Intrinsic ultrasmall nanoscale silicon turns n-/p-type with SiO₂/Si₃N₄-coating

Dirk König*¹,², Daniel Hiller²,³, Noël Wilck⁴, Birger Berghoff⁴, Merlin Müller⁵, Sangeeta Thakur⁶, Giovanni Di Santo⁶, Luca Petaccia⁶, Joachim Mayer⁵, Sean Smith¹,⁷ and Joachim Knoch⁴

Abstract

Impurity doping of ultrasmall nanoscale (usn) silicon (Si) currently used in ultralarge scale integration (ULSI) 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). Moreover, self-purification and massively increased ionization energy cause doping to fail for Si nano-crystals (NCs) showing quantum confinement. To introduce electron- (n-) or hole- (p-) type conductivity, usn-Si may not require doping, but an energy shift of electronic states with respect to the vacuum energy between different regions of usn-Si. We show in theory and experiment that usn-Si can experience a considerable energy offset of electronic states by embedding it in silicon dioxide (SiO₂) or silicon nitride (Si₃N₄), whereby a few monolayers (MLs) of SiO₂ or Si₃N₄ are enough to achieve these offsets. Our findings present an alternative to conventional impurity doping for ULSI, provide new opportunities for ultralow power electronics and open a whole new vista on the introduction of p- and n-type conductivity into usn-Si.
Introduction

Impurity doping of silicon (Si) has been a key technique and prerequisite for Si-based electronics for decades [1]. Miniaturization in Si ultralarge scale integration (ULSI) became increasingly difficult as device features approached the characteristic lengths of dopant out-diffusion, clustering and inactivation [2]. The considerable broadening of dopant profiles from drain/source regions into gate areas persists [3]. Moreover, required ULSI 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 – i.e., doping of materials adjacent to semiconductors which then provide free carriers to the unperturbed semiconductor – was first used for group III–V semiconductor combinations such as GaAs/AlAs in the late 1970s [10]. Recently, Si modulation doping of adjacent dielectric layers based on nitrides [11] and oxides [12], in analogy to modulation doping of III–V semiconductors, were shown to be an alternative to conventional impurity doping.

It would be ideal to achieve electron- (n-) or hole- (p-) type conductivity in usn-Si without doping, thereby avoiding all dopant-related issues mentioned above. Such conductivity can be induced by an energy offset (ΔE) of the same electronic states (lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO)) between different regions of the same usn-Si system [13,14]. This concept eliminates doping altogether, leading to a lower inelastic carrier scattering rate and higher carrier mobility which allow for decreased heat loss and bias voltages in ULSI. Such properties enable Si-FET technology to work at even smaller structure sizes, potentially enabling Moore’s law to reach the Si-crystallization limit of ca. 1.5 nm [15].

In our present work, we prove by hybrid-density functional theory (h-DFT) simulations and synchrotron-based long-term ultraviolet photoelectron spectroscopy (UPS) that usn-Si indeed can have a massive ΔE of their electronic density of states (DOS) when embedded in SiO₂ or Si₃N₄. We use further h-DFT results of a Si-nanowire (NW) covered in SiO₂ and Si₃N₄ to examine the device behaviour of an undoped Si-NW FET based solely on CMOS-compatible materials (e.g., Si, SiO₂, Si₃N₄) using the nonequilibrium Green’s function (NEGF) approach.

Following an explanation of the theoretical and experimental methods used, we turn to results for Si-NCs obtained from h-DFT. Here, we focus on the electronic structure of Si-NCs as a function of the embedding dielectric and its thickness of up to 3 monolayers (MLs). The latter dependence requires the use of NCs to keep the h-DFT computation effort practicable; NWires with more than 1 ML dielectric embedding are beyond the feasible computation effort at the level of accuracy we use. As an ultimate theoretical test, we present h-DFT results of two Si-NCs, one embedded in SiO₂ and the other embedded in Si₃N₄, presenting the entire system under investigation within one approximant. An interface charge transfer (ICT) of electrons from the usn-Si volume to the anions of the embedding dielectric – nitrogen (N) or oxygen (O) – is at the core of the energy shift [14]. We explain the shift of usn-Si electronic states towards the vacuum level $E_{\text{Vac}}$ when embedded in Si₃N₄ and further below $E_{\text{Vac}}$ when embedded in SiO₂ by the quantum chemistry of N and O with respect to Si. The next section contains experimental results, namely the thickness determination of embedded Si nanowells (NWells) by transmission electron microscopy (TEM) and the measurement of the highest occupied DOS over energy for Si-NWells samples embedded in SiO₂ or Si₃N₄ by synchrotron-based long-term UPS. With this experimental confirmation of our h-DFT results, we present the concept of undoped Si-NW field-effect transistors (FETs). We show further h-DFT results of a Si-NW of 5.2 nm length and 1.4 nm diameter, terminated to 50% with 1 ML of Si₃N₄ (NH₂ groups) and to 50% with 1 ML of SiO₂ (OH groups). These h-DFT results deliver key input data to NEGF device simulations as a proof-of-concept for the undoped Si-NW FET. A wealth of information on h-DFT accuracy as compared to experiment, details of UPS measurements and NEGF are contained in Supporting Information File 1.

Experimental h-DFT material calculations

Hybrid-DFT calculations were carried out in real space with a molecular orbital basis set (MO-BS) and both Hartree–Fock (HF) and h-DFT methods as described below, employing the Gaussian03 and Gaussian09 program packages [16,17]. Initially, the MO-BS wavefunction ensemble was tested and optimized for stability with respect to describing the energy minimum of the approximant (variational principle; stable = opt) with the HF method using a Gaussian-type 3-21G MO-BS [18] (HF/3-21G). This MO wavefunction ensemble was then used for the structural optimisation of the approximant to arrive at its most stable configuration (maximum integral over all bond energies), again following the HF/3-21G route. Using these optimized geometries, their electronic structure was calculated again by testing and optimizing the MO-BS wavefunction ensemble with the B3LYP hybrid DF [19,20] and the Gaussian-type 6-31G(d) MO-BS which contains d-polarization functions (B3LYP/6-31G(d)) [21] to describe the strong polar nature.
of atomic bonds of Si to O and N. The root mean square (RMS) and peak force convergence limits for all atoms were $3 \times 10^{-4}$ Ha/au (Hartrees per Bohr radius) or 80 meV/Åm and $4.5 \times 10^{-4}$ Ha/au or 120 meV/Åm, respectively. Tight convergence criteria were applied to the self-consistent field routine. Ultrafine integration grids were used throughout. During all calculations, no symmetry constraints were applied to MOs. An extensive accuracy evaluation can be found in the Supporting Information File 1 of this article and elsewhere [13,14,22]. The approximants and MOs were visualized with GaussView 5 [23]. The electronic DOS were calculated from MO eigenenergies, applying a Gaussian broadening of 0.2 eV.

Sample preparation
Samples comprising a Si$_3$N$_4$-embedded NW ell were fabricated by plasma-enhanced vapour deposition (PECVD) using SiH$_4$+NH$_3$+N$_2$ for Si$_3$N$_4$ and SiH$_4$+Ar for amorphous Si [24]. As substrates, n-type Si wafers (Sb doping, 5 to $15 \times 10^{15}$ cm$^{-2}$) of (111) surface orientation underwent wet-chemical cleaning. After deposition the wafers were annealed in a quartz tube furnace for 1 min at 1100 °C in pure N$_2$ ambient to induce Si crystallization. Subsequently, the samples were H$_2$-passivated at 450 °C for 1 h. A 4.5 nm thick Si$_3$N$_4$ spacer layer served to suppress excited electrons from the Si wafer to interfere with electrons from the Si-NWell during UPS.

Samples comprising a SiO$_2$-embedded NW ell were processed by etching the top c-Si layer of an Si-on-insulator (SOI) wafer with 200 nm buried SiO$_2$ (BOX) down to ca. 3 nm. The subsequent oxidation resulted in a 1.7 nm Si-NWell and 1.5 nm SiO$_2$ capping.

Si reference samples were processed by etching a 5 to $15 \times 10^{-3}$ Ω cm Sb-doped n-type (111)-Si wafer in buffered hydrofluoric acid, and the sample was immediately mounted under a N$_2$-shower then swiftly loaded into the ultrahigh vacuum (UHV) annealing chamber.

All NW ell samples were contacted via a lateral metal contact frame on the front surface which was processed by photolithographical structuring, wet-chemical mesa etching and thermal evaporation of Al. The reference Si-wafer was contacted directly on its front surface.

Characterization
UPS measurements were carried out at the BaDElPh beamline [25] at the Elettra Synchrotron in Trieste, Italy, in top-up mode (310 mA electron ring current). All samples were subject to a UHV anneal for 90 min at 500 K to desorb water and air-related species from the sample surface prior to the measurements. Single scans of spectra were recorded over 12 h per NW ell sample and subsequently added up for eliminating white noise. Scans for the Si-reference sample were recorded over 2 h and subsequently added up. All NW ell samples were excited with a photon energy of 8.9 eV and a photon flux of $2 \times 10^{12}$ s$^{-1}$. The incident angle of the UV beam onto the sample was 50° with respect to the sample surface normal, and excited electrons were collected with an electron analyzer along the normal vector of the sample surface. The energy calibration of the UPS was realized using a tantalum (Ta) stripe in electrical contact to the sample as a work function reference. Further UPS-data of SiO$_2$ and Si$_3$N$_4$ reference samples as well as UPS signal normalization are available in Supporting Information File 1.

All samples for TEM investigation were capped with a protective SiO$_2$-layer to facilitate the preparation of cross sections by the focused ion beam technique using a FEI Strata FIB 205 workstation. Some samples were further thinned by means of a Fischione NanoMill. The TEM analysis of the cross sections was performed on a FEI Tecnai F20 TEM operated at 200 kV at the Central Facility for Electron Microscopy, RWTH Aachen University, and on the spherical aberration corrected FEI Titan 80-300 TEM operated at 300 kV at Ernst Ruska-Centre, Forschungszentrum Jülich [26].

In addition, the Si-NWell thickness was measured by ellipsometry. The thickness of the Si-NWells in Si$_3$N$_4$ (in SiO$_2$) were measured using a Woollam M-2000 ellipsometer (ACCURION nanofilm ep4se ellipsometer). All thickness measurements confirmed the values obtained from TEM.

NEGF device simulations
A homemade NEGF simulation program was used for simulating nanoscale device characteristics based on h-DFT results of Si-NW ies. The simulations are based on a self-consistent solution of the Poisson and Schrödinger equations on a finite difference grid. A one-dimensional, modified Poisson equation is considered here that provides an adequate description of the electrostatics of wrap-gate nanowire transistors [27]. Buettiker probes, i.e., virtual contacts, are attached to each finite difference site in order to mimic inelastic scattering [28]. To this end, an additional self-consistent calculation of the quasi-Fermi level throughout the device is computed, ensuring that the net current flow into/out of each Buettiker probe is zero. The electrostatics within the gate underlap region has been taken into consideration with a conformal mapping technique that maps the underlap region to a parallel-plate capacitor and allows the extraction of a space-dependent effective oxide thickness that is used in this region. The “doping” due to the presence of the SiO$_2$ coating is taken into consideration as a volume, active dopant concentration (see Supporting Information File 1); the presence of the Si$_3$N$_4$ layer underneath the gate is accounted for
Results and Discussion

h-DFT calculations of embedded Si nanocrystals, fundamentals of energy offset

For evaluating the energy shift $\Delta E$ of the electronic DOS between usn-Si covered with SiO$_2$ or Si$_3$N$_4$, we calculated two Si-NCs ($Si_{10}$, 0.8 nm size) within one approximant; one NC is embedded in SiO$_2$ and one NC resides in Si$_3$N$_4$ (Figure 1). We found earlier that – regarding DFT – $Si_{10}$-NCs are the smallest NCs above the atomic limit below which Si-clusters behave as small molecules in the gas phase [13]. The frontier-OMOs exist within the Si$_3$N$_4$-embedded Si-NC (Figure 1, inset iii), while the frontier-UMO exists within the SiO$_2$-embedded Si-NC (Figure 1, inset ii), with $\Delta E$ of the occupied frontier MOs of 0.5 eV and of 1 eV for the unoccupied frontier MOs between both NCs. These $\Delta E$ values are smaller when compared to individual embedded NCs (see Figure 2c and Supporting Information File 1) due to the inter-NC distance of merely 1 nm, accounting for some ICT convergence from Si NCs to SiO$_2$ or Si$_3$N$_4$. From Figure 2c we see that an ICT saturation is evident for $\geq$ 2 ML SiO$_2$. This saturation is less apparent when Si$_3$N$_4$ is applied as the embedding matrix. We explain this behaviour together with the $\Delta E$ by the quantum-chemical properties of Si, N and O.

Both anions, N and O, dominate electronic bonds to Si by delocalizing a substantial partition of Si valence electrons to form strong polar bonds [13], giving rise to ICT from usn-Si into the respective dielectric (SiO$_2$, Si$_3$N$_4$) [14]. A high ionicity of bond (IOB) and strong negative electron affinity ($X$) of O result in a strong localization of Si-NC valence electrons. This localization corresponds to increased binding energies – the ICT shifts all MOs away from $E_{vac}$ toward $E_{vac}$ (left scale) and total Si$_{10}$-NC ionization (right scale) with increasing thickness of embedding dielectric. For SiO$_2$-embedding, the ICT and the associated shift in HOMO and LUMO energies away from $E_{vac}$ saturate quickly. For Si$_3$N$_4$-embedding, the HOMO energy shifts towards $E_{vac}$. The LUMO energy shift varies around a constant value as shown by a linear fit to LUMO energies (cyan line) as a function of Si thickness. The positive NC ionization remains nearly unchanged. These features are due to the positive electron affinity $X$ and the anionic nature of N, resulting in electron delocalization from the NC (ionization) without strong electron localization at N as is the case for O.

Figure 1: Energy offsets with SiO$_2$- and Si$_3$N$_4$-embedding for one $Si_{10}$-NC (0.8 nm size) embedded in SiO$_2$ and the other $Si_{10}$-NC embedded in Si$_3$N$_4$ within one approximant. The main graph shows the electronic DOS: MOs localized in Si$_3$N$_4$ (SiO$_2$) embedded Si-NC are shown in blue (red); the reduced length of the MOs corresponds to partial localization in Si$_3$N$_4$-SiO$_2$, with the remainder of the MO being localized within the dielectric. The chemical potential of the entire approximant $\mu$ is shown as a dashed-dotted line. Graphs (i) to (iv) show iso-density plots (1 $\times$ 10$^{-3}$ states/a$^3$ = 6.76 states/nm$^3$) of frontier MOs marked by (i) to (iv) in the DOS plot. $Si_{10}$-NCs are shown in cyan, Si in SiO$_2$ and Si$_3$N$_4$ in grey, O in red, N in blue and H in white.

Figure 2: Evolution of energy offsets for SiO$_2$- and Si$_3$N$_4$-embedded $Si_{10}$-NCs (0.8 nm size) as a function of embedding SiO$_2$- or Si$_3$N$_4$-thickness: (a) $Si_{10}$-NC embedded in 3 ML Si$_3$N$_4$ after structural optimization. (b) $Si_{10}$-NC embedded in 3 ML SiO$_2$ after structural optimization. For atoms colors see Figure 1. (c) Evolution of HOMO and LUMO energies relative to vacuum energy $E_{vac}$ (left scale) and total Si$_{10}$-NC ionization (right scale) with increasing thickness of embedding dielectric. For SiO$_2$-embedding, the ICT and the associated shift in HOMO and LUMO energies away from $E_{vac}$ saturate quickly. For Si$_3$N$_4$-embedding, the HOMO energy shifts towards $E_{vac}$. The LUMO energy shift varies around a constant value as shown by a linear fit to LUMO energies (cyan line) as a function of $Si_{10}$N$_4$ thickness. The positive NC ionization remains nearly unchanged. These features are due to the positive electron affinity $X$ and the anionic nature of N, resulting in electron delocalization from the NC (ionization) without strong electron localization at N as is the case for O.
and lower IOB to Si. Such delocalized MOs correspond to states with substantially lowered binding energy, yielding to a shift of MOs towards $E_{\text{vac}}$. Accordingly, frontier-MOs of the Si$_3$N$_4$-embedded NC (Figure 1, insets i and iii) show stronger delocalization as compared to frontier-MOs of the SiO$_2$-embedded Si-NC (Figure 1, inset ii and iv).

Table 1 summarizes the specific properties of Si, O and N relevant to the nature of ICT. The larger bond length of Si–N as compared to Si–O arguably contributes to electron delocalization, while the lower packing fraction of SiO$_2$ is irrelevant in this respect due to strong electron localization at O. Both anions possess about the same ionization due to their IOB to Si together with N and O being trivalent and divalent, respectively. This finding is supported by the virtually identical NC ionization energy of fully NH$_2$- vs OH-terminated Si-NCs (see Supporting Information File 1).

As will be shown experimentally in the next section, the resulting $\Delta E$ of the frontier-MOs induces an n-type (p-type) behaviour in usn-Si by SiO$_2$-embedding (Si$_3$N$_4$-embedding). For the ICT, and thus the intensity of p- or n-type behaviour, the ratio of interface bonds to atoms forming the Si-NWell, -NWire or -NC is an important parameter [31]. It describes the amount of entities (Si atoms) to be ionized over a certain amount of transfer paths (interface bonds) and depends on the interface facet orientation of the usn-Si volume as well as on its surface-to-volume ratio.

**Sample characterization: TEM and synchrotron-based long-term UPS**

We experimentally verified our theoretical findings by characterizing samples comprising 1.7 nm and 2.6 nm thick Si-NWells embedded in SiO$_2$ or Si$_3$N$_4$ together with a Si reference sample (Figure 3a–d) using synchrotron UPS.

Figure 4a–c shows high-resolution cross-section TEM images of each NWell sample. Such ultrathin Si layers require long signal acquisition times in UPS due to the short mean free path of valence electrons excited above $E_{\text{vac}}$[32] in compound with the small Si-volume probed. This is in particular true for

![Figure 3](https://example.com/figure3.png)

**Figure 3:** Structures of samples investigated by synchrotron UPS: (a) Si-reference, (b) 1.7 nm Si-NWell in Si$_3$N$_4$, (c) 1.7 nm Si-NWell in SiO$_2$, (d) 2.6 nm Si-NWell in Si$_3$N$_4$. Sample codes are shown on top of each structure.

![Figure 4](https://example.com/figure4.png)

**Figure 4:** Cross-section HR-TEM images of samples QW-17-N (a), QW-17-O (b) and QW-26-N (c). Semi-transparent strips show layer thicknesses of Si$_3$N$_4$ (cyan), Si-NWells (magenta) and SiO$_2$ (orange).
Figure 5: Experimental evidence of HOMO $\Delta E$ by synchrotron UPS: (a) scans of NWELL samples and a hydrogen-terminated (111) Si wafer as a reference for the Si-NWells. The valence band edges of Si-NWells detected are located within the magenta lines and shown in (b). The bottom energy scales refer to electron kinetic energy up to UV photon energy. The top energy scale shows the energetic position of electrons relative to vacuum level with valence band edges and respective energy values as extracted from the spectra (dashed lines). The light green and cyan lines show the background fit of the amorphous Si$_3$N$_4$-matrix. The lower signal-to-noise ratio for Si-NWells embedded in Si$_3$N$_4$ as compared to SiO$_2$ is comprehensively evaluated and discussed in Supporting Information File 1.

Figure 6: Electronic properties obtained by h-DFT for Si$_{233}$(NH$_2$)$_{87}$(OH)$_{81}$NWire of 1.4 nm diameter and 5.2 nm length, terminated with NH$_2$ on its left half emulating Si$_3$N$_4$-embedding and with OH on its right half emulating SiO$_2$-embedding: (a) DOS over energy relative to vacuum level $E_{\text{vac}}$. Red (blue) lines show HOMO–LUMO gap of OH-terminated (NH$_2$-terminated) NWire section. Global HOMO–LUMO gap shown in grey together with Fermi energy $E_F$ for entire NWire. Magenta DOS sections are enlarged to show MO locations for (b) frontier-OMOs and (c) frontier-UMOs along with $\Delta E$ for exclusive and dominant MO location in the respective NWire section. (d–g) Si$_{233}$(NH$_2$)$_{87}$(OH)$_{81}$ approximant after structural optimization; for atom colours see Figure 1. The approximant is shown with the sum of frontier-MO densities $\rho_{\text{MO}} = \sum (|\Psi_{\text{MO}}|^2)$ as iso-density plots for: (d) frontier-OMOs exclusively located in the NH$_2$-terminated NWire section ($\rho_{\text{MO}} = 1 \times 10^{-3}$ states/$a_0^3 = 6.76$ states/nm$^3$), (e) frontier-OMOs dominantly located in the NH$_2$-terminated NWire section ($\rho_{\text{MO}} = 3 \times 10^{-3}$ states/$a_0^3 = 20.3$ states/nm$^3$). A slight distortion of atomic positions occurs at the OH-terminated end due to electrostatic forces, leading to a minor location of MOs otherwise exclusively residing in the NH$_2$-terminated NWire section. This effect does not occur at NWire devices where SiO$_2$ coverage is followed by a contact layer, see Figure 7. (f) Frontier-UMOs exclusively located in the OH-terminated NWire section ($\rho_{\text{MO}} = 2 \times 10^{-3}$ states/$a_0^3 = 13.5$ states/nm$^3$), and (g) frontier-UMOs dominantly located in the OH-terminated NWire section ($\rho_{\text{MO}} = 3 \times 10^{-3}$ states/$a_0^3 = 20.3$ states/nm$^3$). Values for $\rho_{\text{MO}}$ are scaled to provide $\rho_{\text{MO}} = 1 \times 10^{-4}$ states/$a_0^3 = 0.675$ states/nm$^3$ per MO.
Si-NWells embedded in Si$_3$N$_4$ as discussed in Supporting Information File 1.

UPS spectra are shown in Figure 5. The reference sample (Si-ref) yielded a valence band edge at the ionization energy $E_{\text{ion}} = E_{\text{vac}} - 5.17$ eV as known for bulk Si [33]. We obtained $E_{\text{ion}} = E_{\text{vac}} - 6.01$ eV for the 1.7 nm Si-NWell in SiO$_2$ and $E_{\text{ion}} = E_{\text{vac}} - 5.20$ eV ($E_{\text{vac}} - 5.11$ eV) for the 1.7 (2.6) nm Si-NWell in Si$_3$N$_4$. The difference in ionization energy $\Delta E_{\text{ion}}$ between 1.7 nm Si-NWells in SiO$_2$ and Si$_3$N$_4$ is 0.81 eV which clearly confirms our h-DFT calculations. For the 2.6 nm NWell embedded in Si$_3$N$_4$ we obtain a $E_{\text{ion}}$ of 0.06 eV below the value of bulk Si (Figure 5b). The ICT may thus overcompensate quantum confinement and induce a negative $\Delta E_{\text{ion}}$ to bulk Si.

The ICT impact length on Si-NWells can be related to Si-NWires and Si-NCs to scale 1/2/3 for NWells/NWires/NCs [14]. This relation explains why larger $\Delta E$ values for HOMOs and LUMOs are obtained for Si-NWires (Figure 6) as compared to Si-NWells (Figure 5b).

**Concept of undoped Si nanowire FETs**

With the $\Delta E$ values of the usn-Si coated with SiO$_2$ vs Si$_3$N$_4$ confirmed by synchrotron UPS, we now turn to its application to undoped ULSI Si devices.

NWires are a cornerstone of future ULSI technology development due to their excellent controllability by wrap-around gate architecture [34,35]. However, the ultrasmall NWire diameter required to guarantee the electrostatic integrity of the devices causes conventional doping to fail. Metal–Si contacts formed by, e.g., silicide formation [36] result in rather high Schottky barriers at the source/drain-channel interfaces that deteriorate the switching behaviour and on-state performance.

**h-DFT calculations of Si nanowires relevant to devices**

As we will show below, a Si-NWire with a combined SiO$_2$/Si$_3$N$_4$-coating can work as a highly scalable, high-performance and dopant-free metal-insulator-silicon (MIS) FET device. Using the same h-DFT methods as above, we computed the electronic properties of a Si$_{233}$(NH$_2$)$_{87}$(OH)$_{81}$ approximant manifesting a Si-NWire with 1.4 nm diameter and 5.2 nm length, whereby the two halves of this NWire are terminated with NH$_2$ and OH groups, respectively. These functional groups correspond to 1 ML of the respective dielectric – NH$_2$ groups to 1 ML Si$_3$N$_4$ and OH groups to 1 ML SiO$_2$ (Figure 6).

Figure 6a shows the DOS around the HOMO–LUMO gap. We determined the location of the densities of all frontier-MOs, $n_{\text{MO}} = (\Psi_{\text{MO}}^\dagger \Psi_{\text{MO}})$, within 2 eV from HOMO and LUMO. Frontier-OMOs are located within the NH$_2$-terminated NWire section with a $\Delta E$ to corresponding MOs in the OH-terminated NWire section of $\approx 1.1$ eV. Frontier-UMOs exist in the OH-terminated NWire section, whereby $\Delta E$ from the OH- to NH$_2$-terminated NWire section is $\approx 1.2$ eV. Again, the increased values of $\Delta E$ of respective frontier-MOs as compared to UPS results of Si-NWells confirm geometric effects [14].

**Undoped Si-NWire FETs**

The electronic structure of the Si$_{233}$(NH$_2$)$_{87}$(OH)$_{81}$ NWire allows $\Delta E$ values to be established for NWire electronic devices with a combined SiO$_2$/Si$_3$N$_4$-coating such as an undoped self-blocking p-channel FET (Figure 7).

![Concept of an undoped FET consisting of a Si-NWire with drain/gate (channel)/source regions covered by ultrathin Si$_3$N$_4$/SiO$_2$/Si$_3$N$_4$: (a) physical layout shown for self-blocking n-channel FET. Schematic band diagram of such an FET shown for (b) zero and (c) negative gate bias relative to source voltage, resulting in a conductive channel by shifting the electronic Si-NWire states pinned by SiO$_2$. Interchanging Si$_3$N$_4$ and SiO$_2$ layers yields self-blocking n-channel FETs and thereby CMOS-compatibility. This concept is applicable to other Si nanostructures with a high surface-to-volume ratio like fin-FETs.](image-url)

Using the $\Delta E$ value obtained from the Si$_{233}$(NH$_2$)$_{87}$(OH)$_{81}$ NWire approximant and above-described UPS results,
we derive hole ($p$) and electron ($n$) densities. We obtain $p = 5 \times 10^{19}$ cm$^{-3}$ ($n \approx 0$ cm$^{-3}$) for the Si$_3$N$_4$-coated NWire-regions (drain/source) and $p = 71$ cm$^{-3}$ ($n \approx 0$ cm$^{-3}$) for the SiO$_2$-coated NWire-regions (see Supporting Information File 1). These values will be used in the next section where results on NEGF device simulations are presented.

**NEGF device simulations**

NEGF simulations were realized considering a 1.7 nm thick undoped Si-NWire MISFET with a channel length of $L = 5$ nm in a wrap-gate architecture placed between two metallic contacts (Figure 8a). The channel is insulated by a SiO$_2$ layer, yielding an effective oxide thickness of 2 nm. The source/drain and the gate electrode are insulated from each other by an underlap region of length $l_{con}$ where the NWire is covered with a 2 nm thick Si$_3$N$_4$ (device I) or SiO$_2$ (device II) layer, resulting in dopant concentration equivalents as mentioned above. Ni source/drain contacts are considered to yield effective Schottky-barriers of $-0.05$ eV for hole-injection into the Si-NWire valence band.

Figure 8c shows drain-current versus gate-voltage characteristics of device I and II for an underlap of $l_{con} = 5$ nm. The SiO$_2$ gate insulator yields a built-in potential that results in self-blocking FETs at $V_{GS} = 0$ V. Clearly, device I shows a substantially higher on-state performance, becoming even more obvious with increasing underlap region $l_{con}$. The inset of Figure 8c displays the drive current at $V_{GS} = -1.5$ V, showing that device I exhibits very small current degradation with increasing $l_{con}$ due to effective “doping” (Si$_3$N$_4$-coating) within the underlap region. In contrast, device II strongly depends on $l_{con}$ with substantial drive current degradation if $l_{con}$ increases. Device II only delivers an acceptable performance for $l_{con} < 5$ nm which ensues a very large parasitic capacitance and presents a challenge to ULSI processing. Moreover, any variation in $l_{con}$ translates into a strong variability of drive current. This massive deterioration of device II is caused by the lack of “doping”, yielding a substantial increase in potential barriers (cf. Figure 8b) in particular at the gate-channel/gate-underlap interface and at the Ni-contact–Si interfaces, both depending on $l_{con}$ (see Supporting Information File 1). Without the energy shift caused by Si$_3$N$_4$-coatings in source/drain, we obtain substantially higher Schottky-barriers for device II, resulting in severely deteriorated device performance. Our simulations underline the great importance of alternatives to conventional doping for increased performance of future ULSI transistors.

![Figure 8](image-url)
Conclusion
We demonstrated quantitatively in theory and experiment that the intrinsic electronic properties of usn-Si can yield p- (n-) type behaviour by shifting the electronic DOS towards (away from) $E_{\text{vac}}$ using ultrathin Si$_3$N$_4$- (SiO$_2$-) coatings. The key parameters for this phenomenon are the electron affinities $X$ of N and O together with their IOB and bond length to Si. Using NEGF device simulations we compared two undoped Si-NWire-FETs with SiO$_2$- or Si$_3$N$_4$-coating in the source/drain regions and SiO$_2$-coated gate area. We demonstrated that devices with Si$_3$N$_4$-coating exhibit substantially better on-state performance and strongly reduced dependence on the length of the source/drain regions, showing that high performance small-scale MISFETs can be realized using undoped ultrathin Si-NWires with a combined SiO$_2$-/Si$_3$N$_4$-coating. Our findings open a whole new vista on Si-based ULSI operating at lower voltages.

Supporting Information
Supporting Information features the comparison of h-DFT results to experimental data, further information on the interface impact on Si nanocrystal electronic structure and its connection to quantum-chemical nature of N and O, details of UPS scans with further reference data, the derivation of charge carrier densities for nonequilibrium Green’s function (NEGF) transport simulation of undoped Si-nanowire MISFET devices and details on NEGF device simulations.

Supporting Information File 1
Further discussion and data of h-DFT, UPS, and NEGF simulations.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-9-210-S1.pdf]

Acknowledgements
D. K. acknowledges use of Leonard mainframe, engineering faculty, use of Abacus mainframe, IMDC, UNSW and funding by the 2018 Theodore-von-Kârmán Fellowship of RWTH Aachen University, Germany and by the 2015 UNSW Blue Sky Research Grant. D. K. and D. H. acknowledge funding by 2012, 2014 and 2016 DAAD-Go8 joint research cooperation schemes. D.H. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship, acknowledges the German Research Foundation (DFG) for funding (HI 1779/3-1) and acknowledges the IMTEK clean room team (RSC) and L. Sancin at Eletra Synchrotron for technical support. N. W., B. B. and J. K. acknowledge support by the Impulse and Networking Fund of the Helmholtz Association.

ORCID® iDs
Dirk Königs - https://orcid.org/0000-0001-7845-9142
Daniel Hiller - https://orcid.org/0000-0001-8774-4069
Birger Berghoff - https://orcid.org/0000-0003-5657-8121
Sangeeta Thakur - https://orcid.org/0000-0003-9394-2563
Lucia Petaccia - https://orcid.org/0000-0001-8696-1468

References
1. Pearson, G. L.; Bardeen, J. Phys. Rev. 1949, 75, 865–883. doi:10.1103/physrev.75.865
2. Koelling, S.; Richard, O.; Bender, H.; Uematsu, M.; Schulze, A.; Zschaetzsch, G.; Gilbert, M.; Vandervorst, W. Nano Lett. 2013, 13, 2458–2462. doi:10.1021/nl400447d
3. Kambham, A. K.; Kumar, A.; Florakis, A.; Vandervorst, W. Nanotechnology 2013, 24, 275705. doi:10.1088/0957-4484/24/27/275705
4. Heitmann, J.; Müller, F.; Zacharias, M.; Gösele, U. Adv. Mater. 2005, 17, 795–803. doi:10.1002/adma.200401126
5. Dalpian, G. M.; Chelikowsky, J. R. Phys. Rev. Lett. 2006, 96, 226802. doi:10.1103/physrevlett.96.226802
6. Stegner, A. R.; Pereira, R. N.; Lechner, R.; Klein, K.; Wiggers, H.; Stutzmann, M.; Brandt, M. S. Phys. Rev. B 2009, 80, 165326. doi:10.1103/physrevb.80.165326
7. Chan, T.-L.; Tiago, M. L.; Kaxiras, E.; Chelikowsky, J. R. Nano Lett. 2008, 8, 596–600. doi:10.1021/nl072997a
8. König, D.; Gutsch, S.; Gnasar, H.; Wahl, M.; Kopnarski, M.; Göttlicher, J.; Steininger, R.; Zacharias, M.; Hiller, D. Sci. Rep. 2015, 5, 9702. doi:10.1038/srep09702
9. Pereira, R. N.; Almeida, A. J.; Stegner, A. R.; Brandt, M. S.; Wiggers, H. Phys. Rev. Lett. 2012, 106, 126806. doi:10.1103/PhysRevLett.106.126806
10. Dingle, R.; Störmer, H. L.; Gossard, A. C.; Wiegmann, W. Appl. Phys. Lett. 1978, 33, 665–667. doi:10.1063/1.90457
11. König, D.; Rudd, J. AIP Adv. 2013, 3, 012109. doi:10.1063/1.4789397
12. König, D.; Hiller, D.; Gutsch, S.; Zacharias, M.; Smith, S. Sci. Rep. 2017, 7, 46703. doi:10.1038/srep46703
13. König, D.; Rudd, J.; Green, M. A.; Conibeer, G. Phys. Rev. B 2008, 78, 035339. doi:10.1103/PhysRevB.78.035339
14. König, D.; Hiller, D.; Gutsch, S.; Zacharias, M. Adv. Mater. Interfaces 2014, 1, 1400359. doi:10.1002/admi.201400359
15. Schuppler, S.; Friedman, S. L.; Marcus, M. A.; Adler, D. L.; Xie, Y.-H.; Ross, F. M.; Harris, T. D.; Brown, W. L.; Chabal, Y. J.; Brus, L. E.; Citrin, P. H. Phys. Rev. Lett. 1994, 72, 2648–2651. doi:10.1103/physrevlett.72.2648
16. Gaussian 03, Revision D.02; Gaussian, Inc.: Wallingford, CT, U.S.A., 2004.
17. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, U.S.A., 2012.
18. Gordon, M. S.; Binkley, J. S.; Pope, J. A.; Pietro, W. J.; Hehre, W. J. Am. Chem. Soc. 1982, 104, 2797–2803. doi:10.1021/ja00374a017
19. Becke, A. D. Phys. Rev. A 1988, 38, 3098–3100. doi:10.1103/physreva.38.3098
20. Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. A 1988, 37, 785–789. doi:10.1103/PhysRevA.37.785
21. Franch, M. M.; Pietro, W. J.; Hreh, W. J.; Binkley, J. S.; Gordon, M. S.; DeFreese, D. J.; Pope, J. A. J. Chem. Phys. 1982, 77, 3654–3665. doi:10.1063/1.444267
22. Hiller, D.; López-Vidrier, J.; Gutsch, S.; Zacharias, M.; Wahl, M.; Bock, W.; Brodyanski, A.; Kopnarsi, M.; Nomoto, K.; Valenta, J.; König, D. Sci. Rep. 2017, 7, 8337. doi:10.1038/s41598-017-08814-0
23. GaussView, 5.0.8; Semichem Inc.: Shawnee Mission, KS, U.S.A., 2009.
24. Hiller, D.; Zelenina, A.; Gutsch, S.; Dyakov, S. A.; López-Conesa, L.; López-Vidrier, J.; Estradé, S.; Peró, F.; Garrido, B.; Valenta, J.; Kofrinek, M.; Trojánek, F.; Malý, P.; Schnabel, M.; Weiss, C.; Janz, S.; Zacharias, M. J. Appl. Phys. 2014, 115, 204301. doi:10.1063/1.4878699
25. Petaccia, L.; Vilmercati, P.; Gorovikov, S.; Barnaba, M.; Bianco, A.; Cocco, D.; Masciovecchio, C.; Goldoni, A. Nucl. Instrum. Methods Phys. Res., Sect. A 2009, 606, 780–784. doi:10.1016/j.nima.2009.05.001
26. Thust, A.; Barthal, J.; Tillmann, K. J. Large-Scale Res. Facil. 2016, 2, A41. doi:10.17815/jlsrf-2-66
27. Auth, C. P.; Plummer, J. D. IEEE Electron Device Lett. 1997, 18, 74–76. doi:10.1109/55.553049
28. Venugopal, R.; Paulsson, M.; Goasguen, S.; Datta, S.; Lundstrom, M. S. J. Appl. Phys. 2003, 93, 5613–5625. doi:10.1063/1.1563298
29. Holleman, A. F.; Wiberg, E.; Wiberg, N. Lehrbuch der Anorganischen Chemie, 101st ed.; Walter deGruyter: Berlin, Germany, 1995.
30. The NIST Reference on Constants, Units and Uncertainties – Fundamental Physical Constants (2014 edition). https://physics.nist.gov/cgi-bin/cuu/Value?asil (accessed Aug 16, 2018).
31. König, D. AIP Adv. 2016, 6, 085306. doi:10.1063/1.4960994
32. Offi, F.; Iacobucci, S.; Vilmercati, P.; Rizzo, A.; Goldoni, A.; Sacchi, M.; Panaccione, G. Phys. Rev. B 2008, 77, 201101. doi:10.1103/PhysRevB.77.201101
33. Böer, K. W. Survey of Semiconductor Physics; Van Nostrand Reinhold: New York, NY, U.S.A., 1992; Vol. 2. doi:10.1007/978-94-011-2912-1
34. Suk, S. D.; Lee, S.-Y.; Kim, S.-M.; Yoon, E.-J.; Kim, M.-S.; Li, M.; Oh, C. W.; Yeo, K. H.; Kim, S. H.; Shin, D.-S.; Lee, K.-H.; Park, H. S.; Han, J. N.; Park, C. J.; Park, J.-B.; Kim, D.-W.; Park, D.; Ryu, B.-I. High performance 5nm radius Twin Silicon Nanowire MOSFET (TSNWFET) fabrication on bulk silicon wafer, characteristics, and reliability. In IEEE International Electron Devices Meeting 2005, 2005; pp 717-720.
35. Bangsaruntip, S.; Majumdar. A.; Cohen, G. M.; Engelman, S. U.; Zhang, Y.; Guillemot, M.; Gignac, L. M.; Mittal, S.; Graham, W. S.; Joseph, E. A.; Klaus, D. P.; Chang, J.; Cartier, E. A.; Sleight, J. W. Gate-all-around silicon nanowire 25-stage CMOS ring oscillators with diameter down to 3 nm. In 2010 Symposium on VLSI Technology, 2010; pp 21–22.
36. Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M. Nature 2004, 430, 61–65. doi:10.1038/nature02674