Fluorination Effects on the Structural Stability and Electronic Properties of sp^3 Type Silicon Nanotubes

Supplementary Material

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Exchange-correlation functional dependence of the stability analysis

For completeness, we present a comparative view of the stability analysis results obtained using Eq. 1 of the main text and the three exchange-correlation functional approximations considered. Results presented for the HSE functional approximation match those given in Fig. 2 of the main text. All functional approximations considered produce a similar qualitative picture with minor quantitative differences.

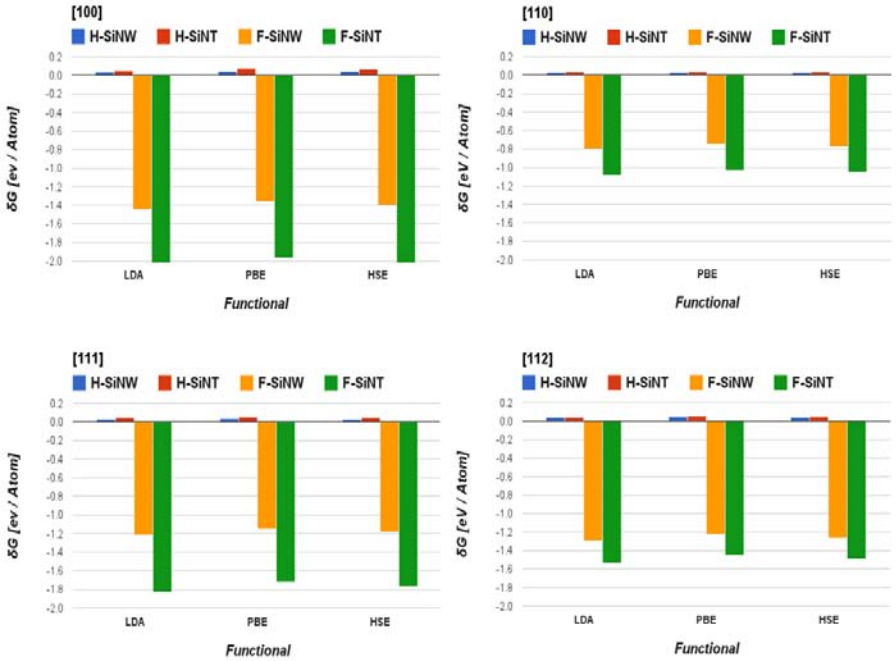

Figure S1: *Comparison between δG values obtained using the LDA, PBE, and HSE functional approximations and the 6-31G** basis set for the [100] (upper left panel),[110] (upper right panel), [111] (lower left panel), and [112] (lower right panel) fully fluorinated SiNWs and SiNTs considered. Result presented for the fully hydrogenated systems are adopted from Ref. 70 of the main text and are brought for comparison purposes.*

Exchange-correlation functional dependence of the bandgap analysis

For completeness, we present a comparative view of the bandgap results obtained using the three exchange-correlation functional approximations considered. Results presented for the HSE functional approximation match those given in Fig. 4 of the main text. As may be expected the HSE screened hybrid exchange-correlation density functional predicts higher bandgap values than those obtained using the LDA and PBE counterparts and generally speaking the PBE functional gives slightly larger values than those obtained using the LDA.

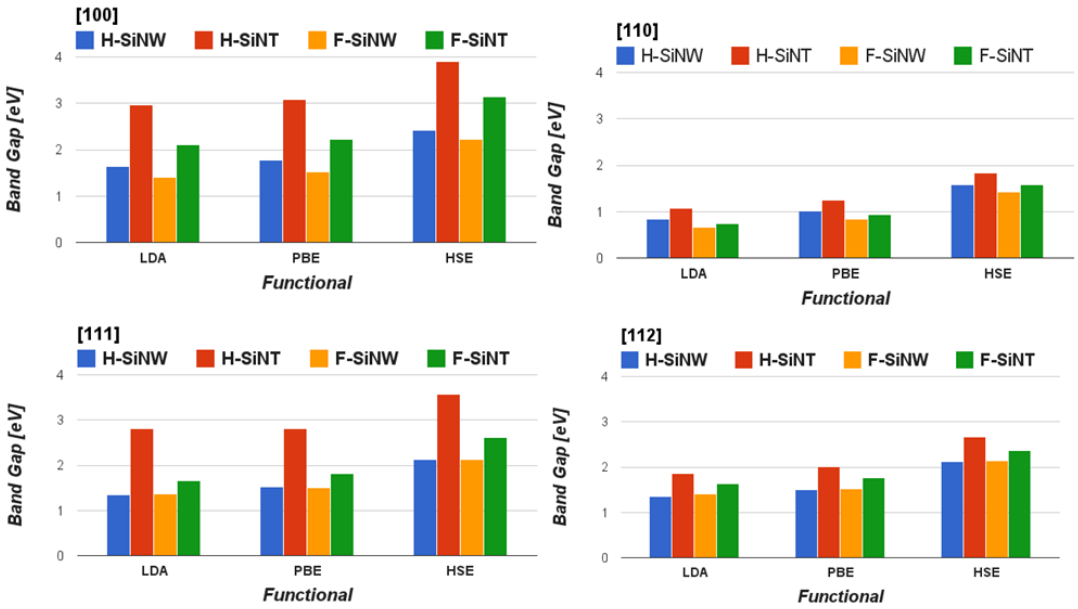

Figure S2: *Comparison between bandgap values obtained using the LDA, PBE, and HSE functional approximations and the 6-31G** basis set for the [100] (upper left panel), [110] (upper right panel), [111] (lower left panel), and [112] (lower right panel) fully fluorinated SiNWs and SiNTs considered. Result presented for the fully hydrogenated systems are adopted from Ref. 70 of the main text and are brought for comparison purposes.*

Evaluation of the performance of small basis sets

In order to reduce the computational burden, geometry optimization of the fluorinated [110] SiNW and SiNT has been performed at the LDA/3-21G and HSE/3-21G level of theory, respectively. This was followed by single-point calculations performed at the HSE/6-31G** level of theory using the obtained geometries of both structures for the evaluation of the relative stability and the bandgaps of these systems. We estimate the error that this procedure introduces by repeating it for the hydrogenated and fluorinated [100] SiNT and for bulk silicon where full geometry optimization at the HSE/6-31G** level of theory can be readily performed and the results can be compared to those obtained with lower level optimized structures. As can be seen, bandgap variations of up to 8% and δG errors of up to 40% may occur.

Level of Theory												
Functional / Basis-Set				Total Energy			Band Gap			δG		
Optimization		Single Point		Value [a.u]	Δ [a.u]	Change [%]	Value [eV]	Δ [eV]	Change [%]	Value [eV]	Δ [eV]	Change [%]
HSE	6-31G**	HSE	6-31G**	-12766.59521	0.000000	0.0000000	3.880488	0.000000	0.00	0.0674	0.0000	0.00
LDA	3-21G	HSE	6-31G**	-12766.54986	0.045349	-0.0003552	3.837642	-0.042846	-1.12	0.0757	0.0083	12.31
HSE	3-21G	HSE	6-31G**	-12766.58454	0.010669	-0.0000836	3.868426	-0.012062	-0.31	0.0702	0.0028	4.15

*Table S1: Comparison of the total energy, bandgap, and δG of the hydrogenated [100] SiNT as calculated at the HSE/6-31G** level of theory using optimized geometries obtained at the LDA/3-21G, HSE/3-21G, and HSE/6-31G** levels of theory.*

Level of Theory												
Functional / Basis-Set				Total Energy			Band Gap			δG		
Optimization		Single Point		Value [a.u]	Δ [a.u]	Change [%]	Value [eV]	Δ [eV]	Change [%]	Value [eV]	Δ [eV]	Change [%]
HSE	6-31G**	HSE	6-31G**	-18322.87922	0.000000	0.0000000	3.136538	0.000000	0.00	-2.0368	0.0000	0.00
LDA	3-21G	HSE	6-31G**	-18319.83038	3.048842	-0.0238814	3.392624	0.256086	8.16	-1.2254	0.8114	-39.84
HSE	3-21G	HSE	6-31G**	-18320.07487	2.804349	-0.0219663	3.297049	0.160511	5.12	-1.2891	0.7477	-36.71

*Table S2: Comparison of the total energy, bandgap, and δG of the fluorinated [100] SiNT as calculated at the HSE/6-31G** level of theory using optimized geometries obtained at the LDA/3-21G, HSE/3-21G, and HSE/6-31G** levels of theory.*

Level of Theory												
Functional / Basis-Set				Total Energy			Band Gap			δG		
Optimization		Single Point		Value [a.u]	Δ [a.u]	Change [%]	Value [eV]	Δ [eV]	Change [%]	Value [eV]	Δ [eV]	Change [%]
HSE	6-31G**	HSE	6-31G**	-578.8254042	0.000000	0.0000000	1.227498	0.000000	0.00	-0.2160	0.0000	0.00
LDA	3-21G	HSE	6-31G**	-578.825198	-0.000206	0.0000356	1.192479	0.035019	0.25	-0.2159	-0.0001	0.05
HSE	3-21G	HSE	6-31G**	-578.8254035	-0.000001	0.0000001	1.224381	0.003117	2.85	-0.2160	0.0000	0.00

*Table S3: Comparison of the total energy, bandgap, and δG of bulk silicon as calculated at the HSE/6-31G** level of theory using optimized geometries obtained at the LDA/3-21G, HSE/3-21G, and HSE/6-31G** levels of theory.*

Systems coordinate

Optimized geometries (coordinates given in units of Å) of all SiNWs and SiNTs studied obtained using the LDA, PBE, and HSE functional approximations with the 6-31G** atomic centered Gaussian basis set (the 3-21G basis set was used for the [110] SiNT and SiNW) are presented in supplementary Excel worksheet.