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Electronic Structure Shift of Deep Nanoscale Silicon by SiO₂- vs. Si₃N₄-Embedding as Alternative to Impurity Doping

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Conventional impurity doping of deep nanoscale silicon (dns-Si) used in ultra large scale integration (ULSI) faces serious challenges below the 14 nm technology node. We report on a new fundamental effect in theory and experiment, namely the electronic structure of dns-Si experiencing energy offsets of ca. 1 eV as a function of SiO₂- vs. Si₃N₄-embedding with a few monolayers (MLs). An interface charge transfer (ICT) from dns-Si specific to the anion type of the dielectric is at the core of this effect and arguably nested in quantum-chemical properties of oxygen (O) and nitrogen (N) vs. Si. We investigate the size up to which this energy offset defines the electronic structure of dns-Si by density functional theory (DFT), considering interface orientation, embedding layer thickness, and approximants featuring two Si nanocrystals (NCs); one embedded in SiO₂ and the other in Si₃N₄. Working with synchrotron ultraviolet photoelectron spectroscopy (UPS), we use SiO₂- vs. Si₃N₄-embedded Si nanowells (NWells) to obtain their energy of the top valence band states. These results confirm our theoretical findings and gauge an analytic model for projecting maximum dns-Si sizes for NCs, nanowires (NWires) and NWells where the energy offset reaches full scale, yielding to a clear preference for electrons or holes as majority carriers in dns-Si. Our findings can replace impurity doping for n/p-type dns-Si as used in ultra-low power electronics and ULSI, eliminating dopant-related issues such as inelastic carrier scattering, thermal ionization, clustering, out-diffusion and defect generation. As far as majority carrier preference is concerned, the elimination of those issues effectively shifts the lower size limit of Si-based ULSI devices to the crystallization limit of Si of ca. 1.5 nm and enables them to work also under cryogenic conditions.

I. INTRODUCTION

Impurity doping of Si has been a prerequisite for Si-based electronics for about 70 years [1]. Over the last decade, impurity doping gradually became a major issue in ultra-large scale integration (ULSI) as fin/nanowire (NWire) device features approached the characteristic lengths of dopant out-diffusion, clustering and inactivation [2]. Considerable broadening of dopant profiles from drain/source regions into gate areas persists even when using self-regulatory plasma doping combined with rapid spike annealing [3]. To add, required ULSI transistor functionality [4] and emerging applications of Si-nanocrystals (NCs) [5] unveiled additional doping issues such as self-purification [6, 7], dopant ionization failing at room temperature [8, 9] and dopant-associated defect states [9–12].

In the late 1970s, modulation doping of III-V semiconductor combinations such as GaAs/AlAs was discovered

[13]. Lately, this concept was applied successfully to Si by acceptor doping of adjacent SiO₂ [14–16] and proposed for donor-doping Al_xGa_{1-x}N barriers from adjacent Si-rich Si₃N₄ during Si-NC formation anneal [17].

Ideally, majority carrier preference for electrons/holes and thus n/p-type conductivity would not require doping if the electronic structure of deep nanoscale Si (dns-Si) could be shifted over energy as per n/p-type section of an electronic device. Such an energy offset ΔE would avoid all dopant-related issues mentioned above, leading to lower inelastic carrier scattering rates and higher carrier mobilities which allow for decreased heat loss and bias voltages in ULSI. Together with directed self-assembly of block copolymers as new lithography approach to dns-Si structures [18], such properties enable Si-FET technology to work at yet smaller structure sizes potentially enabling Moore's Law to approach the Si-crystallization limit of ca. 1.5 nm [19]. In a recent paper [20] we were able to demonstrate in theory and experiment that ΔE exists in dns-Si when embedding one part of the Si nanovolume in SiO₂ and another part in Si₃N₄. However, a detailed investigation of the impact originating from interface bond densities per square, thickness of embedding dielectric and sample size on the magnitude of the effect is missing. The latter is very important for the applicability of the effect in real devices. As an effect

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induced via the interface of dns-Si, the extension of the p/n-junction is on the order of ca. 15 Å, allowing for a leap in device miniaturization. Moreover, we deliver a detailed phenomenological description of the fundamental quantum-chemical origin of ΔE which is underpinned by experimental data and DFT results.

In our work presented here, we consider SiO₂- and Si₃N₄-embedding of Si-NCs as a function of shape, size, interface orientation and thickness of embedding dielectric by using density functional theory (DFT) to calculate their electronic structure. As the next step, we compute DFT approximants containing two NCs, one embedded in SiO₂ and the other in Si₃N₄, to verify the ΔE we found for single Si-NCs within one system, accounting for interactions of both Si-NCs. From there, we present experimental data on Si-nanowells (NWells) embedded in SiO₂ vs. Si₃N₄, namely information on the ionization energy of the valence band edge of the Si-NWells by long-term synchrotron ultraviolet photoelectron spectroscopy (UPS)[20–25]. With this wealth of theoretical and experimental data, we propose a model explaining the interface impact of oxygen (O) and nitrogen (N) onto dns-Si, the associated characteristic impact length and other prominent features observed in the electronic structure of dns-Si. The massive ΔE observed in theory and experiment presents a new fundamental effect which can replace doping by forcing dns-Si into p- or n-type carrier preference as a function of embedding dielectric. Thereby, advantages of fully depleted field effect transistor (FET) ULSI devices can be combined with carrier preferences hitherto only achieved by impurity doping.

II. METHODS

A. Density Functional Theory Calculations

Hybrid density functional theory (h-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 GAUSSIAN09 program suite [26]. 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 3-21G MO-BS [27] (HF/3-21G). This MO wavefunction ensemble was then used for the structural optimization 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 [28, 29] and the 6-31G(d) MO-BS [30] (B3LYP/6-31G(d)). Root mean square (RMS) and peak force convergence limits were 8 meV/Å and 12 meV/Å, 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. Extensive accuracy evaluations can be found elsewhere [25, 31, 32]. We note that in real-space DFT calculations, exact calibration to an absolute energy scale (the vacuum level E_{vac}) is known to be ambiguous [33]. Nevertheless, relative changes of energy values such as ΔE or fundamental energy gaps E_{gap} between approximants with different interface termination are accurate within the same computation route, leaving a constant energy shift to all states with respect to E_{vac} as the only uncertainty. Approximants and MOs were visualized with GVIEW 5 [34]. Electronic density of states (DOS) were calculated from MO eigenenergies, applying a Gaussian broadening of 0.2 eV. The sizes given for NCs d_{NC} were calculated as the product of atomic volume of Si and the number of Si atoms forming the NC, assuming a spherical shape. This approach allows for a direct comparison of results between approximants of different shape.

B. Sample Preparation

Samples comprising a Si₃N₄-embedded NWell were fabricated by plasma enhanced chemical vapour deposition (PECVD) using SiH₄+NH₃+N₂ for Si₃N₄ buffer and top layers (thickness 5.5 and 1.5 nm, respectively) and SiH₄+ Ar for amorphous Si [35]. The Si₃N₄ spacer layer served to suppress excited electrons from the Si wafer to interfere with electrons from the Si-NWell during UPS. The substrates, i. e. n-type Si wafers (Sb doping, 5 to 15 × 10⁻³ Ωcm) of (111)-surface orientation, were wet-chemically cleaned. After deposition the wafers were annealed in a quartz tube furnace for 1 min at 1100 °C in pure N₂ ambient to induce Si-crystallization. Subsequently, samples were H₂-passivated at 450 °C for 1 hour.

Samples comprising a SiO₂-embedded NWell were dry-etched with an isotropic SF₆/O₂ plasma to thin down a 85 nm thick top c-Si layer of an Si-on-insulator (SOI) wafer with 200 nm buried SiO₂ (BOX), arriving at ca. 2.7 to 6.5 nm thick c-Si on top. The back-etch was followed by oxidation in 68 wt-% HNO₃ at 120 °C, resulting in a 1.1 to 5.0 nm Si-NWell with 1.4 nm SiO₂ capping.

Si reference samples were processed by etching a 001-Si wafer (Sb-doped n-type, 5 to 15 × 10⁻³ Ωcm) in 1 wt-% buffered hydrofluoric acid and immediate sample mounting under a N₂-shower with swift loading into the ultra-high vacuum (UHV) annealing chamber.

All NWell samples were contacted via a lateral metal contact frame on the front surface which was processed by photolithographical structuring, wet-chemical etching in 50 % HF plus 0.1 % HNO₃ for opening the top Si₃N₄ or in 1 wt-% hydrofluoric acid for opening the top SiO₂ layer and thermal evaporation of 300 nm Al, followed by a lift-off in dimethyl-sulfoxide (H₃C–(S=O)–CH₃). The Si reference samples were contacted directly on their front surface. Fig. 1 shows the structure of the mesa samples.

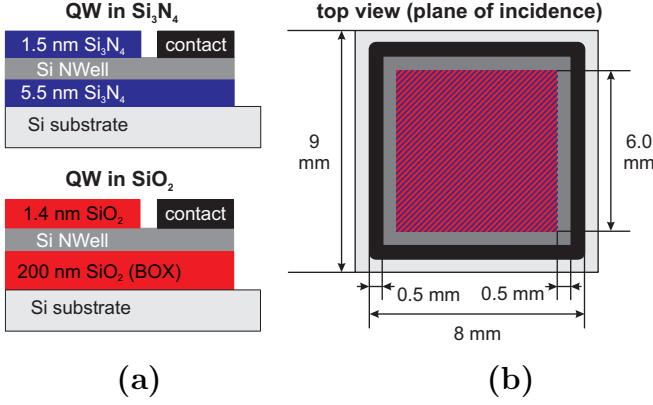


FIG. 1. Cross section view of sample layout of Si NWells embedded in Si_3N_4 or SiO_2 for synchrotron UPS measurements, showing the edge region of samples (a). Top view on the plane of incidence with mesa structure inside the contact frame (b). Hatched area stands for respective dielectric.

C. Characterization

Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out at the BaDElPh beamline [36] at the Elettra Synchrotron in Trieste, Italy, see [20] for details. 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 measurements. Single scans of spectra were recorded over 12 h per NWell sample and sub-sequently added up for eliminating white noise. Scans for the Si-reference sample were recorded over 2 h and sub-sequently added up [20]. All samples of beamtime 1 were excited with photon energies of $h\nu = 8.7$ eV and a photon flux of $2 \times 10^{12} \text{ s}^{-1}$. Samples of beamtime 2 were excited with $h\nu = 8.0$ eV and a photon flux of $2 \times 10^{12} \text{ s}^{-1}$, yielding to slightly better signal-to-noise ratio (SNR) due to an increased inelastic mean free path λ_{imfp} of escaping electrons. The incident angle of the UV beam onto the sample was 50° with respect to the sample surface normal, 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 a work function reference. Further UPS-data of SiO_2 and Si_3N_4 reference samples as well as on UPS signal normalization and background subtraction are available in [20, 25] and in Appendix Sec. A.

All samples for transmission electron microscopy (TEM) investigation were capped with a protective 100 nm thick SiO_2 -layer to facilitate the preparation of cross sections by the focused ion beam (FIB) technique using a FEI Strata FIB 205 workstation. Some samples were further thinned by means of a Fischione NanoMill. TEM analysis of the cross 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 [37].

In addition, Si-NWell thicknesses were measured by ellipsometry. The thickness of Si-NWells in Si_3N_4 and in SiO_2 were measured using a Woollam M-2000 ellipsometer and an ACCURION nanofilm ep4se ellipsometer, respectively. All thickness measurements were confirmed by values obtained from TEM. Yet, samples were given a standard deviation in NWell thickness of ± 1 monolayer (ML) due to the large extension of the measurement spot during UPS as compared to NWell thickness.

III. DFT RESULTS

A. Single Si-NCs coated with SiO_2 vs. Si_3N_4

With the interface charge transfer (ICT) at the core of ΔE , we investigate the nature of the interface and the interface-to-volume ratio of dns-Si as key parameters defined by system size. The latter can be expressed by the ratio of interface bonds to the number of Si-NC atoms $N_{\text{IF}}/N_{\text{NC}}$ [38], whereby this ratio can be applied to other dns-Si volumes such as NWires or fins [39]. Apart from its termination with OH- vs. NH_2 -groups, the nature of the interface is defined by its orientation with characteristic bond densities per square. We choose the $\langle 111 \rangle$ - and $\langle 001 \rangle$ -orientations with their interface bond densities per cm^2 of $\square N_{111} = 7.8 \times 10^{14} \text{ cm}^{-2}$ and $\square N_{001} = 13.6 \times 10^{14} \text{ cm}^{-2}$ [40], respectively, for two reasons. First, the technologically most relevant interface orientations of dns-Si are $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. Second, $\square N_{110} = 9.6 \times 10^{14} \text{ cm}^{-2}$ for $\langle 110 \rangle$ -orientations of Si interfaces [40] is close to $\square N_{111}$ whereby a significant difference of its impact onto the ICT is not given. We calculated octahedral approximants with exclusive $\langle 111 \rangle$ -orientations up to $d_{\text{NC}} = 25.9 \text{ \AA}$ – $\text{Si}_{455}\text{X}_{196}$ with $\text{X} = \text{OH}$, NH_2 , see Fig. 2a – and cubic approximants with exclusive $\langle 001 \rangle$ -orientations and associated bridge bonds ($>$) of NH- and O-groups up to $d_{\text{NC}} = 20.2 \text{ \AA}$ – $\text{Si}_{216}(>\text{XH}_{-1})_{75}\text{X}_{48}$ with $\text{XH}_{-1} = >\text{O}/>\text{NH}$, see Fig. 2b. Computations of bigger cubic NCs such as $\text{Si}_{512}(>\text{XH}_{-1})_{75}\text{X}_{48}$ were not successful due to excessive strain induced by $>\text{NH}$ and in particular $>\text{O}$ disintegrating the cubic shape.

Another important parameter is the thickness of the embedding dielectric. We calculated octahedral Si-NCs with exclusive $\langle 111 \rangle$ -orientations as above, but covered in 1.5 ML SiO_2 or Si_3N_4 up to Si_{286} NCs ($d_{\text{NC}} = 22.2 \text{ \AA}$). Thereby, we can directly compare the electronic structure of both approximant cohorts. Fig 2c shows such approximants where the NCs have been highlighted.

We now focus on the ionization of Si-NCs, see Fig. 3. It provides a blueprint of the strength of the ICT which is closely linked to ΔE . All total NC ionizations $Q_{\text{ion}}^{\text{NC}}$ over d_{NC} show a quadratic dependence which clearly points to a surface effect [32, 38]. In general, O-terminated species have a slightly higher ionization although the difference in ionicity of the bond Si—O with ca. 53 % ionic vs. Si—

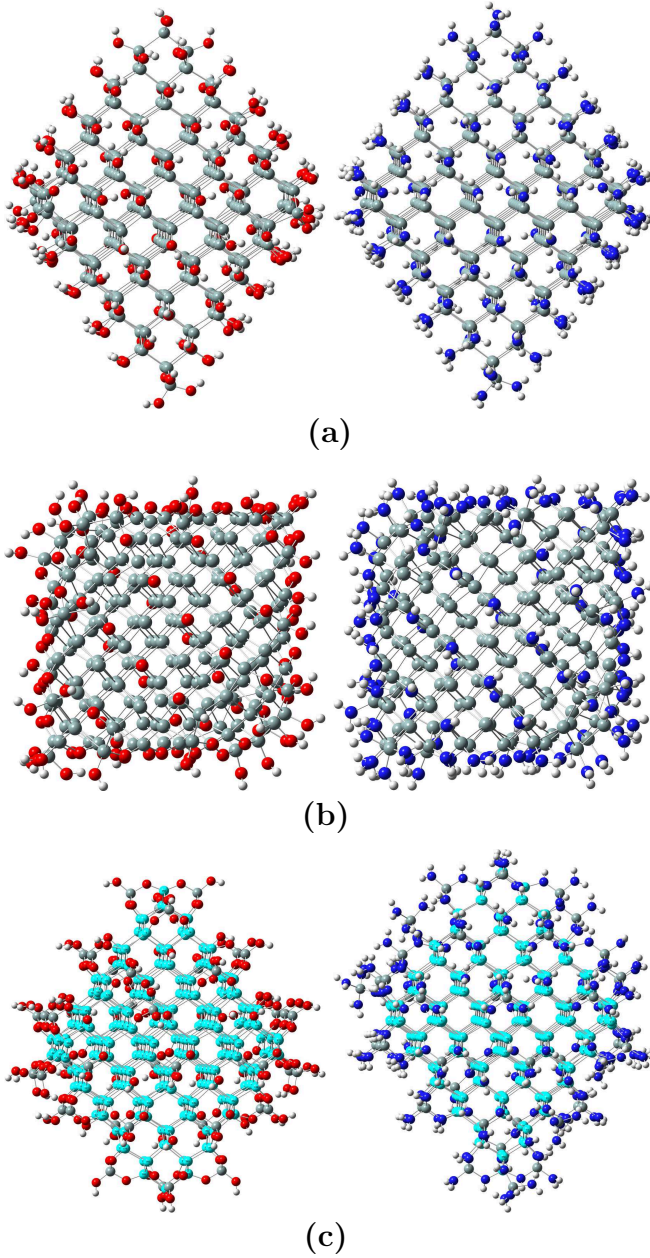


FIG. 2. Approximants to explore the impact of interface modification on electronic structure of Si-NCs. Octahedral $\langle 111 \rangle$ -faceted Si-NCs ($\text{Si}_{286}\text{X}_{144}$, $\text{X}=\text{OH}$, NH_2) of 22 Å size (a). Cubic $\langle 001 \rangle$ -faceted Si-NCs ($\text{Si}_{216}(>\text{XH}_{-1})_{75}\text{X}_{48}$, $>\text{XH}_{-1} = >\text{O}/\text{NH}$) of 20.2 Å size (b). Same Si-NCs as shown in (a), embedded in 1.5 ML SiO_2 or Si_3N_4 . NC atoms are highlighted in cyan (c). Atoms colors: Si is grey, O is red, N is blue and H is white.

N with ca. 35 % is significant [31, 41]. The minute difference for OH-/NH₂-terminated octahedral NCs shows that the ICT is saturated for $d_{\text{NC}} \leq 25.9$ Å. As we will see in Sec. V, this value is merely limited by tractable DFT system size and surpassed roughly 3-fold when feeding experimental results into an analytic impact model of ΔE [32]. Accordingly, the embedding of Si-NCs into

1.5 ML SiO_2 does only yield to a slightly higher $Q_{\text{ion}}^{\text{NC}}$, whereby ionization drops notably for coating in 1.5 ML Si_3N_4 . The origin of the latter is due to the positive electron affinity X of N which deflects the valence electron wavefunctions originating from Si-NC atoms back into the NC, resulting in a delocalization of these wavefunctions, see Sec. V for details. Due to MO hybridization, the unoccupied states follow suit. Considering $Q_{\text{ion}}^{\text{NC}}$ as a function of interface orientation, it becomes apparent that $\langle 001 \rangle$ -faceted interfaces with their increased bond density yield a stronger ICT. A direct comparison of $N_{\text{IF}}/N_{\text{NC}}$ between $\langle 001 \rangle$ -cubic vs. $\langle 111 \rangle$ -octahedral NCs cannot be accomplished due to their different d_{NC} . As a good estimate, we can compare the average value of the $\text{Si}_{165}\text{X}_{100}$ and $\text{Si}_{286}\text{X}_{144}$ NCs of $N_{\text{IF}}/N_{\text{NC}} = 0.555$ with their average size of $d_{\text{NC}} = 20.4$ Å to $N_{\text{IF}}/N_{\text{NC}} = 0.917$ of the $\langle 001 \rangle$ -cubic approximant $\text{Si}_{216}(>\text{XH}_{-1})_{75}\text{X}_{48}$ with $d_{\text{NC}} = 20.2$ Å [38]. We thus arrive at $5/3$ of the number of interface bonds per NC atom when going from $\langle 111 \rangle$ -octahedral to $\langle 001 \rangle$ -cubic NCs. Accordingly, $\langle 001 \rangle$ -cubic NCs are significantly more ionized than $\langle 111 \rangle$ -octahedral NCs which can be seen in Fig. 3.

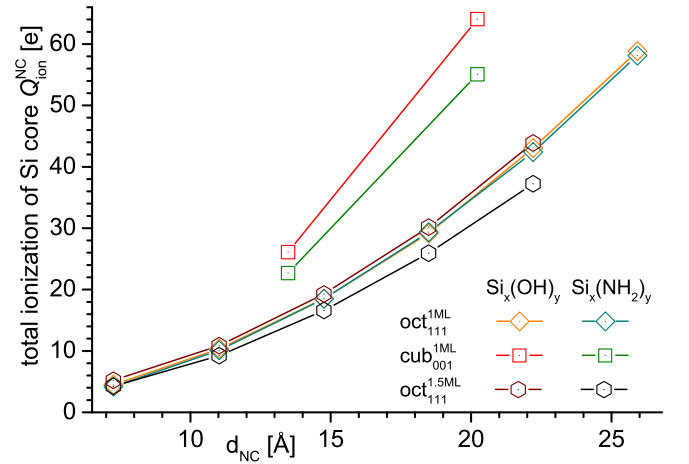


FIG. 3. Total ionization of Si-NCs of NC classes shown in Fig. 2. Terminations with OH (NH_2) are considered to present 1ML of SiO_2 (Si_3N_4).

Alternations of the ICT as function of interface orientation and thickness of embedding dielectric result in a modification of the NC electronic structure, namely energies of the highest occupied MO (HOMO) E_{HOMO} and of the lowest unoccupied MO (LUMO) E_{LUMO} , see Fig. 4. The increased ICT due to a higher ratio $N_{\text{IF}}/N_{\text{NC}}$ for $\langle 001 \rangle$ -cubic NCs or by increasing the dielectric embedding from 1 to 1.5 ML results in a more pronounced shift with respect to the vacuum level E_{vac} . For N-terminated NCs, a more pronounced shift towards E_{vac} is clearly visible for the $\langle 111 \rangle$ -octahedral NCs embedded in 1.5 ML Si_3N_4 and in particular for the $\langle 001 \rangle$ -cubic NCs. The results for O-terminated $\langle 111 \rangle$ -octahedral NCs show the same trend with more pronounced shifts further below E_{vac} . The cubic NCs $\text{Si}_{64}(>\text{O})_{27}(\text{OH})_{30}$ ($d_{\text{NC}} = 13.5$ Å)

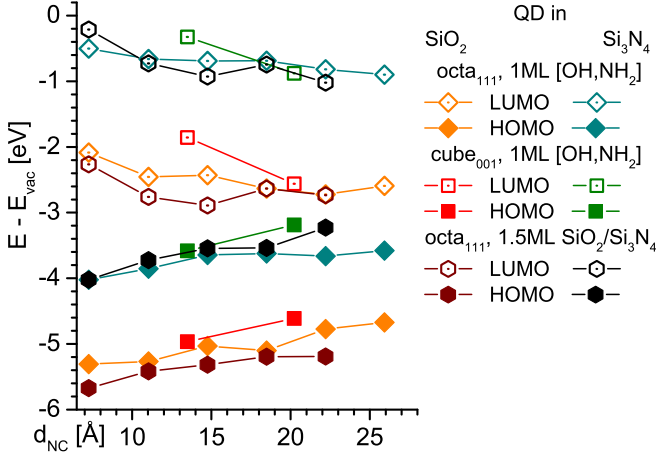


FIG. 4. HOMO and LUMO energies relative to E_{vac} of NC classes shown in Fig. 2. Terminations with OH (NH_2) are considered to present 1ML of SiO_2 (Si_3N_4).

and $\text{Si}_{216}(>\text{O})_{75}(\text{OH})_{48}$ do not follow the trend which appears surprising on a first glance. When looking at the latter cubic Si-NC (see Fig. 2b), it becomes apparent that considerable strain deforms the NC cube. For $\langle 111 \rangle$ -octahedral NCs, strain has only a minor influence on their electronic structure even with embedding – see Fig 2 and [20]. However, with many $>\text{O}$ bond configurations on $\langle 001 \rangle$ interfaces, strain may become more influential on the electronic structure. Such strain becomes evident when comparing bond lengths and angles as listed in Table I. The bond length of $\text{O}-\text{Si}$ bonds in ultrathin SiO_2 at the NC is ca. 7.4 % longer when compared to SiO_2 , while the value for $\text{Si}-\text{N}$ bonds is only stretched by ca. 3.8 % with respect to Si_3N_4 [25]. A similar situation exists with bond angles of Si atoms when going from the NC center to its interface. Together with a bond energy of $E_{\text{bond}}(\text{Si}-\text{O}) \approx 4.72$ eV vs. $E_{\text{bond}}(\text{Si}-\text{N}) \approx 3.89$ eV [41], the combination of higher E_{bond} and shorter bond lengths shows that $>\text{O}$ bond configurations to Si are capable of generating notably more local strain as opposed to $>\text{NH}$ bond configurations. With O-terminated $\langle 001 \rangle$ -cubic NCs, it appears that significant strain lowers the binding energy of the system which is reflected in a slight shift towards E_{vac} , see Fig. 4. It was reported that strain dominates the electronic structure of even $\langle 111 \rangle$ -octahedral Si-NCs embedded in SiO_2 [42], although we cannot confirm such results with own calculations of such Si-NCs in up to 3 ML of SiO_2 [20]. Hence, only massive strain emerges as modifier to the electronic structure, though still exceeded considerably by the impact of embedding dielectric via ICT. Bigger $\langle 001 \rangle$ -cubic approximants such as $\text{Si}_{512}(>\text{O})_{147}(\text{OH})_{66}$ with $d_{\text{NC}} = 27.0$ Å get partially disintegrated by strain due to $>\text{O}$ bonds, showing that stress destroys the NC before becoming dominant over the ICT.

In summary, we observed a substantial energy offset of

TABLE I. Bond lengths $d_{\text{Si}-\text{X}}$ ($\text{X} = \text{O}, \text{N}$) of bridging anion species $>\text{O}$ or $>\text{NH}$, bond angles over associated Si atoms $\angle_{\text{X}-\text{Si}-\text{X}}$, and bond angles $\angle_{\text{Si}-\text{Si}-\text{Si}}$ over Si-Si-Si in the center of cubic NCs shown for 20.2 Å cubic Si-NCs with exclusively $\langle 001 \rangle$ -oriented interfaces, *cf.* Fig. 2b. For comparison, $d_{\text{Si}-\text{X}}$ bond lengths of SiO_2 and Si_3N_4 approximants are listed. All lengths and angles are given as average values with absolute standard deviations. All approximants had identical parameters in HF/3-21G structural optimization.

	$\text{Si}_{216}(>\text{O})_{75}(\text{OH})_{48}$	SiO_2 [$\text{Si}_{29}\text{O}_{76}\text{H}_{36}$]
$d_{\text{Si}-\text{O}}$ [Å] ^a	1.732 ± 0.031	1.612 ± 0.009 [25]
$\angle_{\text{O}-\text{Si}-\text{O}}$ [°]	132.86 ± 1.24	
$\angle_{\text{Si}-\text{Si}-\text{Si}}$ [°] ^b	109.76 ± 0.91	
	$\text{Si}_{216}(>\text{NH})_{75}(\text{NH}_2)_{48}$	Si_3N_4 [$\text{Si}_{40}\text{N}_{86}\text{H}_{98}$]
$d_{\text{Si}-\text{N}}$ [Å] ^c	1.824 ± 0.032	1.757 ± 0.016 [25]
$\angle_{\text{N}-\text{Si}-\text{N}}$ [°]	125.19 ± 1.27	
$\angle_{\text{Si}-\text{Si}-\text{Si}}$ [°] ^b	109.75 ± 0.96	

^a excluding $-\text{OH}$ groups

^b angles from central Si atom up to 2-nn Si

^c excluding $-\text{NH}_2$ groups

the electronic structure of Si-NCs terminated with O vs. N, yielding to $\Delta E_{\text{HOMO}} \approx 1.75$ eV and $\Delta E_{\text{LUMO}} \approx 1.93$ eV with 1.5 ML coating by SiO_2 vs. Si_3N_4 . These values correspond to ca. 75 % and 55 %, respectively, of the nominal HOMO-LUMO gap of Si-NCs in the size range of 20 Å. We found that the ICT is dominated by bond densities per square given by interface orientation via the ratio $N_{\text{IF}}/N_{\text{NC}}$ and to a lesser degree by the thickness of the embedding dielectric. Interface strain originating from $>\text{O}$ bonds does have a minor influence on the electronic structure by decreasing binding energies of $\langle 001 \rangle$ -cubic NCs, shifting their electronic structure slightly towards E_{vac} , opposing the downshift of the electronic structure by SiO_2 -embedding to some extent.

B. One Approximant Featuring a Si-NC in SiO_2 Adjacent to a Si-NC in Si_3N_4

An approximant consisting of two Si-NCs, with the first (second) NC embedded in SiO_2 (Si_3N_4), presents the ultimate DFT system to test the energy offset ΔE and to gain further insight into its working principle. We calculated four approximants which mainly differ in the size of embedded Si-NCs: $2 \times \text{Si}_{10}$ (7.2 Å each) [20], $2 \times \text{Si}_{35}$ (11.0 Å each), $2 \times \text{Si}_{84}$ (14.8 Å each) and $2 \times \text{Si}_{165}$ (18.5 Å each). The latter two NC sizes overlap with experimental observations, thus providing a solid ground for Sec. V where we estimate the size range up to which dns-Si systems are dominated by ΔE .

Fig. 5 shows the results for the $2 \times \text{Si}_{35}$, $2 \times \text{Si}_{84}$ and $2 \times \text{Si}_{165}$ approximants, with respective DOS ranges enlarged to show the localization of the electronic states within the approximants. Underneath these DOS ranges, iso-density plots of the partial DOS located dominantly

within one of the NCs are shown as a function of their embedding. We can clearly see two effects: ΔE_{HOMO} and ΔE_{LUMO} increase with NC separation growing with NC size [43]. The global energy gap of the entire approximant $E_{\text{gap}}^{\text{global}}$ decreases with NC size. Both effects lead to a superlinear increase in n/p-type preference for charge carriers with increasing NC size, *cf.* Fig. 6, and in general with the size of dns-Si systems up to a certain limit, see Sec. V. We note that ΔE_{HOMO} and ΔE_{LUMO} of the $2 \times \text{Si}_n$ approximants ($n = 10, 35, 84, 165$) do not reach the values obtained for individual NCs in Sec. III A. The proximity of SiO_2 to Si_3N_4 results in a transient region where the electron-localizing nature of O cancels out with the electron-delocalizing nature of N [20]. Since the combined thickness of SiO_2 and Si_3N_4 between NCs gets thicker with increasing NC size, this effect diminishes to yield to increased ΔE_{HOMO} and ΔE_{LUMO} .

The total NC ionization in Fig. 6 only shows minor deviations from the ionization of $\langle 111 \rangle$ -octahedral N Cs with OH/ NH_2 -termination, see Fig. 3, confirming that both 18.5 Å Si-NCs (Si_{165}) are still within range of ICT saturation. These minor deviations are instructive to understand the impact of O vs. N onto dns-Si, see Sec. V.

For all NC sizes, N-terminated Si-NCs slightly increase their ionization from coverage with all-around 1.5 ML Si_3N_4 via inclusion into 1 to 3 ML Si_3N_4 in $2 \times \text{Si}_n$ approximants up to all-around 1 ML Si_3N_4 coverage. As pointed out in Sec. III A, this increase with decreasing thickness of Si_3N_4 -embedding originates from the positive electron affinity X of N. The 1 to 3 ML Si_3N_4 coverage takes an intermediate position between full coverages with 1 and 1.5 ML Si_3N_4 . In other words, the 1 ML Si_3N_4 coverage of the outer NC interface in $2 \times \text{Si}_n$ approximants does not delocate and/or deflect valence electron wavefunctions originating from Si-NC atoms enough to provide a full upshift of energy levels. Arguably, and backed by experimental data (Sec. IV), the electronic states of Si_3N_4 -embedded NCs in the $2 \times \text{Si}_n$ approximants could be located nearer E_{vac} if a complete multi-ML embedding in Si_3N_4 with $> 1,500$ heavy atoms could be computed.

For Si-NCs in SiO_2 , NC ionization increases from 1 ML via 1.5 ML SiO_2 to embedding in 1 to 3 ML SiO_2 in $2 \times \text{Si}_n$ approximants. Here, the strong localization of valence electrons from Si-NCs at O drives the ionization process and thus the shift of valence electron wavefunctions of the Si-NC to higher binding energies. We thus can presume an average 2 ML embedding in SiO_2 for the $2 \times \text{Si}_n$ approximants, yielding 1, 1.5 and 2 ML for the increasing ionization of Si-NCs by SiO_2 , clearly correlating with the number of O atoms per Si-NC atom.

To recapitalize, ΔE also exists in the complete system manifested by $2 \times \text{Si}_n$ approximants, one embedded each in SiO_2 and Si_3N_4 . The strength of ΔE increases with NC separation given by the combined inter-NC thickness of SiO_2 and Si_3N_4 , though not quite reaching the values for individual NCs in SiO_2 vs. Si_3N_4 . As a likely cause we identified the transition range between SiO_2 and Si_3N_4 where the nature of both anions – O and N – tend to can-

cel each others impact on the electronic structure. Apart from proving the full scale of ΔE in a complete system, the $2 \times \text{Si}_n$ approximants investigated in this section yield to a more detailed evaluations of NC ionization and ΔE .

IV. EXPERIMENTAL RESULTS: SYNCHROTRON UPS

After an initial UPS measurements confirming the effect of ΔE for Si-NWells in SiO_2 vs. Si_3N_4 [20], we characterized 10 SiO_2 - and 4 Si_3N_4 -embedded NWells with thicknesses ranging from 11 to 50 Å. Since we work with NWells and thus quasi-2D band structures, we replace E_{HOMO} and E_{LUMO} with the energy of the highest occupied *viz.* top valence band states E_V and of the lowest unoccupied states *viz.* bottom conduction band E_C , respectively, to account for the limits on continuous electronic DOS. Details on deriving the ionization energy $E_{\text{ion}} = E_V$ of such valence band states and respective standard deviations are treated in Appendix Sec. A and in [25]. Fig. 7 shows E_V values as a function of NWell thickness d_{NWell} for SiO_2 - and Si_3N_4 -embedding.

For $d_{\text{NWell}} = 11$ to 15 Å, we obtained $E_V \approx E_{\text{vac}} - 5.85$ eV for NWells in SiO_2 and $E_V \approx E_{\text{vac}} - 4.96$ eV for NWells in Si_3N_4 . For SiO_2 -embedding, a minute change to $E_V \approx E_{\text{vac}} - 5.82$ eV occurs for $d_{\text{NWell}} = 25 \pm 1$ Å. Changes are more notable for Si_3N_4 -embedding where we obtained $E_V \approx E_{\text{vac}} - 5.08$ eV for $d_{\text{NWell}} = 27$ Å. We also note that $E_V(d_{\text{NWell}})$ changes rather continuously as compared to NWells embedded in SiO_2 which is subject to discussion in Sec. V. In the range of $d_{\text{NWell}} \approx 30$ to 40 Å, E_V of Si-NWells in SiO_2 and Si_3N_4 change to approach the common value $E_V = E_{\text{vac}} - 5.17$ eV as known for bulk-Si. Expressing these values in terms of ΔE_V , we get $\Delta E_V(d_{\text{NWell}} = 11 \text{ to } 20 \text{ Å}, \text{SiO}_2) = -0.68$ eV and $\Delta E_V(d_{\text{NWell}} = 11 \text{ to } 20 \text{ Å}, \text{Si}_3\text{N}_4) = +0.21$ eV, decreasing to $\Delta E_V(d_{\text{NWell}} = 25 \pm 1 \text{ Å}, \text{SiO}_2) = -0.65$ eV and $\Delta E_V(d_{\text{NWell}} = 25 \pm 1 \text{ Å}, \text{Si}_3\text{N}_4) = +0.09$ eV. The difference in E_V for Si-NWells embedded in SiO_2 vs. Si_3N_4 thus undergoes a minor decrease from 0.89 eV for $d_{\text{NWell}} = 11$ to 15 Å to 0.74 eV for $d_{\text{NWell}} = 25 \pm 1$ Å. Since Si-NWells have significantly lower fundamental gaps as compared to Si-NCs (*cf.* Figs. 4 and 5), a pronounced n/p-type charge carrier preference arises from the energy offsets above for $d_{\text{NWell}} \leq 28$ Å.

We are planning to measure the conduction band states of NWell samples along with UPS characterizations on the same samples, motivated by Zimina *et al.* [44] who characterized E_C of Si-NCs embedded in SiO_2 for $d_{\text{NC}} = 16$ to 40 Å by soft X-ray emission spectroscopy (SXES). A *downshift* of E_C up to 0.2 eV *below the conduction band edge E_C of bulk-Si* was obtained [44]. Conventional quantum physics strongly suggests E_C to be located a few 100 meV above E_C of bulk-Si which already includes contributions from excitonic binding and dielectric screening. The same work also noted that the interface of Si-NCs is not abrupt but rather gradual, with

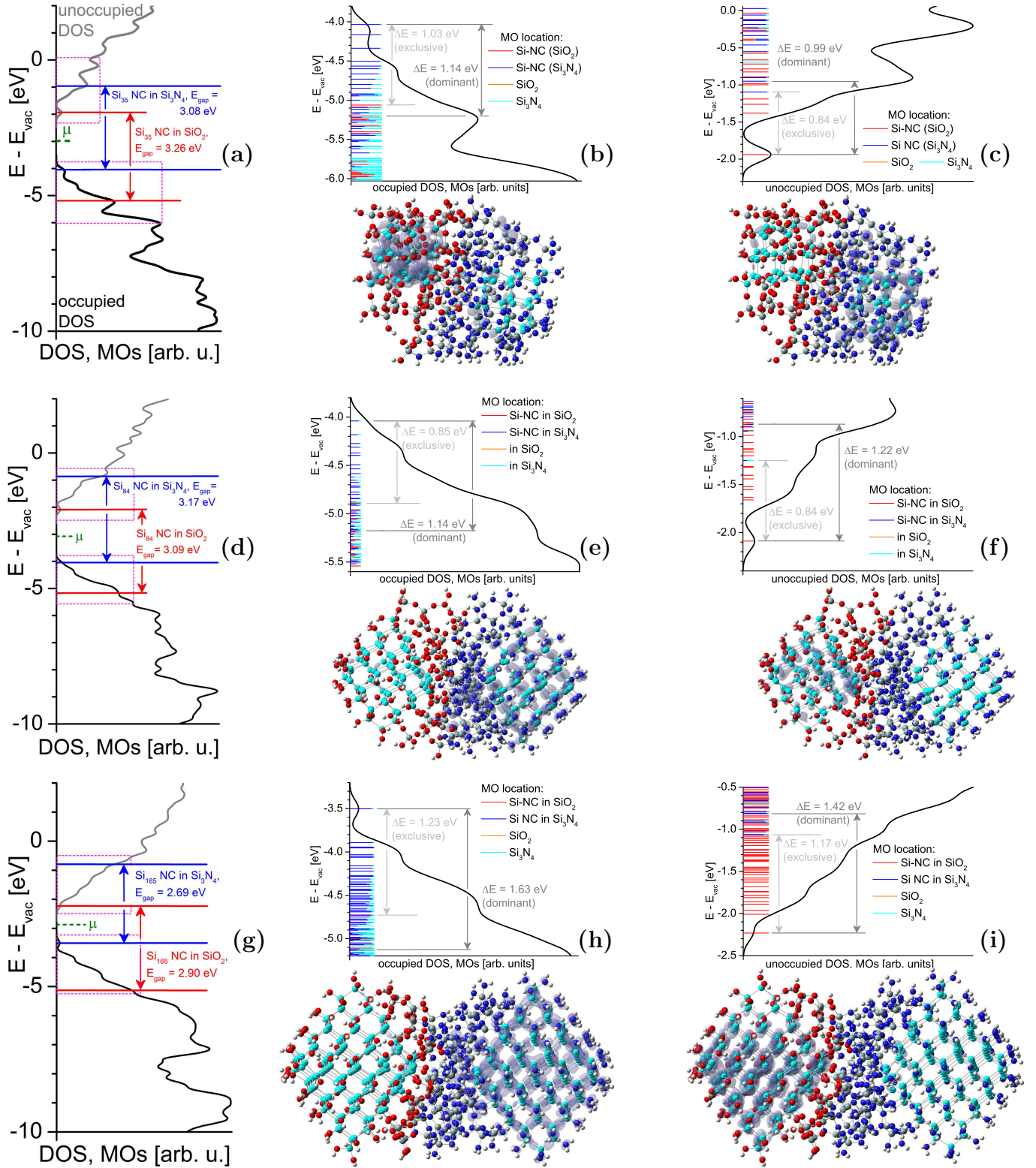


FIG. 5. **DFT results of two embedded Si-NCs in $\text{SiO}_2/\text{Si}_3\text{N}_4$ within one approximant.** DOS of $2 \times \text{Si}_{35}$ NCs, of 11.0 Å size (a). The green dashed line shows the chemical potential μ of the approximant. Detailed DOS of frontier OMOs contained in magenta rectangle, showing their localization, together with iso-density plot of OMOs [$4.6 \times 10^{-3} e/a_{\text{B},0}$] within energy window where NC in Si_3N_4 dominates electronic structure (b). Detailed DOS of frontier UMOs contained in magenta rectangle, showing their localization, together with iso-density plot of UMOs [$3.2 \times 10^{-3} e/a_{\text{B},0}$] within energy window where NC in SiO_2 dominates electronic structure (c). All iso-density plots have the same value per frontier OMOs/UMOs. Graphs (d)-(f) show results for $2 \times \text{Si}_{84}$ NCs of 14.8 Å size, graphs (g)-(i) for $2 \times \text{Si}_{165}$ NCs of 18.5 Å size. For atom colors see Fig. 2.

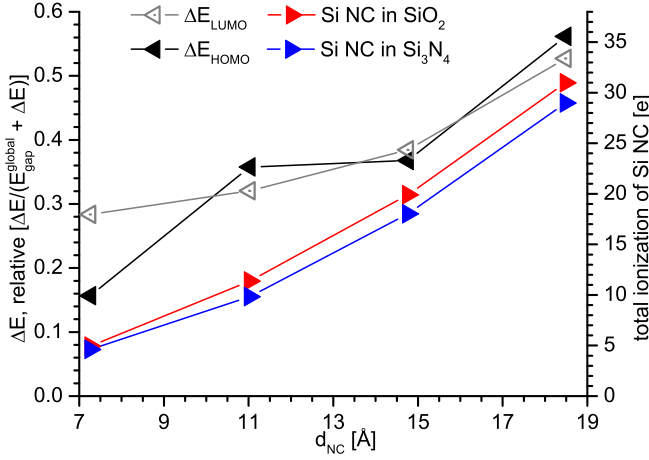


FIG. 6. Relative change in OMO and UMO energy offsets due to SiO_2 - vs. Si_3N_4 -embedding as function of NC size, referring to global HOMO-LUMO gap of Si-NCs in SiO_2 vs. Si_3N_4 , see Fig. 5. Colored symbols show total Si-NC ionization as function of NC size and embedding and refer to right scale.

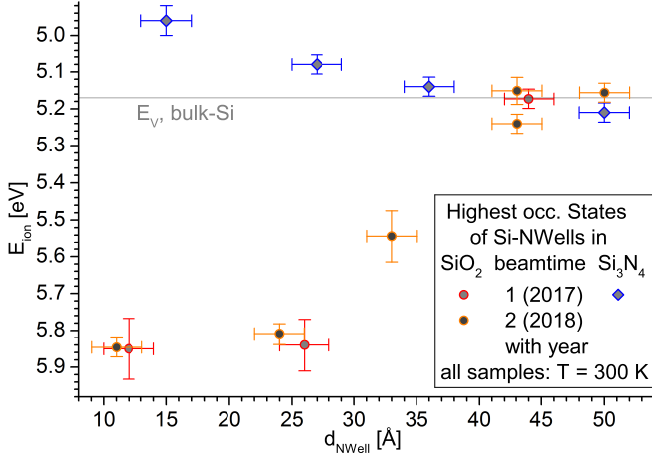


FIG. 7. Ionization energies E_{ion} , representing E_V of Si-NWells embedded in SiO_2 or in Si_3N_4 as a function of d_{NWell} . Each point represents a different sample. Valence band edge of bulk-Si is shown as reference. Error bars refer to standard deviations in thickness and in energy, see Sec. A and [25]).

sub-oxide shells in a thickness range of 3 to 5 Å. This value is likely underestimated since similar superlattices of Si-NCs with sub-oxide shells characterized by atom probe tomography were found to have sub-oxide shells of ca. 8 Å [9, 45]. Such thicker sub-oxide shells will attenuate the ICT and thus ΔE due to the sub-oxide not having the full ΔE impact onto dns-Si and working as an electrostatic buffer between the Si-NC and SiO_2 at the same time. Since our NWell samples have plane interfaces and were not processed by excess Si segregation from a sub-oxide [5], the interface thickness is on the order of 5 Å as occurring in conventional c-Si oxidation [46]. Hence, it appears that higher energy offsets ΔE_C and consequently ΔE_V exist for NWells as compared to Si-NCs formed by

TABLE II. Fundamental properties of N, O and Si: Ionization energy (E_{ion}), electron affinity (X), electronegativity (EN), ensuing ionicity of bond (IOB) to Si and experimental values of characteristic bond lengths [41].

\in	$E_{\text{ion}}^{\text{a}}$ [eV]	X [eV]	EN^{b}	IOB [%]	$d_{\text{bond to Si}}$ [Å]
N	14.53	+0.07	3.07	36	0.1743 (Si_3N_4)
O	13.36	-1.46	3.50	54	0.1626 (SiO_2)
Si	8.15	-2.08	1.74	0	0.2387 (bulk Si) ^c

^a refers to first valence electron

^b values after Allred & Rochow

^c with unit cell length of 0.5431 nm [47]

segregation from Si-rich dielectrics [5, 35].

To sum up, $E_V = E_{\text{vac}} - 5.17 \text{ eV} = E_V(\text{bulk-Si})$ for NWells with $d_{\text{NWell}} = 40$ to 50 Å in both, SiO_2 and Si_3N_4 . We take this value as the common baseline from which to count ΔE_V with decreasing d_{NWell} as per dielectric. For $d_{\text{NWell}} = 30$ to 40 Å , a transition range exists with increasing ΔE_V between NWells in SiO_2 vs. Si_3N_4 . At $d_{\text{NWell}} = 25 \pm 1 \text{ Å}$, the respective E_V are fully developed with $\Delta E_V \approx 0.74 \text{ eV}$, still increasing to $\approx 0.9 \text{ eV}$ for $d_{\text{NWell}} = 11$ to 15 Å . Thus, a strong n/p-type carrier preference exists for dns-Si in $\text{SiO}_2/\text{Si}_3\text{N}_4$ which can induce a p/n junction for $d_{\text{NWell}} \leq 28 \text{ Å}$, cf. Fig. 5g-i. Published characterisation data on Si-NCs prepared by segregation anneal from Si-rich SiO_2 [44] show *negative* ΔE_C , resulting in $E_C \approx E_C(\text{bulk-Si}) - 0.2 \text{ eV}$. As electronic quality and abruptness of the interface of Si-NWells is notably superior to segregated Si-NCs having warped/multi-faceted interfaces, the negative ΔE_C of NWells should be more pronounced in SXES measurements.

V. PROPOSED MECHANISM OF ENERGY OFFSET

With the quantitative theoretical and experimental data presented above, we propose a qualitative model for the energy offsets ΔE_V and ΔE_C induced by embedding in SiO_2 vs. Si_3N_4 . From there, we determine the impact length of ΔE_V and ΔE_C in dns-Si systems.

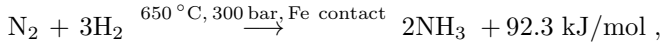
A. Basic Principle

A brief look at some element-specific quantum-chemical parameters of O, N and Si as listed in Table II is very helpful to explain ΔE .

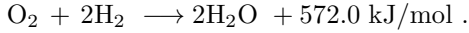
For O, the explanation of ΔE is fairly straightforward. With a high negative X and an ionicity of bond (IOB) to Si of ca. 53 %, O localizes electronic charge from dns-Si, thereby increasing the binding energy of such electrons which present the valence states of dns-Si with the lowest binding energy. As a consequence, $E_V(\text{dns-Si})$ is shifted

further below E_{vac} . Since Si atoms have a reasonably high E_{ion} which counteracts electron removal, the ICT feeding into electron localization at O decreases from its saturation value (maximum positive ionization) after a few MLs of the dns-Si system. Eventually, the impact of the ICT due to O at the dns-Si interface vanishes, whereby $E_V(\text{dns-Si}) \rightarrow E_V(\text{bulk-Si})$. The top graph of Fig. 8 illustrates this behavior.

The situation with N requires some broader considerations of its properties. Out of all chemical elements which are known to expose anionic properties (main groups IV to VII of the periodic table), N is the only element which possesses a *positive* electron affinity X , meaning that turning N into a negative ion (a Lewis acid [41]) requires a significant activation energy. Therefore, N is very reluctant to accept negative charge as from dns-Si, which becomes even more prominent when compared to O. This fact is well known from some basic chemical reactions such as creating ammonia (NH_3) from the elements,



requiring a catalytic iron contact at 300 bar and 650 °C to trigger above reaction known as Haber-Bosch synthesis [41]. In contrast, O reacts violently with H at room temperature at 1 bar (oxyhydrogen reaction) [41]:



Considering Si, oxidation of Si surfaces to SiO_2 in elemental O_2 proceeds readily at room temperature and is promoted by the presence of H_2O . In contrast, the nitridation reaction requires Si surfaces to be offered atomic/ionic N in a plasma several 100 °C above room temperature to achieve the reaction.

This uncommon behavior of N is at the heart of the energy offset: While N delocalizes electrons of a dns-Si system at the top of its valence band, it does not localize such electrons, but rather deflects them back into the dns-Si and adjacent Si_3N_4 . This delocalization results in a lower binding energy of these valence electrons. From Fig. 7 we also see that the delocalizing impact of N onto $E_V(\text{dns-Si})$ does not show a strict saturation for $d_{\text{NWell}} \leq 25\text{ \AA}$ as is the case for SiO_2 -embedding. This behavior has to be seen in the context of electron delocalization which is more sensitive to environmental changes such as an increase of the number of NWell Si atoms per N atom in Si_3N_4 . We can therefore state that ΔE generated by Si_3N_4 -embedding is not as robust as ΔE due to SiO_2 .

The partial deflection of delocalized electrons into the first couple of ML of Si_3N_4 explains the stronger shift of E_{HOMO} and E_{LUMO} towards E_{vac} for $\langle 111 \rangle$ -octahedral Si-NCs in 1.5 ML vs. 1 ML Si_3N_4 , cf. Fig. 4. The same consequence occurs when going from $\langle 111 \rangle$ -octahedral to $\langle 001 \rangle$ -cubic Si-NCs, where the ratio $N_{\text{IF}}/N_{\text{NC}}$ increases significantly. To add, such behavior can clearly be seen for the frontier OMOs at approximants featuring a Si-NC in Si_3N_4 plus a Si-NC in SiO_2 , see Sec. IIIB and Fig. 5b, e and h. The resulting shift of $E_V(\text{dns-Si})$ towards

E_{vac} within the first few MLs of dns-Si is shown in the bottom graph of Fig. 8.

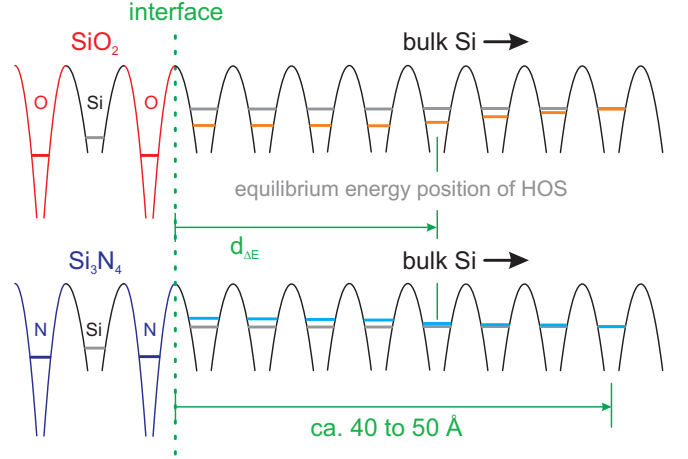


FIG. 8. Principle of how the energy offset in dns-Si is induced on the quantum scale. Top graph shows atomic potential at SiO_2/Si interface, bottom graph shows the situation at $\text{Si}_3\text{N}_4/\text{Si}$ interface. Gray valence levels refer to equilibrium positions in bulk-Si. The impact length of the energy offset $d_{\Delta E}$ defines the distance from the interface where ΔE leaves the saturation regime as obtained from UPS measurements. For further explanations see text.

Fig. 7 shows that $|\Delta E_V(\text{SiO}_2)| \approx 5 \pm 2 \times |\Delta E_V(\text{Si}_3\text{N}_4)|$. This finding correlates qualitatively with the IOB of N vs. O to Si. Other factors as anion-to-Si ratio, positive $X(\text{N})$ vs. negative $X(\text{O})$, bond length and packing fraction in the dielectric have an influence on this ratio as well.

Since we intent to use the ΔE for undoped p/n junctions, we consider it useful to define its impact length $d_{\Delta E}$ as the distance from the dns-Si interface to the point where E_V comes out of saturation. This definition of $d_{\Delta E}$ provides the optimum impact for undoped p/n-junctions since the global energy gap of the dns-Si system decreases with its increasing size, see Fig. 9.

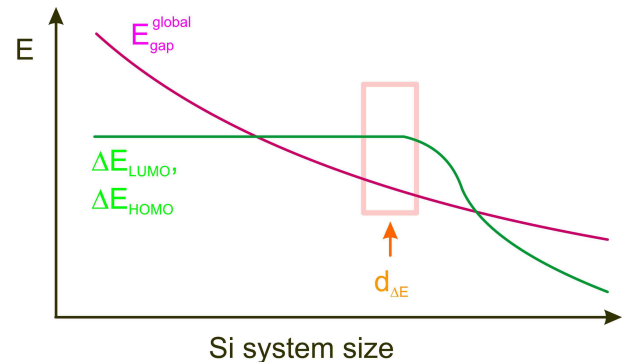


FIG. 9. Qualitative scheme to explain the dependence of energy offset and global energy gap as function of dns-Si system size. The technological optimum for maximum n/p-type carrier preference is shown by the semi-transparent pink frame, defining $d_{\Delta E}$ as per explanation in text.

B. Calculation of Impact Length of ΔE in dns-Si

From the measurements of $E_V(d_{\text{NWWell}})$ by synchrotron UPS, we derived $d_{\text{NWWell}} \approx 28 \text{ \AA}$ as the saturation limit beyond which ΔE decreases significantly. NWells have two adjacent interfaces which immediately yields $d_{\Delta E}(\text{bulk-Si}) = 1/2 \times d_{\text{NWWell}} \approx 14 \text{ \AA}$. This value presents the limit for the semi-infinite case, *id est* an interface to bulk-Si. The volume element defining $d_{\Delta E}(\text{bulk-Si})$ is a cubicle of height $d_{\Delta E}(\text{bulk-Si})$, its width and length is defined by the smallest periodic unit in the respective direction. For NWells, we thus get $d_{\Delta E}(\text{Si-NWWell}) = 2 \times d_{\Delta E}(\text{bulk-Si})$, arriving at the value obtained by synchrotron UPS, see right graph in Fig 10.

As an approximation, NWires and NCs have warped interfaces which do not allow for a straightforward derivation of dV as is the case for NWells and bulk-Si. Therefore, we derive the gauge for these dns-Si systems by simple geometric arguments of volume integration via Riemann's sums [48]. For NWires, we cut out a slab which presents the smallest periodic unit along the NWire axis. This slab is then filled with volume elements $dV(i)$, presenting the Riemann sum $\sum_i dV$ of the slab volume. For NWires, these $dV(i)$ are wedges, see center graph in Fig. 10. With $i \rightarrow \infty$, we achieve the transition from the Riemann sum to the volume integral, resulting in an infinite number of wedges with vanishing base area. With equal base areas, the volume of a wedge equals the volume of a cubicle if the height of the wedge is twice the height of the cubicle. Consequently, the impact length of ΔE doubles when going from NWells to NWires, resulting in $d_{\Delta E}(\text{Si-NWire}) = 2 \times d_{\Delta E}(\text{Si-NWWell})$. For NCs, it is straightforward that we get pyramids as volume elements dV , see left graph in Fig. 10. With the same base area, a pyramid has the same volume as a cubicle if its height is three times the height of the cubicle. Accordingly, we obtain $d_{\Delta E}(\text{Si-NC}) = 2 \times d_{\Delta E}(\text{Si-NWire})$. Summarizing all dV definitions, we get $d_{\Delta E}$ scaling with bulk-Si: NWWell: NWire: NC like 1:2:4:6. With $d_{\Delta E}(\text{Si-NWWell}) \approx 28 \text{ \AA}$, we get $d_{\Delta E}(\text{Si-NWire}) \approx 56 \text{ \AA}$ and $d_{\Delta E}(\text{Si-NC}) \approx 84 \text{ \AA}$.

In real systems, the rise in $d_{\Delta E}$ with decreasing dimensionality of the dns-Si system should be sublinear, originating from a higher defect density due to warped interfaces which has to be controlled by ΔE as well. We can account for this effect by exploiting the fact that fundamental gaps E_{gap} of Si-NCs are significantly bigger for Si_3N_4 -embedding vs. SiO_2 -embedding if such NCs are small enough [31, 32]. Experimental data showed E_{gap} of both embeddings to converge at $d_{\text{NC}} \approx 56 \text{ \AA}$ [49]. Assuming a reduction factor per reduced dimension DF and using $d_{\Delta E}(\text{Si-NC}) = DF^2 \times 4 \times d_{\Delta E}(\text{Si-NWWell})$, we arrive at $DF \approx 1/\sqrt{2}$, yielding $d_{\Delta E}(\text{Si-NWire}) \approx 40 \text{ \AA}$ and $d_{\Delta E}(\text{Si-NC}) \approx 56 \text{ \AA}$ below which ΔE is saturated.

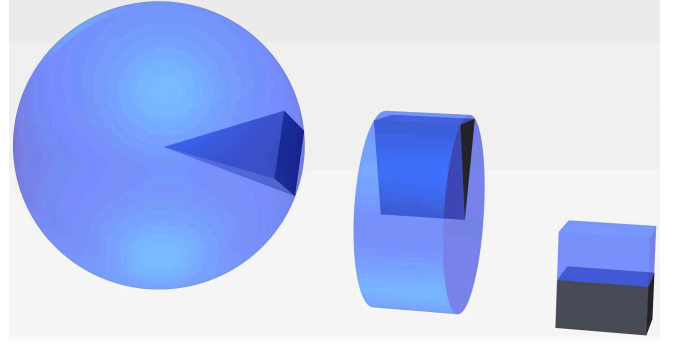


FIG. 10. Illustration of volume elements dV to describe the volume of NCs (left), NWires (center), and NWells (right). For NWires and NCs having warped surfaces, the Riemann sum over all $dV(i)$ converges against the volume integral of the dns-Si system for $i \rightarrow \infty$, resulting in the base areas of dV to converge to zero. Scaling of system sizes matches dV shape with constant volume and is thus 3:2:1 from left to right.

VI. CONCLUSIONS

We presented a detailed quantitative study of considerable energy offsets of frontier electronic states as a new fundamental effect arising from deep nanoscale (dns-) Si volumes when embedded/coated in SiO_2 vs. Si_3N_4 .

Using DFT, we investigated single Si-NCs as a function of interface orientation and thickness of embedding SiO_2 vs. Si_3N_4 up to $d_{\text{NC}} = 26 \text{ \AA}$. We found E_{HOMO} and E_{LUMO} to have little dependence on NC size in the range considered, showing a strong offset due to 1.5 ML SiO_2 - vs. Si_3N_4 -embedding of $\Delta E_{\text{HOMO}} \approx 1.75 \text{ eV}$ and $\Delta E_{\text{LUMO}} \approx 1.93 \text{ eV}$. These offsets push E_{HOMO} and E_{LUMO} of SiO_2 -embedded Si-NCs further below E_{vac} , while shifting E_{HOMO} and E_{LUMO} of Si_3N_4 -embedded Si-NCs towards E_{vac} . Extending the embedding in $\text{SiO}_2/\text{Si}_3\text{N}_4$ beyond 1 ML and in particular increasing the ratio of interface bonds per NC atom $N_{\text{IF}}/N_{\text{NC}}$ by going from (111)-octahedral to (001)-cubic NCs increased ΔE further. As ultimate theoretical test, we computed approximants featuring two Si-NCs of up to 18.5 \AA size, one each embedded in SiO_2 and Si_3N_4 , respectively, confirming ΔE within one system.

We characterized 14 samples, each featuring one Si-NWWell of $d_{\text{NWWell}} = 11$ to 50 \AA embedded in SiO_2 or in Si_3N_4 , by long-term synchrotron UPS to measure the energy of the top valence band states E_V . For $d_{\text{NWWell}} \lesssim 28 \text{ \AA}$, we obtained $\Delta E_V \approx 0.9$ to 0.74 eV for SiO_2 - vs. Si_3N_4 -embedding. After a transition range at $d_{\text{NWWell}} \approx 30$ to 40 \AA , Si-NWells in both embeddings converge to $E_V = E_V(\text{bulk-Si})$. Zimina *et al.* [44] found the energy of the lowest unoccupied states at $E_C \approx E_C(\text{bulk-Si}) - 0.2 \text{ eV}$ for SiO_2 -embedded Si-NCs, whereby attractive interactions like exciton binding energy and screening were already included in this value. This finding is consistent with our results on E_V of thin Si-NWells in SiO_2 .

Investigating the quantum chemistry of O and N with

respect to Si, we proposed a model for ΔE . The uncommon situation of N as the only anionic element with an electron affinity $X > 0$ eV and a yet fairly high electronegativity EN inducing a strong polar bond to Si is one cornerstone of the newly discovered effect. While N delocalizes valence electrons from dns-Si, it does *not* localize such electrons but deflects these back into dns-Si or surrounding Si_3N_4 as also evident from frontier OMO density plots in DFT calculations spreading well into Si_3N_4 . As a consequence, such delocalized NWell valence band states have a lower binding energy which is equivalent to an upshift of $E_V(\text{NWell})$ towards E_{vac} . As expected, the strong conventional anionic nature of O results in strong localization of valence electrons from dns-Si at O in SiO_2 and an associated downshift of $E_V(\text{NWell})$ below E_{vac} .

With a straightforward geometrical Riemann model, we calculated the impact length $l_{\Delta E}$ up to which ΔE governs the electronic structure of dns-Si to scale 1:2:4:6 for bulk-Si:NWell:NWire:NC. With $l_{\Delta E}(\text{NWell}) \approx 28$ Å, we thus arrived at $l_{\Delta E}(\text{NWire}) \approx 56$ Å and $l_{\Delta E}(\text{NC}) \approx 84$ Å. The latter two dns-Si structures have warped interfaces which are more prone to defects; experimental data from the literature on the difference on the fundamental gap of Si-NCs embedded in SiO_2 vs. Si_3N_4 yielded $l_{\Delta E}(\text{NC}) \approx 56$ Å. We introduced a dimensionality factor DF per reduced dimension (NWells $\xrightarrow{\times DF}$ NWires $\xrightarrow{\times DF}$ NCs) of $DF \approx 1/\sqrt{2}$, accounting for an increased number of defects at warped interfaces, yielding $l_{\Delta E}(\text{NWire}) \approx 40$ Å and matching $l_{\Delta E}(\text{NC}) \approx 56$ Å.

The ΔE in dns-Si by coating with or embedding in SiO_2 (Si_3N_4) induces a strong preference for electrons (holes) and thus to n(p)-type Si. Application to dns-Si would eliminate all issues of impurity doping – out-diffusion, clustering, self-purification, ionization at room and cryogenic temperatures, inelastic carrier scattering – and extend device miniaturization potentially down to the minimum size of Si crystallites of ca. 1.5 nm [19] along with much reduced bias voltages and heat loss.

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Appendix A: Evaluation of UPS Data

In our recent publication, we discussed the calibration of UPS-Scans and data extraction by local fitting of amorphous backgrounds using Si_3N_4 -embedded Si-NWells of 17 and 27 Å thickness in much detail [25].

Here, we just focus on one SiO_2 - and one Si_3N_4 -embedded sample for determining the valence band edge, its standard deviation over energy and associated local background fitting per scan to explain the principle. We further explain several plausibility tests as an additional means to arrive at the correct data. As examples, we pick UPS scans of sample N-15-D, comprising a 15 Å Si-NWell in Si_3N_4 , and of sample SOO-15, comprising a 12 Å Si-NWell in SiO_2 . Both scans have the lowest signal-to-noise ratio (SNR) against the background due to secondary electrons and $\text{SiO}_2/\text{Si}_3\text{N}_4$. This circumstance predestines both samples to demonstrate the UPS data filtering algorithm to obtain the valence band edge of buried Si-NWells. Fig. 11 shows the global UPS scans of both samples which were measured during beamtime 1 at the BaDElPh beamline at the Elettra Sincrotrone Trieste, Italy, *cf.* Fig. 7. Common parameters are the UV photon energy of $h\nu = 8.7$ eV and the background cps value of 1950 which was derived in the E_{kin} interval of $[h\nu; h\nu - 0.5]$ eV = $[8.7; 8.2]$ eV. This background cps value derived from the Si reference serves as calibration standard and thus sets the cps intercept for all UPS scans, see [25] for details.

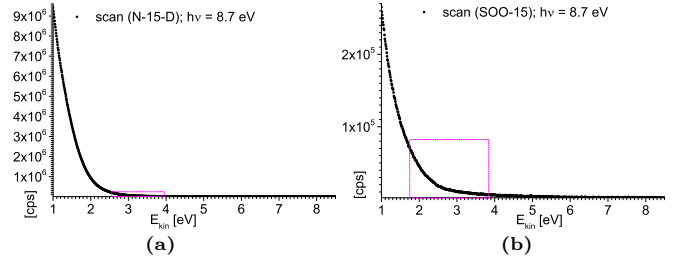


FIG. 11. Complete UPS scan of sample N-15-D (a) and SOO-15 (b), shown with respective region of interest marked as magenta frame. Photoexcitation energy was $h\nu = 8.7$ eV.

Below, we describe the algorithm to determine the valence band edge of a Si-NWell embedded in Si_3N_4 or SiO_2 . We begin by checking the UPS scan for regions of reasonably linear values with ≥ 15 points, equivalent to an E_{kin} range of 0.15 eV. The following steps are applied to every linear region found. We assign the number of points forming the linear region to N_{pts} . We then run a linear fit over the edge region, calculate its sum of residual squares (RS) $\sum [\text{data}(E_{\text{kin}}) - \text{fit}(E_{\text{kin}})]^2$ and its average cps value $\text{cps}_{\text{avg}} = 1/N_{\text{pts}} \sum \text{data}(E_{\text{kin}})$. With these three values, we can calculate the normalized RS (nRS) which takes into account the signal intensity and length of the linear region: $\text{nRS} = \text{RS} / [N_{\text{pts}} \text{cps}_{\text{avg}}]$. The linear region with the minimum nRS is the edge of the Si-NWell, subject to passing a number of plausibility tests lined out below. The intercept of the linear fit provides the E_{kin} value

which yields to the valence band top of the Si-NWell via $E_V = h\nu - E_{\text{kin}}$ (intercept). Fig. 12 shows the range of interest per UPS scan with all linear regions detected.

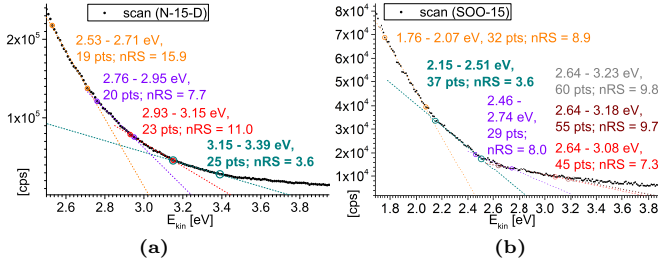


FIG. 12. Range of interest of UPS scans of sample N-15-D (a) and SOO-15 (b), shown with all linear region found as per definition in text. Range of E_{kin} , N_{pts} and nRS are shown per linear fit. Bold printed parameters in dark cyan and associated fit are valence band edge of embedded Si-NWell.

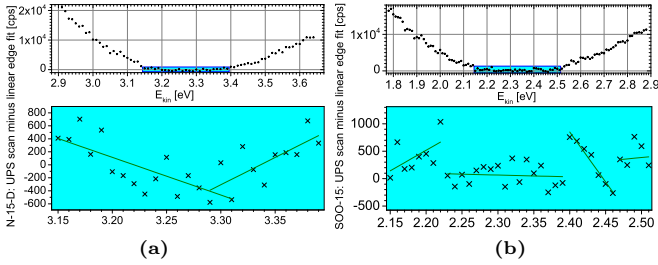


FIG. 13. Difference between UPS signal and linear fit to the edge region, shown in $\pm 1 E_{\text{kin}}$ (edge) interval for sample N-15-D (a) and SOO-15 (b); see text for details. The lower graphs show the edge region, including linear fits to local point groups with associated alignment. These fits are used for estimating the standard deviation of the valence band edge over E_{kin} .

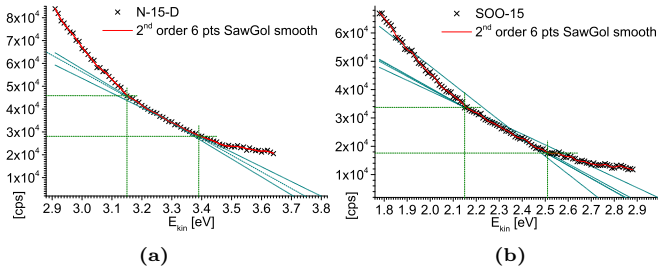


FIG. 14. UPS scan and its Sawitzky-Golay smoothed version of edge region $\pm 1 E_{\text{kin}}$ (edge) interval around it, shown for sample N-15-D (a) and SOO-15 (b). Thick dashed lines show valence band edge of Si-NWell, thin dashed lines show local linear fits to point groups showing local alignment within edge region. The latter are used to calculate the standard deviation of the edge over E_{kin} and thus E_V . Green dashed lines show cps and E_{kin} limits of edge region.

Next, we calculate the standard deviation $\sigma(E_{\text{kin}})$, using the difference between the UPS signal and its linear fit, *cf.* Fig. 13. Within the edge region, we group points with associated alignment. For these, we calculate local fits and determine their intercepts, *cf.* Fig.

14. The resulting E_{kin} values are used together with the value of the linear fit to the entire edge region to determine $\sigma(E_{\text{kin}}) = \sqrt{1/n \sum_{i=1}^n [\bar{E}_{\text{kin}} - E_{\text{kin}}(i)]^2}$ [48] and are shown as error bars of E_{ion} in Fig. 7. We note that – as samples were measured at $T = 300$ K – the minimum error bar for E_{kin} , E_{ion} is set to $k_B T = 0.026$ eV.

Since the algorithm on its own may yield a couple of possible solutions, we carry out additional plausibility tests. One of them is a combination of the smoothed UPS signal, an associated background fit and the interpolation of the resulting differential signal. First, we take the UPS data of the edge region plus one energy range as defined by the edge region above and below the edge (e.g. N-15-D has an edge from $E_{\text{kin}} = 3.15$ to 3.39 eV [25 pts], we now pick UPS data from 2.90 to 3.64 eV [25 + 25 + 25 = 75 pts]). To this data set, we apply a Sawitzky-Golay smoothing [50] over 6 points with a 2nd order polynomial as an effective means to *remove single point runaways without altering the spectral information*, *cf.* Fig. 14. Thereby, we get less noisy UPS data in the range of interest. This smoothed UPS data is used for a background fit, whereby we exclude the actual edge region ($E_{\text{kin}} = 3.15$ to 3.39 eV [25 pts] for sample N-15-D). Since higher order polynomials can be interpreted as the finite Taylor series of an exponential function, $\exp(x) = \sum_{i=0}^{\infty} [x^i / i!]$, we choose polynomials to fit the background and use the signal calibration intercept of 1950 cps as the coefficient for $i = 0$, see Fig. 15. While the coefficients of the x^i decrease from $i > 1$, qualitatively agreeing with the Taylor series of an exponential function, there is still some degree of freedom to adapt to local deviations. These are evident even after Sawitzky-Golay smoothing, *cf.* Figs. 12 and 15. An exponential behavior of the signal background originates from the Urbach tails of the amorphous dielectric [51], with additional contributions due to inelastic electron scattering.

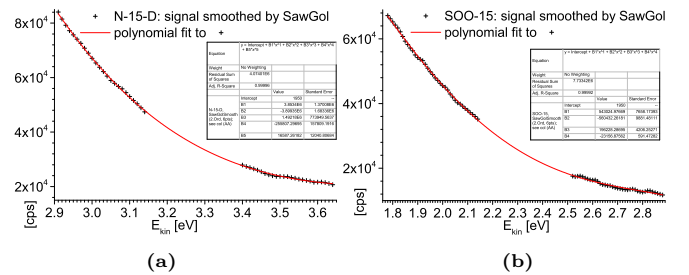


FIG. 15. Sawitzky-Golay smoothed data of UPS scan in $\pm 1 E_{\text{kin}}$ (edge) interval, shown for sample N-15-D (a) and SOO-15 (b), see text for details. The red line shows the polynomial fit to the smoothed UPS data which present the local surrounding of the edge region, serving as local background with lower SNR.

We now can calculate the difference between the smoothed UPS signal and the background fit where the edge region shows up above the noise, *cf.* Fig. 16. Due to the finite error in background fitting, there are local

deviations of the fit from data points in the local environment of the edge region which cannot be accounted for. As a consequence, the first few points outside the edge region tend to be further away from the background fit which can cause a dumping of the first few data points within the edge region. We also note that the fit does not account for an irregular, rather rapid low amplitude oscillation of the UPS signal. Hence, we have to look for positive signals – the edge signal occurs on top of the background – on a prolonged energy scale, ruling out rapid oscillations. To this end, we run a cubic B-Spline interpolation [48] on the differential signal which minimizes the oscillatory behavior, *cf.* Fig. 16.

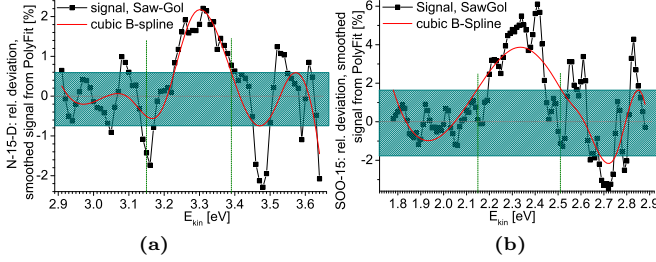


FIG. 16. Difference between Sawitzky-Golay smoothed UPS scan and background fit (*cf.* Fig. 15) of edge region ± 1 E_{kin} (edge) interval around it, shown together with a cubic B-Spline interpolation to minimize noise for sample N-15-D (a) and SOO-15 (b). Green dashed lines show E_{kin} limits of edge region. Hashed dark cyan area is a guide to noise limit.

Another plausibility test is given by measuring NWell samples of different d_{NWell} with a dielectric top layer of possibly constant thickness. Assuming that the dielectric top layer and its interface to the NWell have exactly the same thickness for all samples per dielectric type and all measurement conditions are constant, the signal intensity (cps) of the NWell is related to the layer thickness of the top dielectric layer $d_{\text{diel}}^{\text{top}}$ and d_{NWell} via $\text{cps}(d_{\text{NWell}}) \propto \exp(-d_{\text{diel}}^{\text{top}}/\lambda_{\text{imfp}})[1 - \exp(-d_{\text{NWell}}/\lambda_{\text{imfp}})]$, reducing to $\text{cps}(d_{\text{NWell}}) \propto 1 - \exp(-d_{\text{NWell}}/\lambda_{\text{imfp}})$ for $d_{\text{diel}}^{\text{top}} = \text{const.}$ The average inelastic mean free path of excited electrons is presented by λ_{imfp} . For brevity, we introduce one value

for Si-NWell and the respective dielectric. It is interesting to note that λ_{imfp} has been overestimated in UPS for several compounds [52, 53] since its widely used empirical description by Seah and Dench [54] was derived for many chemical elements and compounds for $h\nu \geq 150$ eV but only for three compound materials using $h\nu \leq 40$ eV. In a perfect world, we should see a cps increasing asymptotically with d_{NWell} . In reality, minor thickness deviations in particular of the top dielectric layer will soften this asymptotic behavior into a cps monotonically increasing with d_{NWell} , *cf.* Fig. 17.

As for UPS signal quality, we can state that the SNR is higher for Si-NWells embedded in SiO_2 vs. Si_3N_4 . This finding may come as a surprise as the average cps per edge region is higher for NWells embedded in Si_3N_4 vs. SiO_2 . However, the difference in valence band top energies is $E_V(\text{bulk-Si}) - E_V(\text{Si}_3\text{N}_4) = 1.78$ to 1.88 eV [25, 55] and $E_V(\text{bulk-Si}) - E_V(\text{SiO}_2) = 4.53$ to 4.54 eV [25, 55]. As a consequence, the Urbach tails of the amorphous Si_3N_4 layers deliver a significantly higher contribution to the UPS signal as opposed to SiO_2 , *cf.* Fig. 11. To add, the packing fraction of Si_3N_4 and the density of electronic defects is notably higher as compared to SiO_2 . This finding is also reflected in the bigger range of the valence band offset from Si_3N_4 to bulk-Si of ca. 0.1 eV as opposed to the value from SiO_2 to bulk-Si (0.01 eV).

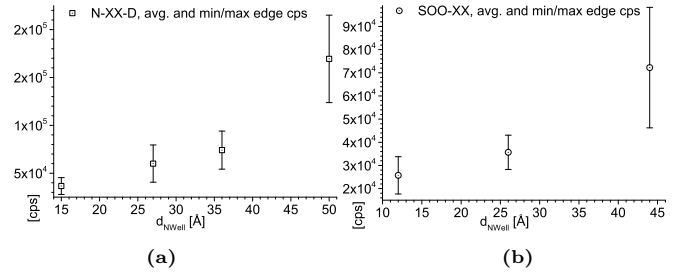


FIG. 17. Average value of cps of edge region per sample of beamtime 1, *cf.* 7 for results, for Si-NWells embedded in Si_3N_4 (a) and in SiO_2 (b). Error bars show mini- and maximum cps values per edge region.

- [1] G. L. Pearson and J. Bardeen, Phys. Rev. **17**, 865 (1949).
- [2] S. Koelling, O. Richard, H. Bender, M. Uematsu, A. Schulze, G. Zschaetzsch, M. Gilbert, and W. Vandervorst, Nano Letters **13**, 2458 (2013).
- [3] A. K. Kambham, A. Kumar, A. Florakis, and W. Vandervorst, Nanotechnology **24**, 275705 (2013).
- [4] R. Duffy, A. Ricchio, R. Murphy, G. Maxwell, R. Murphy, G. Piaszenski, N. Petkov, A. Hydes, D. O'Connell, C. Lyons, N. Kennedy, B. Sheehan, M. Schmidt, F. Crupi, J. D. Holmes, P. K. Hurley, J. Connolly, C. Hatem, and B. Long, J. Appl. Phys. **123**, 125701 (2018).
- [5] J. Heitmann, F. Müller, M. Zacharias, and U. Gösele, Adv. Mater. **17**, 795 (2005).
- [6] G. M. Dalpian and J. R. Chelikowsky, Phys. Rev. Lett. **96**, 226802 (2006).
- [7] A. R. Stegner, R. N. Pereira, R. Lechner, K. Klein, H. Wiggers, M. Stutzmann, and M. S. Brandt, Phys. Rev. B **80**, 165326 (2009).
- [8] T.-L. Chan, M. L. Tiago, E. Kaxiras, and J. R. Chelikowsky, Nano Lett. **8**, 596 (2008).
- [9] D. König, S. Gutsch, H. Gnaser, M. Wahl, M. Kopnarski, J. Göttlicher, R. Steininger, M. Zacharias, and D. Hiller, Sci. Rep. **5**, 09702 (2015).
- [10] R. N. Pereira, A. J. Almeida, A. R. Stegner, M. S. Brandt, and H. Wiggers, Phys. Rev. Lett. **108**, 126806 (2012).
- [11] D. Hiller, J. López-Vidrier, S. Gutsch, M. Zacharias,

