Origin and Quantitative Description of the NESSIAS Effect at Si Nanostructures

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The electronic structure of SiO₂ versus Si₃N₄-coated low nanoscale intrinsic silicon (Si) shifts away from versus toward the vacuum level $E_{\text{vac}}$, originating from the Nanoscale Electronic Structure Shift Induced by Anions at Surfaces (NESSIAS). Using the quantum chemical properties of the elements involved to explain NESSIAS, an analytic parameter $\Delta$ is derived to predict the highest occupied energy level of Si nanocrystals (NCs) as verified by various hybrid-density functional calculations and NC sizes. First experimental data of Si nanowells (NWells) embedded in SiO₂ versus Si₃N₄ were measured by X-ray absorption spectroscopy in total fluorescence yield mode (XAS-TFY), complemented by ultraviolet photoelectron spectroscopy (UPS), characterizing their conduction band and valence band edge energies $E_C$ and $E_V$, respectively. Scanning the valence band sub-structure over NWell thickness yields an accurate estimate of $E_V$ shifted purely by spatial confinement, and thus the actual $E_V$ shift due to NESSIAS. Offsets of $\Delta E_C = 0.56$ eV and $\Delta E_V = 0.89$ eV were obtained for 1.9 nm thick NWells in SiO₂ versus Si₃N₄, demonstrating an intrinsic Si type II homojunction. This $p/n$ junction generated by NESSIAS eliminates any deteriorating impact of impurity dopants, offering undoped ultrasmall Si electronic devices with much reduced physical gate lengths and CMOS-compatible materials.

1. Introduction

Si NWells with a thickness of $d_{\text{well}} \leq \text{ca. 3.3 nm}$ embedded in silicon dioxide (SiO₂) versus silicon nitride (Si₃N₄) show an electronic structure shift with respect to the vacuum energy level $E_{\text{vac}}$ as measured by UPS and XAS-TFY.[1–3] NWells embedded in SiO₂ (Si₃N₄) get shifted to higher (lower) binding energies, that is, away from (towards to) $E_{\text{vac}}$. This NESSIAS effect is caused by quantum chemical properties of the anions forming the dielectric which surrounds the low nanoscale Si. While the NESSIAS effect has been established in theory and experiment, its exact origin and quantitative description are still elusive. Here, we deliver a detailed quantum chemical explanation of the NESSIAS effect, complemented with its semi-quantitative description which serves to predict NESSIAS in low nanoscale intrinsic Si for a variety of anions in embedding/coating dielectrics. To this end, we provide
experimental evidence and details of the quantum-chemical concept which leads to the NESSIAS effect.

The NESSIAS effect induces a p/n junction on semiconductor nanostructures such as fins, nanowires (NWires), or NCs by enabling an electron flooding of the nanostructure when coated with SiO$_2$\cite{1} or a virtually complete electron drainage from the nanostructure when coated with Si$_3$N$_4$\cite{2,12} introducing a high density of holes into the nanovolume by the latter process. This re-arrangement of charge carrier densities has far-reaching consequences for semiconductor devices in very large scale integration (VLSI), ultra-low power and cryo-electronics. Spatial fluctuations of dopant densities, out-diffusion and self-purification impose a size limit onto VLSI devices as evident from physical gate lengths hovering around 20 nm since ca. 2014\cite{14}. With thermal dopant ionization not required, junctions induced by the NESSIAS effect should remain fully functional down to extremely low temperatures as useful for peripheral electronics in qubit manipulation\cite{5}.

The detection of the NESSIAS in low nanoscale intrinsic Si requires an absolute assignment of energies to $E_{\text{vac}}$, combined with elaborate UPS and XAS-TFY measurements and refined data processing for improved signal-to-noise ratios\cite{1-3}. To this end, the structures under investigation have to be in the range of the NESSIAS impact length. Many published Density Functional Theory (DFT) calculations\cite{6-9} lack an energy assignment on an absolute scale. Possibly identical low nanoscale intrinsic Si NWell systems near the low end of the one-digit nm range embedded in different dielectrics pose a challenge in experiment. The common perception of Si$_3$N$_4$ as an inferior dielectric on grounds of interface defect density\cite{10} and its more complex technology as opposed to SiO$_2$\cite{11} are likely reasons for the literature on low nanoscale Si embedded in or coated with Si$_3$N$_4$ being rather scarce. Indeed, standard Si$_3$N$_4$ has an interface defect density to low nanoscale Si which exceeds values of SiO$_2$/Si interfaces ca. 13-fold\cite{10,12,13} though refined preparation techniques for high-quality H-passivated Si$_3$N$_4$-coatings rival trap densities on SiO$_2$/Si interfaces\cite{14}. This complex situation may explain why the NESSIAS might have been overlooked in the past.

We deliver a phenomenological and qualitative explanation of the NESSIAS effect in Section 2.1, resorting to quantum chemical properties of involved chemical elements. In Section 2.2, we derive an analytic parameter $\Lambda$ of the NESSIAS effect to describe the energy of the highest occupied molecular orbital (HOMO) $E_{\text{HOMO}}$ as a function of anion-specific quantum chemical properties combined with the charge of these main anions $q_{\text{main}}$ of the ligand groups attached to Si NCs. In Section 2.3, we test $\Lambda$ with a variety of density functionals (DFs) and most anionic elements of the first and second row of the periodic table with respect to Si, subject to the availability of experimental quantum chemical data. Our discussion is complemented with synchrotron data in Section 2.4. Since the electronic structure of NWells shifts as a function of quantum confinement, it is essential to separate this phenomenon induced by a spatial limit from the NESSIAS brought about by the quantum-chemical nature of embedding dielectric versus Si. To this end, we evaluate our results from synchrotron UPS measurements in Section 2.4.2, revealing substructures of the valence band which serve to estimate the actual quantum confinement. This true quantum confinement is revealed by the shift of the valence band (VB) edge to higher binding energies as a sole function of NWell thickness, occurring in all samples irrespective of the embedding dielectric. We use this VB edge as a reference level to estimate the actual NESSIAS as per embedding dielectric in the quantum confinement regime. Next, we evaluate our experimental data of the VB and conduction band edges as measured by synchrotron XAS-TFY in Section 2.4.3, establishing the link between bulk Si and SiO$_2$ versus Si$_3$N$_4$ as given by ultrathin Si NWells coated with the respective dielectric. Section 3 delivers a conclusion.

### 2. Results and Discussion

#### 2.1. Qualitative Explanation of the NESSIAS Effect

When a common boundary between two different solids with a bandgap is formed, an interface charge transfer occurs\cite{15} generating an interface electronic structure, which may shift the electron work function of both materials with respect to the intrinsic solid-vacuum interface\cite{15,16}. The solid which accumulates extrinsic electrons experiences an electronic structure shift to lower binding energies $E_{\text{bind}}$, hence to $E_{\text{vac}}$, the other solid which provides the electronic charge experiences an electronic structure shift in the opposite direction. When low nanoscale intrinsic Si is coated with one atomic monolayer (1ML) SiO$_2$ or Si$_3$N$_4$, the interface charge transfer provides about the same amount of electrons to O and N as main interface anions\cite{2} see to Supporting Information. We would thus expect a nearly identical shift of the low nanoscale intrinsic Si electronic structure in accord with interface dipole theory.

However, measurements of Si NCs\cite{17} and nanowells (NWells)$^\dagger$ and DFT calculations of Si NCs\cite{2,18,19} and nanowires (NWires)$^\dagger$ show a very different behavior. The Supporting Information lists energies of the lowest unoccupied MO (LUMO) $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ of Si NCs together with the cumulative charge of the interface charge transfer $\sum q_{\text{ICT}}$ transferred from such Si NCs into the dielectric. These data show that $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ of Si NCs coated with SiO$_2$ (Si$_3$N$_4$) experience a shift to higher (lower) $E_{\text{bind}}$. The apparent contradiction to interface dipole theory can be resolved when looking at the quantum chemical properties of the chemical elements involved. Such elements are Si as the cation providing electrons, and in particular N or O as the anion receiving such electrons. Relevant properties of the anions are the electronegativity and resulting ionicity of bond to Si, the ionization energy $E_{\text{ion}}$, the electron affinity for the neutral anion $X^0$, and the electron affinity of the anion ionized with one electron $X^-$, see Table 1. We focus on N and O as anions to explain the origin of the NESSIAS effect.

Table 1 shows that N has a much more positive $X^0$ and still more positive $X^-$ than O, while its ionicity of bond to Si is ca. 2/3 of the value O provides. This lower ionicity of bond and an associated lower charge of the interface charge transfer $q_{\text{ICT}}$ is nearly cancelled out by N in Si$_3$N$_4$ having 3/2 interface bonds to Si on average due to its trivalent configuration. Thus, values of the cumulative charge transferred to the main anions $\sum q_{\text{ICT}}$ for NCs of same size embedded into 1 ML SiO$_2$ versus Si$_3$N$_4$ are nearly equal.

Evaluating $\sum q_{\text{ICT}}$, $E_{\text{HOMO}}$, and $E_{\text{LUMO}}$ (Supporting Information) shows that the NESSIAS remains in saturation (i.e., at maximum strength) for NCs embedded in 1 ML SiO$_2$ up to $d_{\text{NC}} = 1.85$
nm (Si₃₅(OH)₁₉₆). The Si₂₈₆(OH)₁₄₄ approximant with \( d_{\text{NC}} = 2.2 \) nm shows the onset of \( E_{\text{HOMO}} \) moving toward \( E_{\text{vac}} \) which indicates the size limit limit of NESSIAS saturation. For the Si₃₅(OH)₁₉₆ approximant with \( d_{\text{NC}} = 2.6 \) nm, the NESSIAS is yet weaker as is evident from another slight shift of \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) toward \( E_{\text{vac}} \). Increasing the embedding from 1 to 1.5 ML SiO₂ marginally increases \( \sum q_{\text{ICT}} \) per NC size and pushes the size regime where the NESSIAS becomes unsaturated beyond \( d_{\text{NC}} = 2.2 \) nm.

Although \( \sum q_{\text{ICT}} \) is lower for Si NCs embedded in 1 ML Si₃N₄ versus embedding in 1 ML SiO₂, no NESSIAS saturation occurs for \( d_{\text{NC}} \leq 2.6 \) nm as evident from \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) not moving away from \( E_{\text{vac}} \) to higher \( E_{\text{bind}} \). When going from 1 to 1.5 ML Si₃N₄-embedding, the NC is surrounded by more N atoms in a thicker Si₃N₄ layer. Counterintuitively, \( \sum q_{\text{ICT}} \) drops notably, and \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) slightly move to lower \( E_{\text{bind}} \) which contradicts the presence of significantly more N atoms.

We thus can state for SiO₂-embedding that the NESSIAS effect looks rather spatially compact and comes out of saturation fairly quickly with increasing system size of low nanoscale intrinsic Si. For Si₃N₄-embedding, the NESSIAS effect appears to be spatially distributed and the electronic shift is rather smooth, extending over a wider size range of low nanoscale intrinsic Si. In order to understand this peculiar electronic structure, we look at a sketch combining spatial atomic orbital distribution and energy levels, see Figure 1.

Arguably, the delocalizing impact of N versus the localizing impact of O on their acquired electronic charge is the key to the NESSIAS effect. We can interpret a decreased \( \sum q_{\text{ICT}} \) for N which decreased further for a thicker Si₃N₄ layer as a partial reflection of \( d_{\text{ICT}} \) back into the intrinsic Si. These observations are confirmed by experimental results of Si₃N₄ versus SiO₂-embedded Si NWells, see Section 2.4.2 and Figure 8. The atomic nature of the NESSIAS implies a short impact length in accord with other near-field effects such as significant electron tunneling.[25] For intrinsic Si, the extension of the NESSIAS is ca. 1.3 to 1.8 nm per plane interface.[1-3]

2.2. Analytic Relation of the NESSIAS Effect with the HOMO Energy

We consider interfaces constituted by single bonds, such as between Si/SiO₂ and Si/Si₃N₄. A detailed derivation of the equations below and the use \( E_{\text{HOMO}}, X^0 \) and \( X^- \) of the interface main anion of the considered ligand group together with the average charge of the main anion \( q_{\text{avg}} \) as boundary values are given in the Supporting Information. Here, we focus on results to express \( E_{\text{HOMO}} \) with its dependence on the nature of interface bonds as a function of the parameter \( \Lambda_{\text{main}} \). The average charge of the main anion constituting the ligands to Si NCs \( q_{\text{avg}} \) is derived from DFT calculations and presents the only non-analytic input to \( \Lambda_{\text{main}} \). We calculate the parameter for a negative charge transfer to the main anion – which is the most likely case –

\[
\Lambda_{\text{main}} = (1 - |q_{\text{avg}}^{\text{main}}|) X^0_{\text{main}} + |q_{\text{avg}}^{\text{main}}|X^-_{\text{main}} \quad \forall q_{\text{avg}}^{\text{main}} \leq 0 \tag{1}
\]

and a positive charge transfer to the main anion of the ligand (or dielectric)

\[
\Lambda_{\text{main}} = (1 - |q_{\text{avg}}^{\text{main}}|) X^0_{\text{main}} - |q_{\text{avg}}^{\text{main}}| E_{\text{main}} \quad \forall q_{\text{avg}}^{\text{main}} \geq 0. \tag{2}
\]

The parameter \( \Lambda_{\text{main}} \) describes the binding energy of the interface bond and is proportional to \( E_{\text{HOMO}} \), or the energy of the valence band maximum \( E_v \) for sufficiently large low nanoscale intrinsic Si systems like NWells evaluated in Section 2.4.2. We can thus use \( \Lambda_{\text{main}} \) to predict the NESSIAS as a function of the embedding dielectric, thereby providing optimum combinations of Si and dielectrics per design to meet the desired functionality of VLSI electronic devices as briefly discussed below.

Figure 2 shows the result of Equations 1 and 2, together with the data points of all ligands used in DFT calculations of Si₃₅ NCs.
The parameter $\Lambda_{\text{main}}^{q}$ shown as a function of transferred charge from intrinsic Si to main anion $q_{\text{main}}$ for all anionic terminations and their possible outer terminations, see Table 1. $\Lambda_{\text{main}}^{q}$ for Si$_{35}$X$_{36}$ ($X =$ ligand) is shown per main anion for $q_{\text{main}} \in [-1; +1]$, with the respective data point per functional group termination derived from $q_{\text{main}}$ (DFT), see Figure 4 for corresponding data on electronic structure and $\Lambda_{\text{main}}^{q}$. The difference in $\Lambda_{\text{main}}^{q}$ as per main anion which describes the respective dielectric provides an estimate for the strength of the VB offset $\Delta E_{p}$ between accordingly coated low nanoscale intrinsic Si sections, and can be used for VLSI device design.

Since Si and other semiconductors have a significant interatomic charge transfer, the NESSIAS effect will not be limited to a few atomic MLs within intrinsic low nanoscale Si, providing the basis for its use in VLSI electronics. Within the dielectric, a charge transfer over more than four Si–X ($X =$ O, N) MLs becomes unnoticeable in particular for SiO$_{2}$ embedding because of the strong polar nature of the bonds and immobility of local charges due to charge localization and a rather wide bandgap of SiO$_{2}$ and Si$_{3}N_{4}$.

2.3. Verification of the Analytic Relation with DFT Simulations

DFT approximants consist of NCs fully terminated with one ligand type. The main anion forms the center of the ligand and the interface bond to the NC. Relevant properties of main anions are listed in Table 1. Figure 3 shows examples of NCs calculated by DFT. In Figure 4, the dependence $E_{\text{HOMO}} \propto \Lambda_{\text{main}}^{q}$ can be clearly seen for Si$_{35}$ NCs with a diameter of $d_{\text{NC}} = 1.1$ nm as a function of their surface termination, where ligands are grouped in accord with their main anion, and specific outer terminations where applicable, arranged for increasing electronegativity from left to right.
CF₃, N₂F, and OF ligands, from Silicon-on-Insulator (SOI) with p-type doping of 1 × 10⁻¹⁶ cm⁻³, rear contact (top, lateral) microtopography and calibrated on selected samples by transmission electron microscopy (TEM), see Figure 5b. All N Wells were processed by a top-down design. For Si NCs fully terminated with BF₂, CF₃, NF₂, and OF ligands, E_HOMO (green and red symbols, respectively, in Figure 4). We extended calculations of Si₃N₅ NCs to other hybrid DFs, the Heyd–Scuseria–Ernzerhof DF with its 2006 parametrization (HSE06),[27] and the B3LYP DF complemented with the Coulomb Attenuation Method (CAM-B3LYP).[28] Detailed results of such calculations are listed in the Supporting Information, further corroborating the accuracy of E_HOMO (green and red symbols, respectively, in Figure 4).

2.4.2. Calibrating the NESSIAS by Measuring the Intrinsic Valence Band Edge with Synchrotron UPS

Figure 6a shows the sample layout used in synchrotron XAS-TFY. The sample layout used for UPS is virtually identical, see Figure 5. The sample layout used in synchrotron XAS-TFY, shown in X-section and top view a). X-section view of 1.7 nm (001)-Si N Well in Si₃N₄ seen along the (110) vector class as obtained by TEM b). Semi-transparent black lines show interfaces to adjacent Si₃N₄ from where the N Well thickness was determined. Right. Recently, H-terminated 1.1 nm size Si NCs were processed by a top-down design.[26] For Si NCs fully terminated with BF₂, CF₃, NF₂, and OF ligands, ΔEVanHove (main) slightly deviates from E_HOMO as discussed in the Supporting Information. All other terminations are described accurately by ΔEVanHove (main) ≈ E_HOMO (green and red symbols, respectively, in Figure 4).

We extended calculations of Si₃N₅ NCs to other hybrid DFs, the Heyd–Scuseria–Ernzerhof DF with its 2006 parametrization (HSE06),[27] and the B3LYP DF complemented with the Coulomb Attenuation Method (CAM-B3LYP).[28] Detailed results of such calculations are listed in the Supporting Information, further corroborating the accuracy of ΔEVanHove (main) in predicting E_HOMO.

2.4.1. Sample Layout

Figure 5a shows the sample layout used in synchrotron XAS-TFY. The sample layout used for UPS is virtually identical, see Figure 2 in Ref. [2]. Layer thicknesses were measured by ellipsometry and calibrated on selected samples by transmission electron microscopy (TEM), see Figure 5b. All N Wells were processed from Silicon-on-Insulator (SOI) with p-type doping of 1 × 10⁻¹⁶ cm⁻³, and an interstitial oxygen (O) concentration of 1 to 2 × 10⁻¹⁵ cm⁻³ equivalent to 2 to 4 ppm O in Si²⁶.³⁰ as required for VLSI processing. As surface roughness, we obtained a standard deviation of σ ≈ ±0.2 nm from the nominal dNWell values as derived from TEM X-section images showing σ ≈ ±1 (001) Si ML, see Figure 5b and to error bars in Figure 8.

2.4.2. Calibrating the NESSIAS by Measuring the Intrinsic Valence Band Edge with Synchrotron UPS

First data of SiO₂- and Si₃N₄-embedded Si NWells were obtained by measuring the VB maximum (leading edge) of bulk Si and embedded Si NWells using scan ensembles of synchrotron UPS²⁻¹ with their statistic data, whereby the VB maximum is located at Γ point; E_V = E₉. We now discuss the fine structure of UPS spectra, revealing a sub-edge which can be assigned to the Van Hove singularity of bulk Si at the L point in the Brillouin zone with its energy Eₗ.[³¹,³²] For NWells with dNWell ≤ 5 nm, the VB subband structure becomes increasingly perturbed by quantum confinement. An assignment of subband Van Hove singularities near E_V becomes a function of dNWell and of specific high symmetry points in the electronic DOS along non-orthogonal k-directions of the NWell plane, in particular X and M, see to Supporting Information. Figure 6 illustrates the change in VB electronic structure with the shrinking size of low nanoscale intrinsic Si using experimentally derived values. We focus on the energy offset between Γ and L point for bulk Si, and between Γ and X, M points for thin NWells, generally expressed by the term ΔE₉VanHove.

Figure 7 shows that ΔE₉VanHove does not depend on the embedding dielectric as should be the case for a pure quantum con-
finement phenomenon with sufficiently high potential walls (i.e., band offsets between respective bulk phases).\textsuperscript{33} cf. Figure 10a. When quantum confinement sets in with decreasing $d_{\text{well}}$, the energy offset between VB-DOS extrema at $\Gamma$ and adjacent Van Hove singularities $\Delta E_{V}^{\text{Van Hove}}$ diminishes as $E_{V}^{\text{bulk Si}}$ is shifted to higher binding energies. Since the adjacent Van Hove singularities already have higher binding energies with respect to the VB maximum, they do not experience a notable energy shift due to quantum confinement even for the minimum energetic distance of $\Delta E_{V}^{\text{Van Hove}} \approx 0.2 \text{ eV}$ for NWells with $d_{\text{well}} = 1.1 \text{ nm}$, see Figure 7. We can, therefore, take $\Delta E_{V}^{\text{Van Hove}}$ as a good estimate for the shift of $E_{V}^{\text{well}}$ to higher binding energies due to quantum confinement only. Interestingly, DFT-GGA calculations of Si NWell superlattices (SLs) with 1.9 nm thick SiO$_2$ barriers\textsuperscript{34} yield very similar values of $\Delta E_{V}^{\text{Van Hove}}(d_{\text{well}})$, cf. Figure 7 and discussion in the Supporting Information. We introduce a VB maximum as a function of NWell thickness,

$$E_{V}^{\text{QC}}(d_{\text{well}}) = E_{V}^{\text{bulk Si}} + \left[ E_{V}^{\text{bulk Si}} - E_{V}^{\text{Van Hove}} \right] - \Delta E_{V}^{\text{Van Hove}} = 5.17 \text{ eV} + 0.455 \text{ eV} - \Delta E_{V}^{\text{Van Hove}}$$

In Figure 7, a quadratic-hyperbolic least residuals fit was used in accord with quantum confinement theory\textsuperscript{33} to estimate the shift of $E_{V}$ as a function of $d_{\text{well}}$.

We present all UPS data together with $E_{V}^{\text{QC}}(d_{\text{well}})$ in Figure 8. The energy offset due to the NESSIAS as per embedding dielectric is clearly visible, saturating for SiO$_2$-embedding for $d_{\text{well}} \leq 2.6 \text{ nm}$, while steadily growing with decreasing $d_{\text{well}}$ for Si$_3$N$_4$-embedding. The VB offset between 1.6 nm thick Si NWells coated with Si$_3$N$_4$ versus SiO$_2$ is $\Delta E_{V} \approx 0.95 \text{ eV}$, facilitating charge carrier separation on a massive scale in analogy to a steep p/n junction induced by impurity doping. Apparently, such experimenta...
occur due to an increased DOS at the energy where $E^\text{C} \left( d_{\text{Well}} \right)$ resides. The situation is very different for Si$_x$N$_y$-embedding, where $|\Delta E_{\text{NESSIAS}}|$ is constantly increasing for a decreasing $d_{\text{Well}}$, getting close to the saturation limit of SiO$_2$-embedding. This behavior is in accord with the quantum-chemical properties of N, see Section 2.1. It is uncertain whether we can proceed to Si$_x$N$_y$-embedded NWells with $d_{\text{Well}} < 1.1$ nm to find a saturation limit in experiment should it exist. What we do know from experiment is that the constant increase of $|\Delta E_{\text{NESSIAS}}|$ with decreasing $d_{\text{Well}}$ results from the electron-attractive, yet delocalizing nature of N which does not suffer from a saturation due to a much bigger volume which can be utilized by N to accommodate extrinsic electrons. As discussed in Section 2.1, this peculiar behavior also results in a part of the interface charge transfer to be reflected back into the NWell as a consequence of the decreased binding energy of extrinsic electrons at N atoms, thereby shifting the electronic structure of the NWell and low nanoscale intrinsic Si in general toward $E_{\text{vac}}$.

We have stated in Section 2.1 that 1 ML SiO$_2$ can keep the NESSIAS saturated for a ratio of low nanoscale intrinsic Si atoms per interface bond of $N_{N_1}/N_{Si} = 196/455 \approx 0.43$ for Si NCs. Figure 8 shows that this saturation is left around $d_{\text{Well}} = 2.6$ nm which corresponds to ca. 19 atomic ML of (001)Si or 38 Si atoms and eight interface bonds per unit cell area, resulting in $N_{N_1}/N_{Si} = 8/38 \approx 0.21$. Assuming an exponential decay in charge transfer through SiO$_2$ when moving away from the interface, we arrive at the estimate of ca. 3 ML or 0.9 nm SiO$_2$, after which the NESSIAS does not increase significantly anymore by increasing the thickness of SiO$_2$. While this is good news for the VLSI technology where ultrathin SiO$_2$ layers are required to chemically passivate sorption Spectroscopy in Total Fluorescence Yield mode (XAS-

2.4.3. A First Glimpse on the Full NESSIAS Picture

We recently started to measure the energy of the conduction band edge $E_C$ of Si NWells embedded in SiO$_2$ by means of X-ray Absorption Spectroscopy in Total Fluorescence Yield mode (XAS-

Figure 10. a) Regions of fundamental band gaps for – left to right – bulk Si$_x$N$_y$,[1,13–37] a 1.9 nm Si-NWell in Si$_x$N$_y$, intrinsic bulk Si,[1,38] a 1.9 nm Si-NWell in SiO$_2$, and bulk SiO$_2$.[1,37–39] Band offsets to dielectrics are shown by labelled red (blue) lines for NWells in SiO$_2$ (Si$_3$N$_4$), and in gray/black for bulk Si. Band edges given contain values of bulk solids from experiment, data for NWells were obtained by UPS and XAS-TFY, see to text, to Supporting Information and to[1–3] with respective supplements. b) Layer system comprising a 1.9 nm thick Si NWell coated with 1.0 nm Si$_x$N$_y$ and SiO$_2$ (top), and its band diagram with energies in units of eV (bottom), derived from experimental data in graph (a).

somewhat asymmetric. A strong shift of $E_C$, $E_V$ to higher binding energies occurs for SiO$_2$. For Si$_x$N$_y$, we see a smaller shift to lower binding energies. Both observations are in accord with our discussion of O and N versus Si in Section 2.1. We thus can track the NESSIAS effect all the way to the bulk phase of the respective dielectric. As a consequence, the entire electronic structure of low nanoscale intrinsic Si such as a sufficiently thin NWell moves toward a more symmetric band offset with the respective dielectric when the NESSIAS effect becomes significant.

From above discussion, the question of a low nanoscale intrinsic Si size limit arises below which it starts to behave like the embedding dielectric to a degree where they depart from the properties of semiconducting Si. Further research efforts will be required to provide a thickness estimate around which the NESSIAS effect can be put to best use for technological applications from the viewpoint of low nanoscale intrinsic Si system size. Moreover, recent DFT calculations[3] showed that other group...
IV semiconductors such as C and Ge – and presumably their alloys SiC and SiGe – strongly respond to the NESSIAS, offering a much broader impact on VLSI device design beyond low nanoscale Si.

3. Conclusion

We quantitatively demonstrated that an energy shift of electronic states defining the conduction band and VB edge of low nanoscale intrinsic Si exists, being considerably different from commonly assumed energy positions. The underlying Nanoscale Electronic Structure Shift Induced by Anions at Surfaces (NESSIAS) is brought about by the embedding dielectric, whereby N in the form of Si₃N₄ and O in the form of SiO₂ are of particular scientific and technological interest. We explained the underlying quantum chemical processes of the NESSIAS which mainly reside with the anion of the dielectric, namely its ability to attract extrinsic electrons such as from low nanoscale intrinsic Si from afar (electronegativity defining the ionicity of bond to Si), and its ability to localize extrinsic electrons in its immediate vicinity (electron affinity X). Electronic states experience a shift to higher binding energies with O as an interface anion, while the delocalization of extrinsic electrons in the immediate vicinity of N reflects such states partly back to Si, lowering the binding energy for low nanoscale intrinsic Si systems. The NESSIAS thus results in an electronic structure shift toward (away from) $E_{\text{vac}}$ for Si₃N₄-SiO₂ embedding. Hence, low nanoscale intrinsic Si systems like NWires or N Wells can be flooded by holes (Si₃N₄-coated) or electrons (SiO₂-coated), a property which readily offers the formation of a type II (p/n) homojunction in low nanoscale intrinsic Si.

We introduced an analytic parameter as a function of the ionization of the main interface anion $\Lambda_{\text{main}}^{\text{(n)}}$ which correctly predicts the HOMO energy $E_{\text{HOMO}}$ of the low nanoscale intrinsic Si system. This parameter is a function of the main interface anion presenting the coating dielectric. A verification of $\Lambda_{\text{main}}^{\text{(n)}}$ with three hybrid DFs showed its accuracy in predicting $E_{\text{HOMO}}$. As main anions to Si, we evaluated the entire first period of the periodic table and Si, with all of these main anions terminated by all possible outer atoms to form ligands. Using $\Lambda_{\text{main}}^{\text{(n)}}$ to predict the NESSIAS as a function of the dielectric coating, we obtain optimum combinations of Si and dielectrics per design to meet the desired functionality of VLSI electronic devices.

Band edges of 1.9 nm thick Si NWells measured by UPS and XAS-TFY revealed band offsets due to Si₃N₄ versus SiO₂-coating of $\Delta E_{\text{C}} = 0.56$ eV and $\Delta E_{\text{V}} = 0.89$ eV. The band gap energies were $E_{\text{gap}} = 1.29$ eV for Si₃N₄ and $E_{\text{gap}} = 1.62$ eV for SiO₂-embedding, respectively. The shift of experimental $E_{\text{C}}$ and $E_{\text{V}}$ values showed band offsets of the NWells to the respective dielectric becoming more symmetric with decreasing $d_{\text{well}}$. It emerged that the absolute position of $E_{\text{C}}$ and $E_{\text{V}}$ residing with the respective dielectric is also a function of the quantum chemical properties at the origin of the NESSIAS. The impact length for a saturation of the NESSIAS is ca. $1.5 \pm 0.2$ nm per plane interface, resulting in a considerable NESSIAS effect for $\leq 2.6 \pm 0.4$ nm thick Si NWells and $\leq 4.4 \pm 0.6$ nm thick Si NWires.[3] With VLSI approaching ultrathin fins and NWires, device dimensions are currently advancing into this thickness range. It should therefore be of high interest to the VLSI research community to carry out device-related research, in particular in the light of the prospective ultra-low power demand and low temperature functionality given by the NESSIAS effect.

4. Experimental Section

Sample Preparation: After determining the Deal-Gove parameters[41] for the furnace oxidation of silicon-on-insulator (SOI) samples, the SOI crystalline Si (c-Si) layers (p-type, 1 $\Omega$cm) on Si wafers with 145 nm buried SiO₂ (BOX) were oxidized to a thickness of 2.1 to 6.0 nm. The SiO₂ was removed by etching in a buffered oxide etch (BOE; 1 wt-% HF buffered with NH₄F), followed by a self-limiting oxidation in 68 wt-% HNO₃ at 120 °C, yielding a 1.1 to 5.0 nm Si-NWells with 1.4 nm SiO₂ capping. A lateral metal contact frame was processed on the front surface by photolithographically structuring, wet-chemical etching in BOE for opening the top SiO₂ layer and thermal evaporation of 300 nm Al, followed by a lift-off in acetone. The Si reference samples were contacted directly on their front surface. NWell samples were coated with photo resist immediately after NWell thickness measurements using Mueller matrix ellipsometry straight after processing to prevent oxidation in air. Resist was removed just prior to sample mounting at the beamline. Si reference samples consisted of (001)-Si wafer (Sb-doped n-type, 0.01 $\Omega$cm) which were treated with a BOE immediately before sample mounting under a N₂ gas flow with swift loading into the ultra-high vacuum (UHV) annealing chamber.

Si-NWells in Si₃N₄ were processed in analogy to the ones in SiO₂, using the same SOI wafers as starting point. The SOI was thinned down to a remnant Si device layer which was 1 nm thicker than the final NWell thickness, accommodating for Si consumption during the growth of Si₃N₄. Next, the SiO₂ capping is removed with BOE immediately before growing 3 nm of Si₃N₄ in an ammonia atmosphere by rapid thermal nitridation (RTN). Afterward, 20 nm of Si₃N₄ and 80 nm of SiO₂ were deposited by plasma enhanced chemical vapor deposition, followed by chemical mechanical polishing of the SiO₂ layer. After an RCA clean,[42] the samples were bonded to a Si wafer[45] covered by SiO₂ of ca. 1.5 nm thickness which was grown by an RCA-SC2 step. The original Si substrate of the SOI samples was etched back using a cyclic deep reactive ion etching process based on passivation with C₄F₈ and etching with SF₆. The BOX served as a stopping layer and was subsequently removed by a BOE immediately before growing 1 nm of Si₃N₄ onto the remnant SOI constituting the NWell by RTN in ammonia atmosphere. Contacts to the NWells were fabricated by photolithography, locally etching the Si₃N₄ with 1 wt-% hydrofluoric acid and deposition of 300 nm Al.

The layout of the samples and a high resolution TEM image of a NWell sample is shown Figure 5. Characterization: For synchrotron-based characterization techniques such as X-ray absorption spectroscopy measurements in total fluorescence yield (XAS-TFY) and UV photoelectron spectroscopy (UPS), all samples were subject to a UHV anneal for 60 min at 500 K to desorb water and air-related species from the sample surface prior to measurements. Synchrotron XAS-TFY measurements were carried out at the BACH CNR beamline[44,45] at the Elettra synchrotron radiation facility in Trieste, Italy, in top-up mode at an electron energy of 2.4 GeV (140 mA electron ring current). The photon energy scale has been calibrated using the energy position of the Si L₃-edge (99.6 eV) measured on a reference (001)-Si wafer. In addition, a gold (Au) layer with its 4f7/2 edge at an 87.6 eV binding energy was used as a calibration standard. A multitude of spectra was recorded per sample to obtain the data ensemble required for statistical post-processing. Further information and data on measurement parameters, measurement geometry, and statistical data post-processing can be found in the Supporting Information.

Synchrotron UPS measurements were realized at the BaDEII beamline[46] at the Elettra synchrotron radiation facility in Trieste, Italy, in top-up mode at an electron energy of 2.0 GeV (300 mA electron ring current). Single scans of spectra were recorded over 1 h per NWell 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 NWell samples were excited with photon energies of initially 8.9 eV and...
of 8.0 eV for subsequent measurements, and a photon flux of ca. $2 \times 10^{12}$ s$^{-1}$. The incident angle of the UV beam onto the sample was 50° with respect to the sample surface normal, the excited electrons were collected with an electron analyzer along the normal vector of the sample surface. Energy calibration of the UPS was realized using a tantalum (Ta) stripe in electrical contact to the sample as work function reference. Details on UPS data and measurement can be found in the Supporting Information as well as in the Supporting Information of [1] and the Appendix of [2].

The thickness of Si-NWells and its adjacent SiO$_2$ layers were measured using an ACCURION nanofilm ep4se ellipsometer$^{[47]}$ using a Mueller matrix approach.$^{[48–50]}$ Additional thickness measurements of the Si NWells and top SiO$_2$ were carried out by Transmission Electron Microscopy (TEM) on selected samples to confirm and/or calibrate ellipsometry measurements, see to representative NWell image in Figure 5b. All TEM samples were capped with a protective 100 nm thick SiO$_2$-layer to facilitate the preparation of X-sections by the focused ion beam (FIB) technique using a FEI Strata FIB 205 workstation. Some samples were further thinned by a Fischione NanoMill. TEM analysis of the X-sections was performed at a FEI Tecnai F20 TEM operated at 200 kV at the Central Facility for Electron Microscopy, RWTH Aachen University, and at the spherical aberration corrected FEI Titan 80-300 TEM operated at 300 kV at Ernst Ruska-Centre, Forschungszentrum Jülich.$^{[51]}$

**Density Functional Theory (DFT) Calculations:** Real space calculations were carried out with a molecular orbital basis set (MO-BS) and Hartree-Fock (HF)/DFT methods, employing the Gaussian09 program package$^{[52]}$ with the GaussView program$^{[53]}$ for visualization. Initially, the MO-BS wavefunction ensemble was tested and optimized for describing the energy minimum of the system (variational principle; stable = opt) with the HF method.$^{[54–56]}$ Exact exchange interaction inherent to HF is crucial in obtaining accurate bond geometries, see Supporting Information of Ref.$^{[1]}$ As MO-BS, we used the Gaussian type 3-21G MO-BS.$^{[57]}$ This HF/3-21G route was used for the structural optimization of approximants to obtain their most stable configuration (maximum integral over all bond energies); root mean square (RMS) and peak force convergence limits were $15.3$ meV Å$^{-1}$ and $23.1$ meV Å$^{-1}$, $(300$ and $450$ μHa/orb), respectively. Optimized geometries were used to calculate their electronic structure by testing and optimizing the MO-BS wavefunction ensemble with the non-local hybrid DF B3LYP,$^{[58–60]}$ its modified form featuring the Coulomb Attenuation Method (CAM-B3LYP) for more accurate asymptotic non-local exchange interactions,$^{[61]}$ and the HSE06 hybrid DF with its parameters from 2006.$^{[62]}$ As MO-BS, we used the Gaussian type 6-31G(d) MO-BS which contains d-polarization functions (B3LYP/6-31G(d))$^{[63]}$ for all chemical elements. For all calculations, tight convergence criteria were set to the self-consistent field routine and no symmetry constraints to MOs were applied. Ultrafine integration grids were used throughout. The Supporting Information of Refs.$^{[1]}$ and $[17]$ contain detailed accuracy assessments.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

- electronic structure shift, NESSIAS, p/n junction, silicon nanoelectronics, Si$_3$N$_4$, SiO$_2$, VLSI

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