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Investigation of single boron acceptors at the cleaved Si:B(111) surface

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The cleaved and (2×1) reconstructed (111) surface of *p*-type Si is investigated by scanning tunneling microscopy (STM). Single B acceptors are identified due to their characteristic voltage-dependent contrast, which is explained by a local energetic shift of the electronic density of states caused by the Coulomb potential of the negatively charged acceptor. In addition, detailed analysis of the STM images shows that apparently one orbital is missing at the B site at sample voltages of 0.4 – 0.6 V, corresponding to the absence of a localized dangling-bond state. Scanning tunneling spectroscopy (STS) confirms a strongly altered density of states at the B atom due to the different electronic structure of B compared to Si.

I. INTRODUCTION

In recent years, much interest has been devoted to identify individual dopant atoms at the surface of doped semiconductors by scanning tunneling microscopy (STM). For instance, on GaAs (110) substitutional Si donors ($\mathrm{Si_{Ga}}$) and Be or Zn acceptors in the top few surface layers appear as protrusions due to the local change of the tip-induced band bending arising from the Coulomb potential of the ionized dopant.[1,2] At low temperatures and negative sample bias circularly modulated structures in the topographic image have been interpreted as Friedel oscillations around the ionized donors induced by the accumulated electrons in the space-charge region.[3] Moreover, quantized subbands associated with bound states of a confined electron system have been observed for *n*-doped GaAs in the band-bending region induced by the STM tip [*x*]. Furthermore, in *n*-doped InAs the scattering states of ionized dopants at low temperatures have been explored.[4]

In addition to the delocalized features in the subsurface region, localized features have also been found, which were attributed to a local change of the electronic structure around dopants at the GaAs (110) surface.[1] Remarkably, *ab initio* calculations predict that the additional electron of the substitutional $\mathrm{Si_{Ga}}$ atom is trapped by a localized midgap level due to a local modification of the electronic structure around the Si atom.[5] Furthermore, different kinds of dopant-induced features and surface defects have been distinguished by voltage-dependent imaging of the occupied and unoccupied electronic states.[6]

Apart from studies of the segregation or adsorption of group-III or group-IV elements on the Si (111) surface, most of the work on the local electronic structure around individual dopant atoms focussed on doped III-V semiconductors rather than on elemental semiconductors like Si, although these surfaces have been investigated in great detail by STM and scanning tunneling spectroscopy (STS).[7] The question of how the dopant atoms are spatially distributed is of crucial interest for the investigation of the metal-insulator transition in Si doped with phosphorus and/or boron.[8] In a previous report we have shown that individual P donors at the (2×1) reconstructed (111) surface of *n*-doped Si can be identified by voltage dependent imaging and STS at room temperature.[9,10] Electronic surface states energetically located in the bulk band gap pin the Fermi level at 0.4 eV above the top of the valence band at the surface. Consequently, the bands are bent upward towards the surface in contrast to GaAs (110) where the bands remain flat at zero bias. In Si:P the Coulomb potential around the ionized donor causes a local down-shift of the electronic density of states (DOS) and the donor appears as a protrusion at positive sample bias and as an indentation at negative bias.

In order to further investigate the change of the local electronic structure around dopant atoms at the Si (111) surface we performed STM and STS measurements on cleaved *p*-doped Si (Si:B) at room temperature. Previous studies on the adsorption of B on Si (111) revealed different stages of B incorporation in the surface depending on coverage and thermal treatment[11,12] in contrast to other group-III adsorbates.[13,14] For the cleaved Si:B (111) surface one might naively expect that apart from the change of the sign of the Coulomb potential the influence of the negatively ionized B acceptor on the electronic structure can be explained in a way similar to Si:P. However, we will show that unlike in Si:P, the DOS in Si:B is strongly modified at the acceptor site possibly due to the different electronic configuration of substitutional B in Si compared to P.

II. EXPERIMENT

Measurements were performed with an Omicron STM in ultrahigh vacuum (UHV) at room temperature. STM tips were prepared from electro-chemically etched tungsten wire and further cleaned in UHV by repeated cycles of annealing and consecutive Ar^+ sputtering. Samples ($0.3\times4\times10\ \mathrm{mm}^3$) with boron concentrations $N_A=7\times10^{18}$ and $4.5\times10^{19}\ \mathrm{cm}^{-3}$ were cut from Czochralski-grown single crystals[15] and cleaved *in situ* to expose the (111) surface to the tip. STM images were acquired directly after cleavage without further heat treatment of the samples to maintain the original dopant distribution at the surface. Images were taken in the constant-current mode with the voltage applied to the sample and the tip grounded. Hence, at positive voltages unoccupied electronic states of the sample are imaged whereas at negative voltages occupied states are imaged, implying that the DOS of the tip varies smoothly with energy. Scans of opposite polarity were acquired quasisimultaneously by scanning each line forward and backward with reversed polarities.

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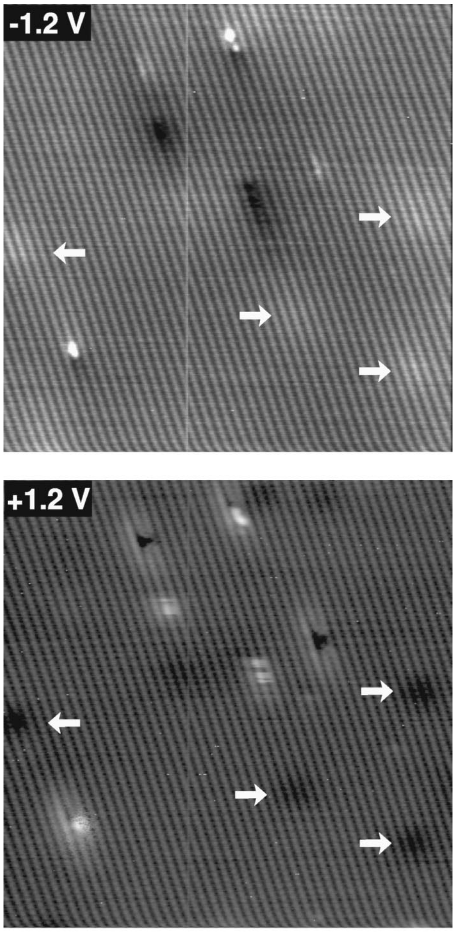

FIG. 1. STM images (30 nm×30 nm) of the cleaved Si:B (111) surface ($N_A=7\times10^{18}$ cm^{-3}) at negative and positive sample voltage U, tunneling current $I=0.7$ nA. White arrows indicate B-induced features.

III. RESULTS AND DISCUSSION

A. Identification and distribution of B acceptors

Figure 1 shows STM images of the cleaved Si(111) surface at $+1.2$ and -1.2 V, respectively. The bright rows are characteristic for the (2×1) reconstruction of the cleaved (111) surface as investigated in detail by Feenstra *et al.*[16] The reconstruction is explained by a revised π-bonded chain model[17,18] where the p_z orbitals representing ‘‘dangling bonds’’ (DB) retain their local character and are therefore ideally suited for imaging with an STM. Figure 2 shows a schematic sketch of this reconstruction where atoms marked 3 and 4 are fourfold coordinated and lowered, while the outer atoms 1 and 2 have one DB each, which is mainly occupied at atom 1 and mainly unoccupied at atom 2.[18] In the STM only the elevated atoms 1 and 2 are imaged. At *negative* sample voltage electrons tunnel out of the mainly occupied orbitals at position 1, which therefore appear as bright chains in the image, separated by dark stripes corresponding to atoms at positions 3 and 4. At low *positive* voltages the electrons are able to tunnel into the mainly unoccupied states located at atom 2, which therefore appear as bright chains. The small shift of the rows along the $[\bar{2}11]$ direction is verified by comparing images of opposite polarity. At even higher positive voltages electrons tunnel into unoccupied states that are located at the bonds between atoms 1 and 2 so that the rows appear as a zigzag chain.

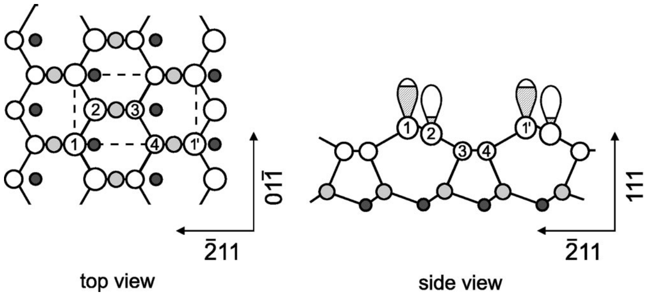

FIG. 2. Schematic sketch of the 2×1 reconstructed (111) surface. The lobes indicate the occupied or unoccupied dangling-bond states at atom 1 or 2, respectively.

Several types of defects are observed. Those marked by arrows have a characteristic voltage-dependent contrast. These defects appear as protrusions (bright) at -1.2 V in contrast to images taken at $+1.2$ V where they appear as indentations (dark). Hence, the contrast is exactly inverted with respect to Si:P. These characteristic defects are observed for both investigated boron concentrations. We count a total of 67 defects in a surface area of 21323 nm^2 for $N_A=7\times10^{18}$ cm^{-3} and 106 defects in 8357 nm^2 for $N_A=4.5\times10^{19}$ cm^{-3}. The values correspond to dopant surface densities of 3.14×10^{-3} nm^{-2} and 1.26×10^{-2} nm^{-2}, in good agreement with the respective surface densities of 2.2×10^{-3} nm^{-2} and 1.4×10^{-2} nm^{-2} obtained from the bulk concentrations, where we assume that only atoms in the outermost layer (atoms 1 to 4, Fig. 2) give rise to a contrast in the image. We therefore ascribe these features as being due to single B acceptors in the surface layer. It is reassuring that structures with this specific voltage-dependent contrast have not been found on the previously investigated Si:P (111) surface.[9,10] Vice versa, the characteristic voltage-dependent contrast ascribed to P donors on Si:P has not been found on the Si:B surface investigated here.

The identification of these defects as individual B dopants allows us to check whether the dopant distribution in Si:B is random. The probability of finding the nearest-neighbor B atom at a distance r from a given atom at the surface is $f(r)=2\pi r\rho e^{-\rho\pi r^2}$, assuming a Poisson distribution of dopants with the dopant surface-density ρ. For the determination of the nearest-neighbor distances, B atoms being nearer to the image border than to any other B atom have been discarded. The distances r have been grouped into 0.665 nm wide intervals corresponding to the unit cell dimension along $[\bar{2}11]$. Figure 3 shows a histogram together with $f(r)$ normalized to the area under the histogram. The behavior does not change considerably when the intervals are shifted by the row-to-row distance of 0.332 nm. We find reasonably good agreement between the statistical and experimental distribution, although there seems to be a cutoff at low r similar to what has been observed for Si:P. The shortest distance between two B atoms was found to be 1.67 nm. This is in reasonable agreement with the distance of 2.3 nm that follows from the solubility limit 1.2 at%($T<1400$ K) of B in Si for a random distribution.[19] The reduced counts at longer distances are likely to be due to the restricted size of the STM images. For this reason, the statistics has been carried

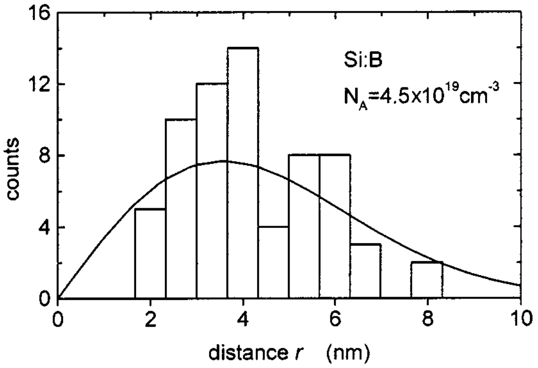

FIG. 3. Distribution of B nearest neighbors as determined from STM images (histogram) and $f(r)$ derived for a random arrangement of B atoms (solid line).

out for the higher concentration of $N_A = 4.5\times10^{19}$ cm^{-3} only, because most of the images taken on the sample with $N_A = 7\times10^{18}$ cm^{-3} showed only one or two B defects. We conclude that B acceptors in Si:B are distributed randomly with a short-distance cutoff similar to P donors in Si:P.

B. Electronic structure of single B acceptors

We now discuss the voltage-dependent contrast in more detail. Figure 4 shows STM images of a B-induced feature for different voltages. At all negative voltages boron appears as an isotropic shallow protrusion with a diameter of ≈ 2 nm. In contrast, at positive voltages B appears as a needle-shaped protrusion at $+0.4$ V but can hardly be distinguished from Si at $+0.9$ V. Further increase of the voltage leads to a reversal of the image contrast compared to $+0.4$ V and the acceptor appears as an indentation. This change in contrast with voltage is explained by a local change of the surface DOS around the acceptor.

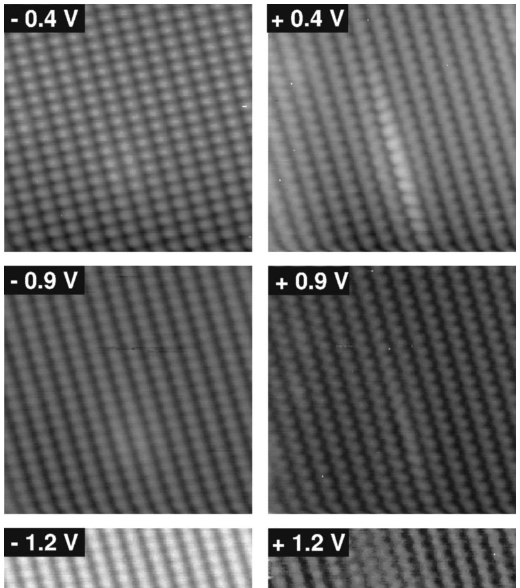

FIG. 4. STM images (7×7 nm^2) of the Si:B (111) surface ($N_A = 7\times10^{18}$ cm^{-3}) at different sample voltages, $I = 0.7$ nA.

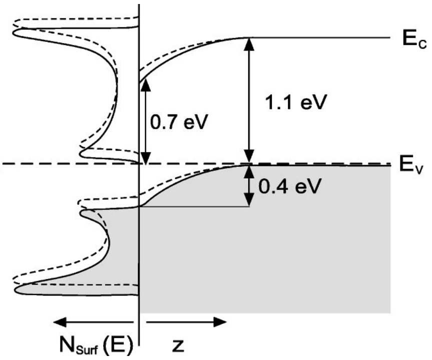

FIG. 5. Surface density of states and energy bands for *p*-doped Si (111) at the Si position (solid line) and at the acceptor position (dashed line). Hatched areas indicate occupied electronic states of Si.

Figure 5 shows the surface DOS for the *p*-type cleaved Si (111) surface together with the near-surface bulk energy bands as inferred from photoemission and STS experiments.[16,20,21] In *p*-type Si, the acceptor level at 45 meV above the valence-band edge is occupied at room temperature and the boron atom is negatively charged. This occurs for B acceptors at the surface as well, due to the low hole binding energy of 25 meV estimated for high-carrier concentrations.[22] In addition, due to the presence of electronic surface states in the bulk band gap (Fig. 5, solid line), holes (majority carriers) are accumulated at the surface and the positive charge is compensated by the formation of a hole depletion layer of depth *d*. The negative space charge of the depletion layer gives rise to a downward band bending towards the surface. Furthermore, the Fermi level is pinned 0.4 eV above the valence-band edge at the surface almost independent of dopant concentration for moderately doped Si.[20,21] For a boron concentration of $N_A = 4.5\times10^{19}$ cm^{-3} and a band bending of -0.4 V a depletion-layer depth $d = 3.4$ nm and a surface charge corresponding to 1.5×10^{13} $e$cm^{-2} are estimated.[23] This charge corresponds to a large hole density of 2.6×10^{20} cm^{-3} near the surface owing to the fact that the surface states decay into the volume with a short decay length of 1–2 lattice constants.[24]

Adopting the simple description which worked successfully for Si:P, the surface DOS at the location of the boron atom is energetically shifted *upward* due to the screened negative Coulomb potential of the B acceptor (Fig. 5, dashed line). For the occupied states below E_F this upward shift leads to a local increase of the surface DOS near the Fermi level. At negative voltages, electrons near the Fermi level of the sample have the highest transmission factor for tunneling into unoccupied states of the tip. Therefore, at the site of the B atom more electrons are able to tunnel into the tip compared to Si sites. Thus, B appears as a protrusion for *all* negative voltages.

At positive voltages, electrons at energies near the Fermi level of the tip have the highest probability for tunneling into unoccupied surface states of the sample. At $+0.4$ V there are more states available at the position of B, which therefore appears as a bright protrusion. At $+0.9$ V the surface DOS

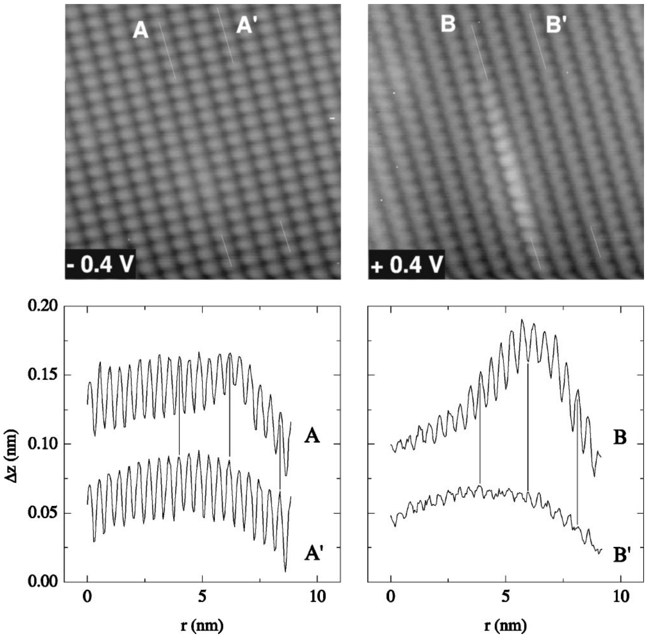

FIG. 6. STM images (7 nm×7 nm) of the boron-induced feature for $U=\pm 0.4$ V (cf. Fig. 4) and height profiles $\Delta z(r)$ along the indicated lines. In the scan along B one orbital is missing at the position of boron compared to the scan along B′.

of B and Si are alike so that B and Si can hardly be distinguished. At even higher voltages (+1.2 V) there are more surface states on Si, leading to a higher tunneling probability at the Si position than at the B position and B appears as an indentation. Hence, in this simple picture of a locally shifted DOS the contrast changes from bright to dark with increasing positive voltage as experimentally observed.

A more detailed analysis of the image taken at +0.4 V shows that apparently one unoccupied orbital in the row containing the defect is missing, compared to the image for $U=-0.4$ V (Fig. 6). The same behavior was found for ±0.6 V bias. The fact that the orbital is present for higher voltages confirms that the feature is not due to a surface vacancy. The missing orbital is better seen in the cross-section lines where each maximum corresponds to an unoccupied orbital (Fig. 6). At the position of the B acceptor a minimum appears at a position where actually a maximum is expected. Counting the number of maxima along the two lines B, B′, i.e., along the $[01\overline{1}]$ direction, one maximum is missing in the line taken across the defect (B) compared to a scan away from the acceptor (B′). We stress that this behavior was found for about 50% of all B-induced features while 50% appeared regular.

In Si:P the appearance of an additional orbital at the position of the P donor at U=−0.4 V (Refs. 9 and 10) was explained as being due to Si surface states just above E_F, which are usually unoccupied but are shifted to below the Fermi level by the Coulomb potential of the *positively* charged P donor. These states refer to the dangling-bond orbital at atom 2 (cf. Fig. 2). Therefore, this orbital becomes occupied and appears as an additional ‘‘atom’’ at negative voltages. As is apparent from Fig. 5, a corresponding explanation invoking simply a local shift of the surface DOS cannot be found to account for a missing orbital at the acceptor site in Si:B. We believe that this is due to different substitutional positions of boron at the surface. Rather, a qualitative change of the surface DOS at the B site must be invoked. For instance, the trivalent B located at position 1 or 2 would participate in three covalent bonds although the preferred flat sp^2-hybrid configuration cannot be realized. In contrast, B at position 3 or 4 has to satisfy four bonds making a charge transfer from adjacent Si atoms very likely. Such an effect of the B substitutional site on the electronic structure has been reported for B deposited on Si (111) where B does indeed occupy immediate subsurface positions.[11,12] In addition, the Si-B bond length is about 12% shorter than the Si-Si bond length mainly due to the smaller covalent radius of B compared to Si.[12] This will lead to a relaxation of the surface structure around B, which could be associated with a charge transfer between Si and B and/or a reformation of the unoccupied DB at/nearest to the B site towards a more back-bonded type. A missing orbital in the STM image at +0.4 V could either be explained by a complete occupation of the orbital at position 2, which then would not be imaged for $U>0$, or by a reformation of the DB towards a more back-bonded character.

Because only atoms 1 or 2 are imaged the effect of B at position 3 or 4 on the image contrast is presumably weaker because the acceptor at position 3 or 4 can only be ‘‘imaged’’ via an electronic interaction to Si atoms at positions 1 or 2. Hence, we conclude that the effect of a missing orbital is presumably due to B located at positions 1 or 2. This is in good agreement with the fact that we found a missing orbital at roughly 50% of the B sites. We emphasize that the topological structure of the B-induced feature clearly requires theoretical calculations. Moreover, a more sophisticated model has to include many-body effects which are important for highly localized electronic states.[14]

The local change of the DOS at the acceptor site is confirmed by scanning tunneling spectroscopy (STS). During $I(U)$ data acquisition the tip was retracted from the surface by 0.05 nm/V to compensate for the exponential increase of current with voltage. Several $I(U)$ curves were averaged to reduce the scatter of the data. As demonstrated earlier, the logarithmic derivative $(dI/dU)/(I/U)$ is independent of the distance and is related to the surface DOS with $U=0$ corresponding to E_{F}.[16] Due to the numerical evaluation of $(dI/dU)/(I/U)$ data points around $U=0$ were omitted because division by zero leads to unreasonable results, while $(dI/dU)/(I/U)|_{U=0}=1$. Figure 7 shows spectra taken above a Si atom away from the acceptor, which exhibits peaks at $U=-0.9,+0.5,+1.4$ V in agreement with previous results for *p*-doped Si where similar peaks were observed at somewhat lower voltages $U=-1.0,-0.35,+0.17,+1.25$ V due to the lower doping level[16] compared to the present samples. These peaks can be attributed to the surface DOS of Si observed in photoemission experiments.[20,21] A peak expected at $U=-0.35$ V corresponding to the occupied DB states could not be resolved due to the numerical difficulties around $U=0$.

In comparison, the spectrum taken above the acceptor is strongly modified, apart from the peak at $U=+1.45$ V, which is slightly shifted by $\Delta U\leqslant 0.1$ V compared to the peak on Si. The most striking result is the strong reduction of the large peak observed on Si at +0.5 V. The corresponding unoccupied electronic states are located at the DB orbitals at

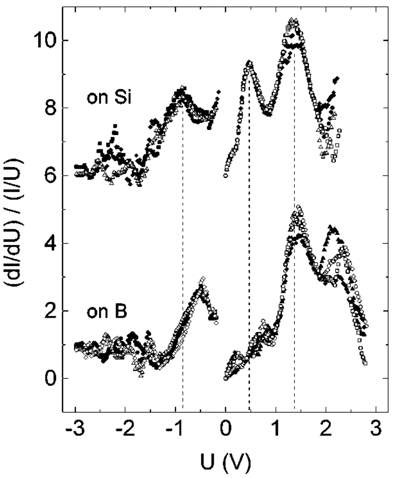

FIG. 7. Normalized tunneling spectra taken away from and on top of the B-induced feature, respectively. Different symbols indicate different tunneling spectra calculated from an averaged set of several $I(U)$ curves.

position 2. Strong modifications of the STS spectra have also been reported for B deposited on Si (111).[11,12] In the present case, the reduction of the surface DOS above E_F confirms the absence of a localized DB state at the B site and the effect of a missing orbital in the STM image at $U=0.4-0.6$ V. Furthermore, the peak at -0.9 V representing the bottom of the occupied surface band is considerably shifted upward by ≈ 0.5 V at the B site. Since, at negative bias, states near E_F of the sample dominate the tunneling current this confirms the bright image contrast at the B site observed for all negative voltages.

A further question concerns the apparent anisotropic shape of the B defect. As mentioned above, at -0.4 V the extension of the B induced feature seems to be isotropic while it appears strongly elongated along the $[01\bar{1}]$ direction at positive voltage. Such an effect could be due to a different electronic interaction between Si and B along the π-bonded chains compared to the perpendicular direction and needs further investigation. We mention that the P-induced feature on Si:P appeared to be isotropic, although its overall extension was smaller. An explanation for the larger extent of the B-derived features could be a different distance between the tip and the surface compared to Si:P caused by a higher tunneling current of 0.7 nA compared to 0.3 nA in the latter case.

IV. SUMMARY

The Si (111) (2×1) surface of cleaved B-doped single crystals has been investigated by STM. The individual B acceptors have been identified by a voltage-dependent contrast and have been further characterized by STS. Similarly to Si:P the general change in contrast is governed by the local shift of the surface DOS due to the Coulomb potential of the charged dopant atom. In addition, the local change of the atomic and electronic structure around the B acceptor gives rise to a missing orbital observed in 50% of the images taken at $U=+0.4$ V. These acceptors are presumably located at the upper positions 1 and 2 of the (2×1) reconstructed surface. The unoccupied DOS of B at the surface as determined by STS is strongly reduced around 0.4 eV, in contrast to Si:P where such drastic changes are not observed. This shows that the electronic configuration of substitutional dopants has a decisive influence on the local electronic structure.

The fact that in Si:B and Si:P the surface-densities of dopants estimated from the STM data are in good agreement with the surface densities derived from the bulk concentrations strongly confirms the assumption that only dopants in the outermost layer are imaged. This is in strong contrast to doped III-V semiconductors, where features arising from dopants in several subsurface layers are observed.[1,2,4] Presumably, the screening of dopants is very different in doped Si and needs to be investigated further.

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