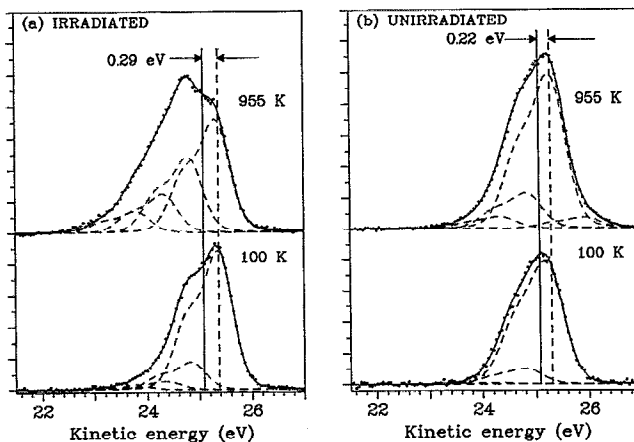

FIG. 2. Lineshape analysis of selected spectra from Fig. 1. The data were analyzed using up to four Gaussian-broadened spin-orbit split Lorentzian doublets (Voigt functions). The solid vertical line shows the energy of the bulk Si $2p_{3/2}$ peak of the clean surface, and the dashed vertical line is at the average energy of that peak for the reacted surface.

visible, and mass spectroscopies. Coverages are given in units of molecules/cm², assuming unity sticking coefficient. Following DB dosing the sample was irradiated with broadband SR ($E < 1200$) eV by setting the monochromator to "zero-order".

RESULTS AND DISCUSSION

Figure 1 shows a series of Si 2p PES spectra of n-type Si(111) under various processing conditions. The bottom spectrum is of a clean Si(111)(7×7) surface at 100 K. (No peak energy shifts were observed between spectra taken at 100 K and those taken at room temperature, which might be expected from a surface photovoltaic effect.[9] This is presumably due to the relatively low flux density transmitted by the Mark V Grasshopper beamline.) Above it are shown two spectra which result from dosing the surface with 2×10^{15} molecules/cm² of DB. The solid curve is the spectrum of a region of the surface that was irradiated with broadband SR, while the dashed curve is a spectrum from a region of the surface that is 2 mm away from the irradiated region. The other spectra in the figure result from successive annealing of the sample to the indicated temperature for 1 min. A cursory analysis of this figure reveals the following two observations: (1) The line shape of the spectrum from the irradiated region is substantially different from that of the unirradiated region. These differences become more pronounced as the sample is annealed. (2) There is a shift toward higher kinetic energy of the main peak following dosing of DB in both the irradiated and unirradiated regions. The shift is greater in the irradiated region and is eliminated following annealing to 1110 K.

More insight into the changes in the peak shapes may be obtained from the lineshape analysis contained in Fig. 2.

For the irradiated region of the surface, the data was best fit by using at least four Gaussian-broadened (0.26 eV) spin-orbit split Lorentzian doublets (0.61 eV spin-orbit splitting). The dominant component is due to Si 2p photoemission from bulk Si, while the other three are due to emission from chemically shifted surface components. The surface components are shifted by − 0.52, − 1.0, and − 1.5 (±0.05 eV). In the unirradiated region, the lower-temperature spectra could be successfully analyzed using two chemically shifted surface components, at − 0.4 and − 0.95 (±0.05 eV); however, at elevated temperature (≳740 K), it was necessary to employ a third component shifted by 0.65±0.05 eV. The clean surface could be satisfactorily fit using two surface-shifted components, at 0.77 eV and − 0.37 eV, in agreement with previous work on the clean Si(111)(7×7) surface.[10]

Initial Si 2p core level PES studies performed on the Si(111)-B($\sqrt{3} \times \sqrt{3}$)R30° surface showed the presence of one surface-shifted component located at − 0.40±0.02 eV from the bulk, and the surface Fermi level shifted downward by ∼0.13 eV from the position of the clean Si(111)(7×7) surface.[4] The − 0.4 eV shift was assigned to surface Si atoms bound to B atoms in surbsurface sites. A subsequent Si 2p PES study of this system was analyzed in terms of three surface components, S_1, S_2, and S_3, shifted from the bulk position by ∼ − 0.2, − 0.5, and − 0.8 eV.[5,6] The largest component, S_2, was assigned to Si atoms bound directly to B atoms, as well as second neighbors in deeper layers. The second most intense component, S_1 was assigned to the 1/3 monolayer (ML) located directly above the subsurface B, while the weak, S_3 component was assigned to third layer Si located directly below B sites.

Previously published valence-level PES studies of DB adsorbed on Si(111) indicate that the initial adsorption state at 100 K is predominately molecular. However, the molecular orbitals are significantly broadened as compared

to the gas phase, and photoemission from surface states is not observed, which indicates a strong adsorbate-substrate interaction.[2] The possibility of some dissociation cannot be excluded. DB exposure beyond a monolayer results in a sharpening of the valence-level PES features, indicating physisorption of the molecules in the multilayer.

The Si $2p$ core level PES data for unirradiated DB adsorbed on Si(111) at 100 K shown in Fig. 2(b) indicate the presence of essentially one weak surface component, shifted by -0.45 eV from the bulk Si position. Annealing of the surface to 955 K results in the formation two other surface species, with core-level shifts of -0.95 and 0.65 eV, and an increase in intensity of the -0.45 eV component. This behavior may be explained as follows. The initial adsorption of DB at 100 K results in bonding of Si to boron, either by direct Si—DB bond formation or DB dissociation and subsequent Si—B bond formation. This accounts for the presence of the -0.45 eV component in the unirradiated 100 K spectrum, although it is also possible that there is some contribution to this component from the -0.37 eV shifted component observed on the clean surface. Annealing of the adsorbed DB to higher temperatures causes dissociation of the adsorbed molecule and additional Si—B bond formation. Subsurface diffusion of boron may also occur. Furthermore it is possible that some silicon atoms may be bound to more than one boron and/or hydrogen, which could explain the presence of the -0.9 eV shifted component, although this component could also be due to strain-induced shifts in subsurface Si as observed on the Si(111)-B($\sqrt{3}\times\sqrt{3}$)$R30°$ surface.[5] The 0.65 eV component, observed following elevated temperature annealing, is assigned to the presence of Si adatoms on the surface,[10] which is supported by the reappearance of surface-state emission in valence level PES (not shown). The slight difference between the surface shift of the clean surface (0.77 eV) and that of the 1100 K annealed surface (0.65 eV) is probably due to the presence of some residual boron in the near surface region.

Dramatically different spectral variations are observed in the the irradiated region [Figs. 1 and 2(a)]. Even at 100 K, three chemically shifted components at -0.52, -1.0, and -1.5 eV are evident [Fig. 2(a)]. As the sample is annealed, the intensities of all three components increase, reaching a maximum at $\sim$950 K (Fig. 3). This behavior is a result of x-ray SR induced decomposition of the adsorbed DB providing a source of highly reactive boron atoms which react with the Si substrate. An Si atom bound to one boron is responsible for the -0.52 eV shifted components, while Si atoms that are multiply coordinated to boron are probably responsible for the higher energy shifted components. As the sample is annealed, more reaction between Si and B occurs, until finally, at 1100 K, the B diffuses into the bulk (Figs. 1 and 3).

The effect of these reactions on the local electronic properties may be inferred by the movement of the bulk Si $2p_{3/2}$ position. This movement is caused by changes in band bending at the surface. For the clean surface of lightly doped p- and n-type Si, it has been determined that the Fermi level is pinned at 0.63–0.65 eV above the valence
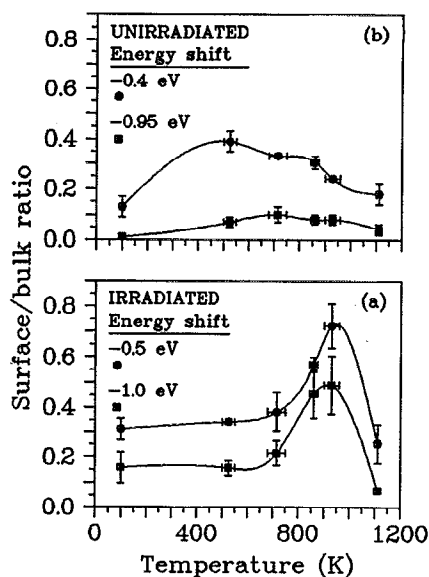

FIG. 3. Annealing temperature dependence of the intensity ratio (surface/bulk) for the two most intense surface components in the (a) irradiated and (b) unirradiated regions of the surface.

band maximum (VBM).[4,11] Analysis of a series of data sets such as those shown in Fig. 1, has enabled us to determine the movement of the Fermi level at the surface for both n- and p-type Si in the irradiated and unirradiated regions. The average shift of the bulk Si $2p$ position to higher kinetic energies (lower binding energies) between the clean and the reacted surface is represented by the space between the solid and dashed vertical lines in Fig. 2. For the n-type Si this shift was 0.29 ± 0.02 eV in the irradiated region and 0.22 ± 0.02 eV in the unirradiated region. Analysis of data on p-type Si (not shown) revealed shifts of 0.22 ± 0.02 eV in the irradiated region and 0.17 ± 0.01 eV in the unirradiated region. [These changes in Fermi level position are close to those observed in studies of the Si(111)-B($\sqrt{3}\times\sqrt{3}$)$R30°$ system.][4] High-temperature annealing (>1100 K) causes diffusion of B into the bulk, resulting in a surface with the Fermi level pinned at the same position as the clean surface (compare top and bottom spectra in Fig. 1). Based on the measured resistivities of the samples, the position of the bulk Fermi level with respect to the VBM is 0.84 eV for the n-type and 0.25 eV for the p-type Si. For the p-type Si, our analysis implies that the position of the Fermi level at the surface changes from 0.65 eV for the clean surface to 0.48 eV in the unirradiated region and to 0.43 eV in the irradiated region. As these values are still larger than that of the bulk, the implication is that these changes are due to a reduction in band bending of the appropriate amount. For the n-type Si, the corresponding surface Fermi level positions are 0.43 eV in the unirradiated region and 0.36 eV in the irradiated region. For n-type doping, electrons are trapped in surface states on the clean surface which causes the bands to bend up. Therefore, either there is an increase in band bending or the surface has become slightly p-type in the unirradiated region and more p-type in the irradiated region. Since boron is an acceptor,

the charge trapped in the surface states would tend to migrate toward boron sites. Therefore, it seems unlikely that band bending would increase, so we conclude that as a result of the reaction with DB the surface has been doped p type, and the amount of doping is larger in the SR irradiated region than in the unirradiated region.

CONCLUSION

In conclusion we have demonstrated that SR-induced reactions may be used to induce localized chemical and electronic changes in semiconductors. With the advent of x-ray lithography using SR, this approach may prove to be a valuable complementary method for device processing.

ACKNOWLEDGMENTS

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