SiO₂ Modulation Doping for Si: Acceptor CandidatesDirk König,^{1,*} Daniel Hiller,² and Sean Smith^{3,†}¹*Integrated Materials Design Centre, University of New South Wales, New South Wales 2052, Australia*²*Research School of Engineering, The Australian National University, Australian Capital Territory 2601, Australia*³*Department of Applied Mathematics, Research School of Physics and Engineering, The Australian National University, Australian Capital Territory 2601, Australia*

(Received 23 May 2018; revised manuscript received 9 August 2018; published 14 November 2018)

Conventional impurity doping of ultrasmall nanoscale silicon (Si) currently used in very-large-scale integration faces serious miniaturization challenges below the 14-nm technology node such as dopant out-diffusion and inactivation by clustering in Si-based field-effect transistors (FETs). For Si nanocrystals showing quantum confinement, self-purification and massively increased ionization energies cause doping to fail. Modulation doping is widely used in group III–group V materials in particular for optoelectronic applications, where high carrier densities at low scattering and nonradiative recombination rates are crucial. Setting out from our recent success to introduce modulation acceptors into SiO₂ with aluminum to provide holes to Si [König *et al.*, *Sci. Rep.* 7, 46703 (2017)], we follow our atomistic concept to investigate other possible modulation acceptors in SiO₂. Using density functional theory and experimental verification of key candidates by capacitance-voltage and deep-level-transient-spectroscopy measurements, we elucidate the role of atomistic parameters that determine the ability of the dopant species to provide modulation-acceptor states to SiO₂ and thus holes to Si. Modulation-doped SiO₂ can replace conventional doping of ultrasmall nanoscale Si from the SiO₂ coating or trench of a FET and have a high potential for carrier-selective tunneling contacts in Si-based heterojunction solar cells and tunnel FETs.

DOI: [10.1103/PhysRevApplied.10.054034](https://doi.org/10.1103/PhysRevApplied.10.054034)

I. INTRODUCTION

Impurity doping of silicon has been a key technique and prerequisite for Si-based electronics for decades [1]. Miniaturizations in Si very-large-scale integration (VLSI) became increasingly difficult as device features approached the characteristic lengths of dopant out-diffusion, clustering, and inactivation [2]. Considerable broadening of dopant profiles from drain and source regions into gate areas persists [3]. Moreover, required VLSI transistor functionality and emerging applications of Si nanocrystals (NCs) [4] unveiled additional doping issues: self-purification [5,6], suppressed dopant ionization [7,8], and dopant-associated defect states [8,9].

Modulation doping—doping of materials adjacent to semiconductors, which then provide free carriers to the unperturbed semiconductor—was first used for group III–group V (III–V) semiconductor combinations such as

GaAs/AlAs in the late 1970s [10]. Recently, Si modulation doping of adjacent dielectric layers based on Al_xGa_{1−x}N [11] and SiO₂ [12] in analogy to modulation doping of III–V semiconductors was shown to be an alternative to conventional impurity doping. Modulation doping of SiO₂ adjacent to Si removes parasitic issues caused by conventional impurity doping, leading to lower inelastic carrier-scattering rates and higher carrier mobilities, which decrease heat loss and bias voltages in VLSI. Such properties enable Si FET technology to work at yet-smaller structure sizes, potentially enabling Moore's law to reach the Si-crystallization limit of approximately 1.5 nm [13,14].

We investigate boron (B) as a special case of a modulation acceptor for Si in SiO₂ using capacitance-voltage (CV) measurements, deep level transient spectroscopy (DLTS), and density functional theory (DFT). The findings, results for scandium (Sc), and previous results for aluminum (Al) [12] are evaluated with respect to their electronic structure to describe their suitability together with the underlying reasons for SiO₂ acceptor modulation doping. Following this detailed investigation, we extend DFT calculations that were proven to be in accord with experimental data as per above to conduct a search for more acceptor candidates. Experimental and DFT data are then evaluated against atomistic data of Si and O in SiO₂

*solidstatedirk@gmail.com

†Also at Institute of Semiconductor Electronics, RWTH Aachen University, 52074 Aachen, Germany

‡Also at Integrated Materials Design Laboratory, The Australian National University, Australian Capital Territory 2601, Australia

and acceptor candidates to arrive at a qualitative atomistic concept of SiO₂ doping. This concept elucidates the mechanisms that allow acceptor states with binding energies high enough to accept an electron from a Si reservoir (bulk Si, NC, nanowire, nanowell).

II. METHODS

Hybrid-DFT calculations are performed in real space with a molecular-orbital (MO) basis set (BS) and Hartree-Fock (HF) and hybrid DFT methods as described below, with use of the Gaussian09 program package [15]. Initially, the MO-BS wavefunction ensemble is tested and optimized for stability with respect to the description of the energy minimum of the approximant (variational principle; *stable = opt*) using the HF method with a 3-21G MO-BS (HF/3-21G) [16]. For modulation acceptors beyond krypton (period 4 of the periodic table), we use the default-2 triple- ζ polarized valence (def2-TZVP) MO-BS [17] with effective core potentials [18–21] throughout all calculations as available from the EMSL Basis Set Exchange project [22]. This MO wavefunction ensemble is then used for the structural optimization of the approximant to arrive at its stablest configuration (maximum integral over all bond energies), again following the HF/3-21G route. Using these optimized geometries, we calculate their electronic structure again by testing and optimizing the MO-BS wavefunction ensemble with the B3LYP hybrid density functional [23,24] and the 6-31G(*d*) MO-BS [B3LYP/6-31G(*d*)] [25]. The root-mean-square-force and peak-force convergence limits are 8 and 12 meV/Å, respectively. Tight convergence criteria are applied to the self-consistent-field routine. Ultrafine integration grids are used throughout. During all calculations, no symmetry constraints are applied to MOs. Extensive accuracy evaluations can be found elsewhere [26–28]. Approximants and MOs are visualized with Gaussview 5 [29]. The electronic density of states (DOS) is calculated from MO eigenenergies by application of a Gaussian broadening of 0.2 eV. DLTS data are evaluated for the energetic position of modulation acceptors with a one-dimensional Poisson solver coded in MATLAB following Nicollian and Bruce [30].

For all samples, wet-chemically-cleaned, front-side-polished, 100-mm Czochralski *n*-type-Si wafers (phosphorus, 1.6 Ω cm) are used as a substrate. For the B-doped sample 1xB, a plasma-enhanced-chemical-vapor-deposition (PECVD) tunnel SiO₂ of 2.0-nm thickness is deposited [31] in a modified Oxford Instruments PlasmaLab–FlexAL cluster. Subsequently, approximately 4 Å of B-doped PECVD oxide, corresponding to approximately two monolayers (MLs) of SiO₂, is deposited with approximately-0.2-at. % B by addition of B₂H₆ gas to the O₂-SiH₄ mixture as determined by secondary-ion mass spectroscopy [32]. This B dose corresponds to

FIG. 1. Cross-section scheme of MOS samples used in this work (a). *X* refers to the modulation acceptor or oxygen for the reference sample. Band structures showing the principle of direct modulation doping for a Si NC in SiO₂ (b) and for bulk Si terminated with a *X*-doped SiO₂ layer (c). Occupation of electronic states is described by the chemical potential μ for a quantum system and the Fermi level E_F for bulk Si.

approximately $6.8 \times 10^{12} \text{ cm}^{-2}$ area density of B in the two MLs of PECVD SiO₂. Reference sample 0xDop and Al-doped sample 1xAl obtain a 1.5-nm-thick rapid thermal oxide (RTO). Then both samples are transferred under a vacuum into the thermal-atomic-layer-deposition chamber for deposition of an Al-O ML (sample 1xAl) and an O ML (sample 0xDop) at 200 °C [12]. Finally, capping SiO₂ layers of 10 nm (samples 0xDop and 1xAl) or 8.5 nm (sample 1xB) are deposited in the PECVD chamber. All wafers undergo a rapid thermal anneal at 1000 °C for 30 s in Ar at ambient pressure with a ramp rate of 25 K/s. Electrical top and substrate contacts (Al) are thermally evaporated and lithographically structured to fabricate MOS capacitors. A schematic cross section of the samples is shown in Fig. 1(a). All silicon oxide thicknesses are measured by ellipsometry with a Woollam M-2000 ellipsometer.

DLTS and high-frequency CV measurements are performed with a PhysTech FT1030 high-energy-resolution-analysis DLTS setup in capacitance mode under isothermal conditions ($T = 100 \text{ K}$) with use of a JANIS VPF 800 cryostat. High-frequency CV curves are measured at a frequency of $f = 1 \text{ MHz}$. Diffusion of B through 1.5-nm SiO₂ of more than one ML can be excluded on the grounds of its minute diffusion coefficient in SiO₂ of approximately $2 \times 10^{-18} \text{ cm}^2/\text{s}$ at $T = 1000 \text{ °C}$ [33] in a compound with the low thermal budget of the processing sequence of the metal-insulator-semiconductor (MIS) structure.

III. PRINCIPLE OF DIRECT MODULATION DOPING IN SILICON DIOXIDE

Direct modulation doping shares the main features with standard modulation doping [10] such as providing carriers into active semiconductor volumes while sparing them from dopants and associated parasitic effects. An important difference is the *direct* ionization of Si [Figs. 1(b)

and 1(c)]. It requires SiO₂ modulation dopants to be adjacent to Si to acquire free carriers by electron relaxation from the modulation donor to Si or from Si to the modulation acceptor, leaving a free hole in Si in the latter process. With relaxation energies of electrons from the top of the valence band in bulk-Si to Al modulation acceptors in SiO₂ of $E_{\text{relax}} = 0.5$ eV through a 1.5-nm SiO₂ tunneling barrier [12], the potential slope for carrier relaxation is represented by the field strength of $F_{\text{relax}}(\text{SiO}_2) \approx 3 \times 10^6$ V/cm. Recent experiments [34] have shown that very high fixed negative charge densities originating from ionized Al modulation acceptors in SiO₂ occur through SiO₂ tunneling barriers up to 3 nm thick, setting the minimum field strength for carrier relaxation at high ionization probabilities P_{ion} to $F_{\text{relax}}(\text{SiO}_2) \approx 1.7 \times 10^6$ V/cm.

As conventional impurity doping, standard modulation doping requires a certain thermal energy $k_B T$ to achieve dopant ionization with sufficiently high P_{ion} at room temperature to the respective band edge of the wider-band-gap semiconductor [10]. For this reason, both doping principles fail at very low temperatures in the nondegenerate regime since $P_{\text{ion}} = \exp(-E_{\text{ion}}/k_B T)$ (dopant freeze-out [35]). Direct modulation doping proceeds from Si straight to the modulation dopant in SiO₂ as shown for a modulation acceptor adjacent to a Si NC [Fig. 1(b)] or bulk Si [Fig. 1(c)]. Since the intermediate ionization step requiring $k_B T$ to be above a certain threshold does not occur, direct modulation doping does not undergo a freeze-out as demonstrated by DLTS for Al in SiO₂ [12].

The total density of Al atoms per ML in SiO₂ $N_{\text{Al}}^{\text{sheet}} \approx 5 \times 10^{14}$ cm⁻² as measured by elastic-recoil-detection analysis. The ionized partition of such acceptors as experienced in Si is given by the fixed negative charge density of $Q_{\text{fix}} = -2.3 \times 10^{12}$ cm⁻² per ML of Al [12]. After multiplication of this value by the ratio of relative dielectric constants $\epsilon_{\text{Si}}/\epsilon_{\text{SiO}_2} = 11.9/3.9 = 3.05$ [35] to account for decreased electrostatic screening in SiO₂, we obtain the density of ionized Al acceptors as $Q_{\text{Al}}^{\text{tot}} = -7.02 \times 10^{12}$ cm⁻². The absolute value of $Q_{\text{Al}}^{\text{tot}}/N_{\text{Al}}^{\text{sheet}}$ yields the ionization probability $P_{\text{ion}} = 1/71$. This low value reflects the low relative dielectric constant of SiO₂, which increases the repulsive Coulomb energy E_{Coulomb} between ionized acceptors to exceed E_{relax} , as can be seen from the modified Fermi-Dirac distribution function:

$$P_{\text{ion}} = 1 - \frac{1}{1 + \exp[(E_{\text{relax}} - E_{\text{Coulomb}})/k_B T]}. \quad (1)$$

Rearrangement to obtain E_{Coulomb} as a function of P_{ion} is straightforward, yielding

$$E_{\text{Coulomb}}(P_{\text{ion}}) = E_{\text{relax}} - k_B T \ln\left(\frac{P_{\text{ion}}}{1 - P_{\text{ion}}}\right). \quad (2)$$

With $P_{\text{ion}} = 1/71$, we obtain $E_{\text{Coulomb}} = E_{\text{relax}} + 4.248 k_B T$, which is $E_{\text{Coulomb}} = E_{\text{relax}} + 0.110$ eV for $T = 300$ K. The

low value of P_{ion} enables self-regulated ionization of direct modulation dopants over a wide density range, leveling any deviations in dopant density in principle down to 0.015 ML of modulation dopants in SiO₂ as there is a massive reserve of unionized acceptors. Hence, direct modulation doping does not suffer from density variabilities as degenerate impurity doping does in VLSI. As a result, the active doping density is set not by the total density of dopants but rather by the dopant-specific value of E_{relax} and the associated change in E_{Coulomb} [see Eq. (1)].

IV. ELECTRONIC PROPERTIES OF BORON IN SILICON DIOXIDE

A. High-frequency CV

The high-frequency CV curves of samples 1xB and 0xDop are shown in Fig. 2 together with the data for sample 1xAl containing one ML of Al in SiO₂ [12]. The CV curve of sample 1xAl shows a significant shift to more positive bias voltages versus sample 0xDop as a result of negatively ionized modulation acceptors induced by the Al atom occupying Si sites in SiO₂ [12]. In contrast, sample 1xB has a slight shift to *more negative* voltages. It appears that if B behaves as a modulation dopant at all, it has a faint donor character since its flat-band voltage V_{FB} is slightly more negative than that of sample 0xDop.

FIG. 2. High-frequency CV data of MIS samples composed of *n*-type-Si(001) wafer (2 Ω cm) with 1.5-nm RTO on which one ML of Al [12] is deposited (1xAl, blue curves) and with 2.0 nm PECVD SiO₂ on which two-ML SiO₂:B (1xB, magenta curves) is deposited. Data for reference sample 0xDop are shown by black curves. Full lines show the forward-bias sweep (fwd) and dashed lines show the backward bias sweep (bwd). The layout for all samples is shown in Fig. 1(a). Arrows with values show the location of V_{FB} . All measurements are performed at $T = 300$ K. The number in parentheses for sample 0xDop is its V_{FB} value corrected for thinner capping SiO₂ of sample 1xB (the total SiO₂ thickness is 10.9 nm for sample 1xB and 11.5 nm for sample 0xDop).

B. Deep-Level Transient Spectroscopy

DLTS is a powerful technique to characterize electronic states within band gaps of semiconductors and insulators if the electronic states in the latter are close enough to a carrier reservoir to be charged by a bias pulse [12]. Fig. 2(a) shows the relevant DLTS scans of sample 1xB and the scan of sample 0xDop under the same conditions. Sample 1xB has a much-weaker signal as opposed to Al in SiO₂ [12]. This raises the question of how much B in SiO₂ is chemically bound to either Si or O and thereby not only present at interstitial sites but potentially undergoes dopant formation. In the third main group of the periodic table, B is by far the most-anionic and most-inert chemical element [36]. While B₂H₆ has a formation enthalpy of +36 kJ/mol and thus easily decomposes into H₂ and B, even amorphous elemental B is so inert that it does not oxidize in air or oxygen (O₂) below $T \approx 700^\circ\text{C}$ [36]. It is therefore likely that even atomic B does not readily react with SiO₂.

To further evaluate DLTS data for B in SiO₂, we calculate the signal difference of sample 1xB to sample 0xDop, which removes all features not due to B for sample 1xB [Fig. 3(b)]. The signal of 0xDop exclusively features the buildup of the space-charge region; we approximate this scan with a quadratic fit to further reduce noise [Fig. 3(a)]. Figure 3(b) clearly shows that there are two signal peaks due to B. With the very low signal intensity as evident from considerations below, we describe these two features with Gaussian fits. Peak 1 occurs at the reference voltage $V_R = -0.53$ V what corresponds to $V_{FB} = -0.37$ V of sample 0xDop, and peak 2 occurs at the reference voltage $V_R = -0.73$ V what corresponds to $V_{FB} = -0.57$ V of sample 0xDop, whereby we use V_{FB} values corrected for the slightly lower SiO₂ thickness of sample 1xB [see Fig. 2].

Using a Poisson solver, we calculate the energy levels of peaks 1 and 2 relative to the Si conduction-band edge at the interface with SiO₂, $E_C^{\text{Si}}(\text{Si/SiO}_2)$, yielding $E_{\text{peak 1}} = E_C^{\text{Si}}(\text{Si/SiO}_2) - 0.28$ eV and $E_{\text{peak 2}} = E_C^{\text{Si}}(\text{Si/SiO}_2) - 0.32$ eV. From these energies located within the band gap of bulk Si, it is apparent that B is not a stable modulation dopant in SiO₂ for Si (see Fig. 4).

Next we calculate the cumulative DOS per peak, performing integration over its transient-capacitance-density signal to get $Q_{\text{peak 1}}^{\text{tot}} = 1.42 \times 10^7 \text{ cm}^{-2}$ for peak 1 and $Q_{\text{peak 2}}^{\text{tot}} = 1.64 \times 10^7 \text{ cm}^{-2}$ for peak 2. As we see in Sec. IV C, the slightly bigger electronic state density of peak 2 is consistent with a slightly-more-negative value of V_{FB} when compared with the reference sample (see Fig. 2). Both total charge densities are about a factor of 10^3 below the midgap trap state densities of high-quality thermal SiO₂ on Si, which explains the rather high noise level. It is interesting to note that the total acceptor DOS for one

FIG. 3. DLTS scan of the electron-escape process in sample 1xB measured at $T = 101$ K (a). Reference sample 0xDop is shown for comparison with a quadratic fit describing the charge buildup in the space charge region without noise. The signal intensity in the subpicofarad-per-square-centimeter range shows that few B atoms occupy atomic sites in SiO₂; see the text for details. The difference between the DLTS signal and the quadratic fit to the reference sample is shown to elucidate the two signal peaks obtained for B in SiO₂ (b). The bias voltage of peak positions is shown together with Gaussian fits.

ML of Al in SiO₂ is $Q_{\text{Al}}^{\text{tot}} = -7.02 \times 10^{12} \text{ cm}^{-2}$, which exceeds by a factor of 4.94×10^5 the value for the acceptor state represented by peak 1 (see Sec. IV C). If we take into account that we have B with an area density of approximately $6.8 \times 10^{12} \text{ cm}^{-2}$ to be incorporated into 4-Å PECVD SiO₂ versus sample 1xAl, having an area density of $5 \times 10^{14} \text{ cm}^{-2}$ in accord with one ML of Al, this factor reduces to 6723. This is a strong argument to support the hypothesis above that the vast majority of B atoms do not form electrically active states with the SiO₂ layer. The peculiar nature of B in SiO₂ of having two peaks (vs one peak for Al in SiO₂) is further elucidated by DFT calculations below.

FIG. 4. Band structure and corresponding diagram of bias voltage versus time, showing electron capture and escape in DLTS from electronic states within SiO₂ due to B.

C. DFT calculations

The comparatively strong anionic character of B in the third main group of the periodic table raises the question of whether B can also be incorporated at an O lattice site in SiO₂. This hypothesis is supported by B having an electronegativity approximately 16% greater than Si (see Table II). In addition, B is ionized by its two first-next-neighbor O atoms to a considerable positive charge q_{ion} , whereby its radius r_{ion} becomes 40% smaller than that of Si at this site (see Table II). In contrast, the ionic radius of B at an O site is merely 8% smaller than that of an O atom in the same location. As a consequence, considerably less strain is generated when O instead of Si is replaced by B, which increases the energy available for binding B at an O lattice site.

We therefore investigate two nearly identical approximants that consist of a Si₁₀ NC in three-ML SiO₂, whereby one approximant has one Si atom in SiO₂ exchanged for B and the other approximant has one O atom exchanged for B. Figures 5(a) and 5(b) show these approximants with isodensity plots of the lowest unoccupied MO (LUMO) and the highest occupied MO (HOMO), respectively. Both locations of B substitutions are located two MLs away from the Si₁₀ NC. Hence, MOs have to penetrate through two MLs of SiO₂ to exist at the modulation dopant and within the Si₁₀ NC. We found earlier that Si₁₀ NCs terminated with functional groups such as OH or embedded in SiO₂ still behave as NCs and not as molecules such as Si cages with very discrete MO energies [26,27]. The fact that both approximants keep the respective configuration of B intact throughout structural optimization shows that B is thermodynamically stable at a Si site as well as at an O site. Identical start configurations of approximants apart from the dopant are used throughout this work and for the investigation of Al as a modulation donor in SiO₂, whereby we

FIG. 5. Optimized DFT approximant of Si₁₀ NC (8Å size) seen along the <001> direction in three-ML SiO₂, with B replacing Si in SiO₂ two MLs away from the NC (a). The density of the LUMO (lowest unoccupied state) is associated with B and is shown as an isodensity plot. As shown by DLTS, this acceptor state cannot capture an electron from bulk Si in equilibrium, ruling out such carrier relaxation in a Si NC with quantum confinement as is evident from the missing LUMO density at/in the Si₁₀ NC. Optimized DFT approximant of Si₁₀ NC seen along the <001> direction in three-ML SiO₂, with B replacing O in SiO₂ two MLs away from the NC (b). The density of the HOMO (highest occupied state) is associated with B and is shown as an isodensity plot. This donor state cannot donate an electron to bulk Si as shown by DLTS, again ruling out such carrier relaxation in a Si NC with quantum confinement. Isodensity plots of MO densities are $\langle \psi_{\text{MO}} | \psi_{\text{MO}}^* \rangle = 4 \times 10^{-4} e/a_{B,0}^3$ ($2.7 \times 10^{-3} e/\text{\AA}^3$). Atom colors are cyan for Si₁₀ NC, gray for Si in SiO₂, red for O, white for H, and cyan for B (single atom within SiO₂).

can directly compare results shown here with results from previous work [12]. In addition, we can test the ability of modulation acceptors to ionize the smallest Si NC though two MLs of perfect SiO₂ presenting a tunneling barrier. We can see from Fig. 5 that both of the relevant MOs are

FIG. 6. Electronic DOS of the following approximants: Si_{10} NC in three-ML SiO_2 with B on O site [see Fig. 5(b)], Si_{10} NC in three-ML SiO_2 with B on Si site [see Fig. 5(a)], Si_{10} NC in three-ML pure SiO_2 , and the fully oxidized approximant where the Si_{10} NC is fully converted into SiO_2 [$\text{Si}_{74}\text{O}_{108}(\text{OH})_{64}$]. Gray (light-gray) lines and arrows indicate the onset of the occupied (unoccupied) SiO_2 DOS. The two possible electron-spin orientations are labeled α and β ; they are relevant for the doped approximants presenting spin doublets. MOs associated with B are shown as thick lines in the respective color of the DOS. The α HOMO of B at an O site and the β LUMO of B at a Si site with their energetic distance of approximately 0.8 eV are of special interest with regard to the electronic nature of B in SiO_2 ; see Fig. 5 for MO density distributions and the text for details.

located only at the B site, and not within or even near the Si_{10} NC. This is a first hint that either configuration of B cannot ionize the NC.

When B occupies Si sites, introducing acceptor states as well as O sites introducing donor states, the system can undergo autocompensation if the donor state is located above the acceptor state on the energy scale. This process is well known from polar III-V materials such as high-density Si-doped GaAs [37]. The electronic DOS of both approximants depicted in Fig. 5 are shown in Fig. 6 together with an undoped approximant of the same type (Si_{10} NC in three-ML SiO_2) and of this approximant fully oxidized to SiO_2 , both presenting reference cases to clarify the nature of the electronic states associated with dopants.

Figure 6 shows that B at a Si site indeed presents an acceptor state at the LUMO of the system. However, its energy is 0.65 eV above the highest occupied state of the Si_{10} NC. A similar situation occurs for B at an O site, which introduces a donor level 1.99 eV below the lowest unoccupied state of the Si_{10} NC. The acceptor state induced by B at a Si site in SiO_2 is located 0.82 eV below the donor state due to B at an O site in SiO_2 , corroborating the picture of autocompensation. This finding is in agreement with our experimental data in Secs. IV A and IV B. While the above DFT calculations do not exactly replicate the energy difference between both peaks found by DLTS, they clearly corroborate the concept of B in SiO_2 acting as donor at an O site and as acceptor

FIG. 7. Optimized approximant featuring a Si_{10} NC embedded in three-ML SiO_2 where a Si atom two MLs away from the NC is replaced with Sc, showing the HOMO (a) and LUMO (b) as isodensity plots of $4 \times 10^{-4} e/a_{B,0}^3$ ($2.70 \times 10^{-3} e/\text{\AA}^3$). Both MOs are clearly located within the NC as well as at Sc, representing the modulation-acceptor site. Atom colors are cyan for Si_{10} NC, gray for Si in SiO_2 , red for O, white for H, and cyan for Sc (single atom within SiO_2).

at a Si site. We can therefore assign peak 1 in the DLTS scan to the donor state (B at O site) with an energy of $E_{B,\text{don}}(\text{SiO}_2) = E_C^{\text{Si}}(\text{Si}/\text{SiO}_2) - 0.28$ eV and peak 2 to the acceptor state (B at Si site in SiO_2) with an energy of $E_{B,\text{acc}}(\text{SiO}_2) = E_C^{\text{Si}}(\text{Si}/\text{SiO}_2) - 0.32$ eV. This situation is schematically illustrated in Fig. 4. DLTS further shows that peak 1 (donor) has a slightly bigger cumulative electronic state density than peak 2 (acceptor), resulting in a slight imbalance favoring the donor state of B in SiO_2 . Accordingly, sample 1xB has a slightly-more-negative value of V_{FB} when compared with reference sample 0xDop since the donor states get positively ionized in equilibrium, thereby shifting V_{FB} to a slightly-more-negative value when compared with reference sample 0xDop.

FIG. 8. Electronic DOS of the following approximants: Si₁₀ NC in three-ML SiO₂ with Sc on Si site [see Fig. 7], Si₁₀ NC in three-ML pure SiO₂, and the fully oxidized approximant where the Si₁₀ NC is fully converted into SiO₂ [Si₇₄O₁₀₈(OH)₆₄]. Gray (light-gray) lines and arrows indicate the onset of the occupied (unoccupied) SiO₂ DOS. The two possible electron-spin orientations are labeled α and β ; they are relevant for the doped approximants presenting spin doublets. MOs associated with Sc are shown as thick lines in the respective color of the DOS. The inset shows the β HOMO and the β LUMO of Sc at a Si site and are of special interest with regard to the electronic nature of Sc in SiO₂; see the text.

V. ELECTRONIC PROPERTIES OF SCANDIUM IN SILICON DIOXIDE

The first studies on acceptor modulation doping in SiO₂ were performed with Si NCs in mind and considered Sc as a key candidate due to its specific atomic orbital (AO) configuration [38], which is discussed below. Several attempts were undertaken to process MIS samples with Sc (ion implantation, atomic layer deposition). So far, exact

TABLE I. Energy of acceptor level relative to vacuum level $E_{\text{vac}} - E_{\text{LUMO}}^{\text{acc}}$ as a function of dopant (see Fig. 10).

	B	Al	Ga	In ^a	Sc	Y ^a	La ^a
$E_{\text{vac}} - E_{\text{LUMO}}^{\text{acc}}$ (eV)	5.12	5.36	5.39	5.27	5.51	5.21	4.54

^aDopants described with the def2-TZVP MO-BS for accurate results of heavier elements. While these values are accurate, they may contain a constant small offset from those energies obtained from calculations which have a 3-21G [6-31G(d)] MO-BS for all atoms during optimization [electronic structure calculation].

deposition control to the ML to obtain the required sample quality for precise characterization has not been successful. We therefore resort to DFT calculations to investigate the electronic properties of Sc in SiO₂. The approximant used had a starting configuration identical to that of the approximant in Fig. 5(a), with B substituted for Sc at a Si site in SiO₂ two MLs away from the Si₁₀ NC. Figures 7(a) and 7(b) show isodensity plots of the β -HOMO and β -LUMO densities, respectively. As is the case for Al in SiO₂ [12], a massive presence of both states can be seen at Sc and at/in the Si₁₀ NC, clearly demonstrating that Sc is able to attract an electron partition from the NC.

The electronic DOS of the approximant in Fig. 7 is shown in Fig. 8. While there is a small uncertainty due to E_{relax} in DFT not producing exactly the experimental value (e.g., 0.8 eV vs 0.5 eV for Al in SiO₂; see [12]), it appears that Sc works as a modulation acceptor even surpassing Al in its performance (see Fig. 10 and Table I).

The AO configuration of Sc has a significant influence on its properties as a modulation acceptor in SiO₂. Acceptors belonging to the third main group of the periodic table such as B, Al, Ga, and In have a $\mathcal{V}s \uparrow \downarrow p_1 \uparrow$

TABLE II. Electronic and chemical properties of all chemical elements involved in acceptor modulation doping of SiO₂ [36]: Ionization energies of the first, second, and—where $q_{\text{ion}} > 2e$ —third valence electron (E_{ion}), electronegativity after Allred and Rochow, ionization of species when they replace Si in SiO₂ (q_{ion}), with two values for B, replacing O or Si, ionic radius of species (r_{ion}) ionized as given by q_{ion} , with coordination number given in parentheses, and relative deviation of ionic radius of the species Δr_{ion} from that of Si in the same lattice position (except for B at O site, which refers to the O atom).

Element	E_{ion} (eV)			Electronegativity	q_{ion} (e)	r_{ion}^a (q_{ion}) (Å)	Δr_{ion}^b (q_{ion}) (%)
	1st	2nd	3rd				
O	13.36	35.11		3.50	−1.08	0.92 (2)	
Si	8.15	14.53	33.49	1.74	+2.16	0.75 (4)	
B	9.32	25.15		2.01			
B at O site					−0.04	0.85 (2)	−8.2
B at Si site					+1.66	0.45 (3)	−40
Al	5.98	18.83		1.47	+1.93	0.70 (3)	−6.7
Ga	6.00	20.51		1.82	+1.52	0.88 (3)	+17
In	5.79	18.87		1.49	+1.91	0.93 (3)	+24
Sc	6.54	12.80	24.76	1.20	+2.20	0.93 (3)	+24
Y	6.38	12.24	20.52	1.11	+2.28	1.07 (3)	+43
La	5.58	11.06	19.17	1.08	+2.31	1.15 (3)	+53

^aUsing cubic interpolation between ions with integer charge.

^bRelative to replaced species (all Si, except for B at O site.)

FIG. 9. AO configuration scheme of the Sc atom. The fully occupied $4s \uparrow\downarrow$ shell provides effective electrostatic screening of the $3d_1 \uparrow$ and $3d_2 \uparrow$ states, whereby the latter two are strongly involved in forming the acceptor state [see Figs. 7(a) and 8].

$p_2 \uparrow$ -based ($\mathcal{V} = 2, 3, 4, 5$) hybrid AO to form the acceptor state. A neutral main-group-III acceptor would localize the accepted electron onto its $p_2 \uparrow$ state. Because of the rather-strong positive ionization of these acceptors, (see Table II), the $\mathcal{V}p_1 \uparrow$ state will take the major partition of the accepted electron, and the $\mathcal{V}p_2 \uparrow$ state may participate in its localization. The $\mathcal{V}p_1 \uparrow$ state taking up an electron from Si reservoirs such as the Si_{10} NC has not only the least ionization energy E_{ion} of the positively ionized main-group-III elements but is also located at the outermost position from the nucleus. In this spatial arrangement, the $\mathcal{V}p_1 \uparrow$ state will experience the full electrostatic force of first-next-neighbor atoms such as the first-next-neighbor O with a dangling bond due to the trivalent group-III element. The $2p \downarrow$ state presenting the dangling bond of the first-next-neighbor O atom readily hybridizes with the $\mathcal{V}p_1 \uparrow$ and $\mathcal{V}p_2 \uparrow$ states of the main-group-III element to form the acceptor state. As a consequence of the negative ionization of the O atom, the acceptor state will be delocalized, whereby it is shifted toward the vacuum level E_{vac} . This shift increases with less-positive ionization of the main-group-III element, by which the $\mathcal{V}p_2 \uparrow$ state becomes more dominant and the impact of the $\mathcal{V}p_1 \uparrow$ state decreases. Accordingly, the value of E_{ion} of the acceptor state decreases, with its dominance being shifted from the $\mathcal{V}p_1 \uparrow$ state to the $\mathcal{V}p_2 \uparrow$ state. This E_{ion} shift causes B, as the most-anionic main-group-III element to fail as a modulation acceptor even if it were to exist only at Si lattice sites.

Modulation acceptors in SiO_2 belonging to group-III transition metals (Sc, Y, La) have a key feature in their hybrid AO arrangement that we discuss below for Sc.

Sc has a fully occupied $4s$ shell ($4s \uparrow\downarrow$), with the $3d$ states being located within this shell. The $3d_1 \uparrow$ state dominates in bond formation over the remaining two $4s \uparrow\downarrow$ valence states due to its lower value of E_{ion} . A neutral Sc

atom would localize the accepted electron onto its $3d_2 \uparrow$ state. Since Sc undergoes substantial positive ionization in SiO_2 (see Table II), the $3d_1 \uparrow$ state will take the major partition of the accepted electron, and the $3d_2 \uparrow$ state may participate in its localization. The first-next-neighbor O to the Sc atom has a dangling bond that forms the acceptor state with its $2p \downarrow$ state and the $3d_1 \uparrow$ ($3d_2 \uparrow$) state of Sc. The difference from the main-group-III elements exists in the electrostatic screening of dangling bond of the first-next-neighbor O by the fully occupied $4s \uparrow\downarrow$ electron shell of the Sc atom, which—although having a higher E_{ion} value—surrounds the $3d_1 \uparrow$ and $3d_2 \uparrow$ states, thereby increasing the localization of the acceptor state onto the Sc atom. This stronger localization translates into a higher value of E_{ion} for the acceptor state (see Table I). As a consequence, this acceptor state occurs at an unusually high E_{ion} value, presenting the maximum value of E_{relax} for electrons originating from bulk Si to the modulation acceptor state in SiO_2 . Other factors such as the ionic radius r_{ion} of the doping species as compared with r_{ion} of the substituted Si atom have an influence on E_{ion} for the acceptor state; we discuss this in Sec. VII.

VI. OTHER ACCEPTOR CANDIDATES IN SILICON DIOXIDE

With the results obtained so far, we calculate other acceptor candidates for SiO_2 modulation doping to provide holes to Si NCs and bulk Si. We use the same DFT methods and the approximant as in Figs. 5(a), 7(a) and 7(b), whereby we investigate the main-group-III elements gallium (Ga) and indium (In), and the group-III transition metals yttrium (Y) and lanthanum (La) as candidates for Si in SiO_2 . Thallium (Tl) and actinium (Ac) are not considered since they are scarce, toxic, and—in the case of Ac—radioactive.

From Fig. 10 and Table I we see that Ga performs about as well as Al as a modulation acceptor. In analogy to Al [12,39], the diffusion coefficient for Ga in SiO_2 is minute (less than $6.0 \times 10^{-18} \text{ cm}^2/\text{s}$ at $T = 1000^\circ\text{C}$ [39]), by which we can rule out any Ga diffusion from the ML into SiO_2 .

The deposition of Ga_2O_3 on Si wafers with an ultrathin O-deficient SiO_2 layer leads to acceptor states inducing a fixed negative charge similarly to Ga modulation acceptors in SiO_2 [40]. The cause of this behavior is very different though. Since the wafers in Ref. [40] did not appear to have been cleaned in NH_4F -buffered hydrofluoric acid, they likely have residual and possibly-O-deficient SiO_2 on Si [41] such as about 4 Å SiO_2 on polished Si(001) wafer surfaces following a chemical cleaning sequence of RCA1, RCA2, and a hydrofluoric acid dip in an unbuffered 1-mol% hydrofluoric acid solution [42]. During the initial atomic-layer-deposition cycles of Ga_2O_3 growth, highly reactive species of O (O_3 , atomic O) pulsed onto the

FIG. 10. Electronic DOS of approximants featuring a Si₁₀ NC embedded in three-ML SiO₂ where a Si atom two MLs away from the NC is replaced with the chemical species listed. The top panel shows the DOS of the undoped approximant and its fully oxidized version as references. In every panel, short thick lines in dark cyan (orange) show the HOMO (LUMO) position of a 19-Å Si NC fully terminated with OH groups [Si₁₆₅(OH)₁₀₀ [27]] as and energy gauge. The dotted bright-green line is aligned to the Al acceptor level and serves as another energy gauge based on measured SiO₂:Al data [12].

substrate further promote SiO₂ growth. During postdeposition annealing, additional O may diffuse to the unrelaxed and possibly-O-deficient SiO₂ [43]. Both processes likely result in an ultrathin layer of O-deficient Ga₂O₃ with O vacancies. This phenomenon is well known from F-deficient AlF₃- and O-deficient Al₂O₃ phases. Substantial fixed negative charge densities were also obtained by F vacancies in thin AlF₃ on Si(001) wafers [44], which drop dramatically for oxide thicknesses below approximately 10 Å [42]. Similar observations were made for Al₂O₃ directly deposited onto Si after its cleaning by the standard RCA1-RCA2 process [45] plus a hydrofluoric acid dip [46] as mentioned above [41].

The occurrence of O (F) vacancies in Al₂O₃ (AlF₃) adjacent to SiO₂ results in acceptor states that are ionized with extrinsic electrons from the adjacent Si wafer [47]. They occur over a layer depth of approximately 5 nm

[42,44] and naturally are less flexible as a single electronic state in tailoring their densities and energetic location as compared with acceptor modulation doping of SiO₂ (see Fig. 10 and Table I). More importantly, the layer compounds of these thin O-deficient (F-deficient) Al₂O₃ (AlF₃) bulk phases and the thin SiO₂ layers have a total thickness of approximately 7 nm and are thus too thick to be used as well-defined tunneling contacts such as 3 nm-thick SiO₂ doped with one ML of Al. Such SiO₂:Al layers are an excellent solution for hole-selective contacts in Si-based solar cells and for *p*-type background modulation doping of VLSI Si devices [12].

Acceptor candidates Y, In, and in particular La do not introduce an acceptor level deep enough below the vacuum level to work reliably as a modulation acceptor for Si. However, Y and In could be useful for defined hole tunneling contacts as used in tunnel FETs [48–50] or for hole-selective contacts in analogy to Al-doped SiO₂ [12].

VII. ATOMISTIC CONCEPT OF MODULATION ACCEPTORS IN SILICON DIOXIDE

With the DFT results of the preceding sections and experimental evidence for B above and for Al [12], we now establish a qualitative concept for the suitability of modulation-acceptor candidates in SiO₂. Table II shows the relevant properties of acceptors at a Si substitutional site in SiO₂, with data for B at an O site added due to experimental and DFT findings (see Sec. IV C).

The evaluation of acceptor-state energies in covalent materials such as Si normally proceeds via the electron affinity X of the respective element. The positive ionization of Si atoms and their substitutional-modulation acceptors in SiO₂ by the first-next-neighbor O atoms to $q_{\text{ion}} > +1$ shifts the energetics from X to E_{ion} instead; we take this into account when evaluating the highest occupied AO for Sc as an acceptor state in Sec. V. Hence, we use E_{ion} values to examine the ability of modulation acceptors to localize an extrinsic electron from Si (see Table II). This examination is done with the sum of E_{ion} values over valence electrons and their partitions as per the q_{ion} value of the acceptor. As an example, we get $\sum E_{\text{ion}}(\text{Si})(q_{\text{ion}}[\text{Si}]) = 1 \times 8.15 + 1 \times 14.54 + 0.16 \times 33.49 = 29.85$ eV for Si, which has $q_{\text{ion}}(\text{Si}) = +2.16$. These sums are then compared against the value for Si to qualitatively evaluate on a relative basis where a nonbonding AO of the modulation acceptor could show up within the band gap of SiO₂. The DFT data of acceptor energy levels (Table I) help us to reflect on $\sum E_{\text{ion}}(q_{\text{ion}})$ values of a specific acceptor.

Another aspect that has a significant influence on the energetic position of the modulation-acceptor level is the atomic radius of the dopant species in its ionized state $r_{\text{ion}}(q_{\text{ion}})$ replacing ionized Si in SiO₂. A deviation of the

atomic radius from the Si value results in considerable local stress, which can delocalize the acceptor state. As a consequence, the acceptor state shifts its energy toward E_{vac} and approaches the valence-band edge in Si at the Si/SiO₂ interface, $E_V^{\text{Si}}(\text{Si/SiO}_2)$. The shrinking energy difference $E_V^{\text{Si}}(\text{Si/SiO}_2) - E_{\text{LUMO}}^{\text{acc}}$ reduces the maximum distance for electron relaxation from Si to the acceptor in SiO₂ since $F_{\text{relax}}(\text{SiO}_2) \approx 1.7 \times 10^6$ V/cm must be fulfilled (see the beginning of Sec. III).

Comparing $r_{\text{ion}}(q_{\text{ion}})$ and $\sum E_{\text{ion}}(q_{\text{ion}})$ between dopant species and Si helps us to understand what features are important to introduce a modulation acceptor in SiO₂. A small deviation in the ionic radius of the acceptor considered from that of Si— Δr_{ion} (see Table II)—appears to keep delocalization of the acceptor state due to local stress to a minimum. This minimum delocalization results in an acceptor level with a higher binding energy; Al and Ga are good examples. If Δr_{ion} is large, the opposite effect occurs as can be seen for B, In, Y, and in particular La. The $5s \uparrow \downarrow 4d_1 \uparrow 4d_2 \uparrow (6s \uparrow \downarrow 5d_1 \uparrow 5d_2 \uparrow)$ AO configuration of Y (La) still shifts the energy level of the acceptor state to higher binding energies (see Sec. V). The same effect is even more apparent when we compare In and Sc, which have both $\Delta r_{\text{ion}} = +24\%$ and similar cumulative ionization energies of $\sum E_{\text{ion}}(\text{Sc})(q_{\text{ion}}[\text{Sc}]) = 22.96$ eV and $\sum E_{\text{ion}}(\text{In})(q_{\text{ion}}[\text{In}]) = 24.29$ eV. Hence, Sc should have an acceptor level slightly below that of In, which is corroborated by DFT results (see Table I). From Table II it appears that the influence of $\sum E_{\text{ion}}(q_{\text{ion}})$ is rather small as evident when we compare its rather broadly spread values with the shift of the acceptor levels (see Table I). The three first-next-neighbor O atoms bonded to the acceptor and the first-next-neighbor O atoms with a dangling bond facing the acceptor appear to minimize the effect of $\sum E_{\text{ion}}(q_{\text{ion}})$ on the acceptor level. This is impressively demonstrated for La, where the increase of its ionic radius relative to the ionic radius of Si of $\Delta r_{\text{ion}} = 53\%$ is the main drive in delocalizing its acceptor state, leading to an unusually low value of E_{ion} .

Given the small deviation in DFT of approximately 0.3 eV from experimental values [12], dopant candidates with an elevated acceptor level in SiO₂, such as Y or In, may not be able to accept an electron from a Si reservoir. However, the proximity of the acceptor level to the bulk-Si valence-band edge may result in these dopants surpassing Al or Ga as hole-selective contacts in Si-based solar cells or tunneling FETs because the tunneling barrier for holes is presented by $E_V^{\text{Si}}(\text{Si/SiO}_2) - E_{\text{LUMO}}^{\text{acc}}$ (see Table I).

The results obtained for B in SiO₂ show that chemical elements working as acceptors for bulk Si cannot be simply considered to work as modulation acceptors in SiO₂ for Si reservoirs. The same statement refers to the group-III transition metals Sc, Y, and La, which would not work as thermal dopants in bulk Si but form silicides in analogy to Ti, Zr, and Hf.

VIII. CONCLUSIONS

As an alternative to conventional impurity doping of Si, we investigate candidates for *direct* SiO₂ acceptor modulation doping to provide holes to an adjacent Si reservoir (bulk, NC, nanowire, or nanowell). Direct modulation doping differs from conventional modulation doping and impurity doping in two aspects. Electrons relax from the Si valence-band edge directly into the acceptor states within SiO₂. This relaxation process proceeds readily though SiO₂ barriers without thermal activation. Thereby, holes can be delivered to Si at very low temperatures, which cannot be accomplished by conventional impurity doping in the nondegenerate regime. Moreover, direct modulation doping does not suffer from density variabilities as degenerate impurity doping does in VLSI. This advantage of direct modulation doping comes at the cost of *proximity* between the dopant and the Si reservoir. We found very recently that electron relaxation into Al-induced acceptor states in SiO₂ proceeds readily through 3-nm-thick SiO₂. This thickness covers the range of SiO₂ layers commonly used in CMOS technology as well as hole-selective tunneling contacts for solar cells or tunnel FETs. Since the diffusion coefficients of most acceptor candidates in SiO₂ at $T = 1000^\circ\text{C}$ are minute, out-diffusion of modulation acceptors is not an issue even for 1.5-nm-thick SiO₂ on Si [12].

The detailed evaluation of acceptor candidates shows that Al [12], Sc, and Ga can deliver holes to a Si reservoir from SiO₂. The highest relaxation energy of valence-band electrons from a Si reservoir into SiO₂ acceptor states is accomplished with Sc, owing to its specific AO configuration and its ionic radius being reasonably close to the that of Si in SiO₂. The same AO configuration in higher periods of the periodic table maintains the possibility of Y and La working as SiO₂ modulation acceptors with reduced relaxation energy despite their ionic radius at a Si site substantially exceeding the ionic radius of In at that site and in particular the ionic radius Si itself.

Because of its rather-anionic features, B exists as a donor at an O site 0.29 eV below the Si conduction-band edge and as acceptor at a Si site 0.32 eV below the Si conduction-band edge. Failing as a direct modulation acceptor, B in SiO₂ is very instructive to evaluate the atomistic properties of acceptor candidates and helps to establish their qualitative concept in SiO₂. As a good example, B shows that acceptors for bulk Si cannot simply be transferred to modulation acceptors in SiO₂. The same statement refers to the group-III transition metals Sc, Y, and La.

Our findings offer a much-needed alternative to conventional doping of Si reservoirs in VLSI, where further device miniaturization is prevented by dopant out-diffusion, extending device shrinkage potentially down to the Si-crystallization limit of approximately 1.5 nm

[13,14]. Removing dopants from VLSI Si devices leads to the suppression of inelastic scattering processes, whereby such devices can operate at lower voltages and lower heat loss. Along the same lines, further increase in conversion efficiencies of Si-based solar cells is increasingly difficult due to mature technology and concepts. Here, a hole-selective tunneling contact based on SiO₂ doped with modulation acceptors is a qualitatively new feature which bears great promise to boost efficiencies yet further with little technological effort and low process energy demand.

ACKNOWLEDGMENTS

D.K. thanks J. Rudd for computer-cluster administration and acknowledges use of the Abacus computer cluster, Integrated Materials Design Centre, University of New South Wales, and funding by a 2015 University of New South Wales blue sky research grant and by the 2018 Theodore von Kármán Fellowship of RWTH Aachen University, Germany. D.K. and D.H. acknowledge funding by 2012, 2014, and 2016 DAAD-Go8 joint-research-cooperation schemes. D.H. acknowledges the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship and the German Research Foundation (DFG) for funding (Grant No. HI 1779/3-1) and thanks the IMTEK clean-room team (RSC) for technical support.

- [1] G. L. Pearson and J. Bardeen, Electrical properties of pure silicon and silicon alloys containing boron and phosphorus, *Phys. Rev.* **17**, 865 (1949).
- [2] S. Koelling, O. Richard, H. Bender, M. Uematsu, A. Schulze, G. Zschaetzsch, M. Gilbert, and W. Vandervorst, Direct imaging of 3D atomic-scale dopant-defect clustering processes in ion-implanted silicon, *Nano Lett.* **13**, 2458 (2013).
- [3] A. K. Kambham, A. Kumar, A. Florakis, and W. Vandervorst, Three-dimensional doping and diffusion in nano scaled devices as studied by atom probe tomography, *Nanotechnology* **24**, 275705 (2013).
- [4] J. Heitmann, F. Müller, M. Zacharias, and U. Gösele, Silicon nanocrystals: Size matters, *Adv. Mater.* **17**, 795 (2005).
- [5] Gustavo M. Dalpian and James R. Chelikowsky, Self-Purification in Semiconductor Nanocrystals, *Phys. Rev. Lett.* **96**, 226802 (2006).
- [6] A. R. Stegner, R. N. Pereira, R. Lechner, K. Klein, H. Wiggers, M. Stutzmann, and M. S. Brandt, Doping efficiency in freestanding silicon nanocrystals from the gas phase: Phosphorus incorporation and defect-induced compensation, *Phys. Rev. B* **80**, 165326 (2009).
- [7] T.-L. Chan, Murilo L. Tiago, Efthimios Kaxiras, and James R. Chelikowsky, Size limits on doping phosphorus into silicon nanocrystals, *Nano Lett.* **8**, 596 (2008).
- [8] D. König, S. Gutsch, H. Gnaser, M. Wahl, M. Kopnarski, J. Göttlicher, R. Steininger, M. Zacharias, and D. Hiller, Location and electronic nature of phosphorus in the Si nanocrystal–SiO₂ system, *Sci. Rep.* **5**, 09702 (2015).
- [9] R. N. Pereira, A. J. Almeida, A. R. Stegner, M. S. Brandt, and H. Wiggers, Exchange-Coupled Donor Dimers in Nanocrystal Quantum Dots, *Phys. Rev. Lett.* **108**, 126806 (2012).
- [10] R. Dingle, H. L. Störmer, A. C. Gossard, and W. Wiegmann, Electron mobilities in modulation-doped semiconductor heterojunction superlattices, *Appl. Phys. Lett.* **33**, 665 (1978).
- [11] D. König and J. Rudd, Formation of Si or Ge nanodots in Si₃N₄ with in-situ donor modulation doping of adjacent barrier material, *AIP Adv.* **3**, 012109 (2013).
- [12] D. König, D. Hiller, S. Gutsch, M. Zacharias, and S. Smith, Modulation doping of silicon using aluminium-induced acceptor states in silicon dioxide, *Sci. Rep.* **7**, 46703 (2017).
- [13] S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y. H. Xie, F. M. Ross, T. D. Harris, W. L. Brown, Y. J. Chabal, L. E. Brus, and P. H. Citrin, Dimensions of Luminescent Oxidized and Porous Silicon Structures, *Phys. Rev. Lett.* **72**, 2648 (1994).
- [14] D. König, Number series of atoms, interatomic bonds and interface bonds defining zinc-blende nanocrystals as function of size, shape and surface orientation: Analytic tools to interpret solid state spectroscopy data, *AIP Adv.* **6**, 085306 (2016).
- [15] M. J. Frisch, et al. Gaussian09, revision D.01, Gaussian Inc., Wallingford, CT (2010).
- [16] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, Self-consistent molecular orbital methods. 22. Small split-valence basis sets for second-row elements, *J. Am. Chem. Soc.* **104**, 2797 (1982).
- [17] F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [18] D. Andrae, U. Häusermann, M. Dolg, H. Stoll, and H. Preus, Energy-adjusted ab-initio pseudopotentials for the second and third row transition elements, *Theor. Chim. Acta* **77**, 123 (1990).
- [19] M. Dolg, H. Stoll, A. Savin, and H. Preus, Energy-adjusted pseudopotentials for the rare earth elements, *Theor. Chim. Acta* **75**, 173 (1989).
- [20] M. Dolg, H. Stoll, and H. Preus, Energyadjusted pseudopotentials for the rare earth elements, *J. Chem. Phys.* **90**, 1730 (1989).
- [21] B. Metz, H. Stoll, and M. Dolg, Small-core multiconfiguration-Dirac-Hartree-Fock-adjusted pseudopotentials for post-d main group elements: Application to PbH and PbO, *J. Chem. Phys.* **113**, 2563 (2000).
- [22] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, Basis set exchange: A community database for computational sciences, *J. Chem. Inf. Model.* **47**, 1045 (2007).
- [23] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, *Phys. Rev. A* **38**, 3098 (1988).
- [24] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **37**, 785 (1988).

- [25] M. M. Francel, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, and M. S. Gordon, Self-consistent molecular orbital methods. 23. A polarization-type basis set for 2nd-row elements, *J. Chem. Phys.* **77**, 3654 (1982).
- [26] D. König, J. Rudd, M. A. Green, and G. Conibeer, Role of the interface for the electronic structure of silicon quantum dots, *Phys. Rev. B* **78**, 035339 (2008).
- [27] D. König, D. Hiller, S. Gutsch, and M. Zacharias, Energy offset between silicon quantum structures: Interface impact of embedding dielectrics as doping alternative, *Adv. Mater. Interfaces* **1**, 1400359 (2014).
- [28] supplemental information to D. König, D. Hiller, N. Wilck, B. Berghoff, M. Müller, S. Thakur, G. DiSanto, L. Petaccia, J. Mayer, S. Smith, and J. Knoch, Intrinsic ultrasmall nanoscale silicon turns n-/p-type with SiO₂/Si₃N₄-coating, *Beilstein J. Nanotech.* **9**, 2255 (2018).
- [29] R. Dennington, T. Keith, and J. Millam, GaussView 5.0.8 (2009).
- [30] E. H. Nicollian and J. R. Brews, *MOS (Metal Oxide Semiconductor) Physics and Technology* (Wiley, New York, 1982).
- [31] J. Laube, S. Gutsch, D. Hiller, M. Bruns, C. Kübel, C. Weiss, and M. Zacharias, Formation of size controlled silicon nanocrystals in nitrogen free silicon dioxide matrix prepared by plasma enhanced chemical vapor deposition, *J. Appl. Phys.* **116**, 223501 (2014).
- [32] D. Hiller, J. López-Vidrier, S. Gutsch, M. Zacharias, M. Wahl, W. Bock, A. Brodyanski, M. Kopnarski, K. Nomoto, J. Valenta, and Dirk König, Boron-incorporating silicon nanocrystals embedded in SiO₂: Absence of free carriers vs. B-induced defects, *Sci. Rep.* **7**, 8337 (2017).
- [33] D. Mathiot, A. Straboni, E. Andre, and P. Debenest, Boron diffusion through thin gate oxides: Influence of nitridation and effect on the Si/SiO₂ interface electrical characteristics, *J. Appl. Phys.* **73**, 8215 (1993).
- [34] D. Hiller, J. Göttlicher, R. Steininger, T. Huthwelker, J. Julin, F. Munnik, M. Wahl, W. Bock, B. Schoenaers, A. Stesmans, and D. König, Structural properties of Al-O monolayer stacks in SiO₂ and the maximization of their negative fixed charge density on Si, *ACS Appl. Mat. Interfaces* **10**, 30495 (2018).
- [35] K. W. Böer, *Survey of semiconductor physics* (Van Nostrand Reinhold, New York, 1990), Vol. 1.
- [36] A. F. Holleman, E. Wiberg, and N. Wiberg, *Lehrbuch der anorganischen Chemie* (Walter de Gruyter, Berlin, 1995), 101 Ed. in German
- [37] M. E. Greiner and J. F. Gibbons, Diffusion of silicon in gallium arsenide using rapid thermal processing: Experiment and model, *Appl. Phys. Lett.* **44**, 750 (1984).
- [38] D. König, J. Rudd, S. Shrestha, G. Conibeer, and M. A. Green, in *Proceedings 24th European Photovoltaic Solar Energy Conference (PVSEC)* (WIP Munich, Germany, 2009) presentation 1CV.4.53; <http://www.eupvsec-proceedings.com/proceedings?paper=4050>.
- [39] H. G. Francois-Saint-Cyr, F. A. Stevie, J. M. McKinley, K. Elshot, L. Chow, and K. A. Richardson, Diffusion of 18 elements implanted into thermally grown SiO₂, *J. Appl. Phys.* **94**, 7433 (2003).
- [40] T. G. Allen and A. Cuevas, Electronic passivation of silicon surfaces by thin films of atomic layer deposited gallium oxide, *Appl. Phys. Lett.* **105**, 031601 (2014).
- [41] H. Angermann, W. Henrion, M. Rebien, and A. Rösele, Wet-chemical preparation and spectroscopic characterization of Si interfaces, *Appl. Surf. Sci.* **235**, 322 (2004).
- [42] D. König, Isolatorschichtenanordnungen mit negativen Festladungen und ihre Anwendung an Silicium-Solarzellen (Insulator Layers with Fixed Negative Charges and Their Application to Silicon Solar Cells), https://www.researchgate.net/profile/D_Koenig2/publication/312796601_Insulator_Layers_With_Fixed_Negative_Charge_and_Their_Application_to_Silicon_Solar_Cells (2004), PhD thesis, pp. 34–35 (in German).
- [43] T. G. Allen and A. Cuevas, Plasma enhanced atomic layer deposition of gallium oxide on crystalline silicon: Demonstration of surface passivation and negative interfacial charge, *Phys. Stat. Sol. RRL* **9**, 220 (2015).
- [44] D. König, R. Scholz, and D. R. T. Zahn, Band diagram of the al₃/SiO₂/Si system, *J. Appl. Phys.* **97**, 093707 (2005).
- [45] F. Werner, B. Veith, D. Zielke, L. Kühnemund, C. Tegenkamp, M. Seibt, R. Brendel, and J. Schmidt, Electronic and chemical properties of the C-Si/Al₂O₃ interface, *J. Appl. Phys.* **109**, 113701 (2011).
- [46] B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. vandeSanden, and W. M. M. Kessels, Ultralow surface recombination of C-Si substrates passivated by plasma-assisted atomic layer deposited Al₂O₃, *Appl. Phys. Lett.* **89**, 042112 (2006).
- [47] D. König, M. Rennau, and M. Henker, Direct tunneling effective mass of electrons determined by intrinsic charge-up process, *Sol. Stat. Electron.* **51**, 650 (2007).
- [48] M. T. Björk, J. Knoch, H. Schmid, H. Riel, and W. Riess, Silicon nanowire tunneling field-effect transistors, *Appl. Phys. Lett.* **92**, 193504 (2008).
- [49] J. Appenzeller, Y.-M. Lin, J. Knoch, and P. Avouris, Band-to-Band Tunneling in Carbon Nanotube Field-Effect Transistors, *Phys. Rev. Lett.* **93**, 196805 (2004).
- [50] J. Knoch and J. Appenzeller, Modeling of high-performance p-type III-V heterojunction tunnel fets, *IEEE Electron Device Lett.* **31**, 305 (2010).