Supporting Information

Metallic-like bonding in plasma-born silicon nanocrystals for nanoscale bandgap engineering

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Abstract

Based on *ab initio* molecular dynamics simulations, we show that small nanoclusters of about 1nm size spontaneously generated in a low-temperature silane plasma do not possess tetrahedral structures, but are ultrastable. Apparently small differences in cluster structure result in substantial modifications in their electric, magnetic, and optical properties without the need for any dopants. Their nontetrahedral geometries notably lead to electron deficient bonds that introduce efficient electron delocalization that strongly resembles the one of a homogeneous electron gas leading to metallic-like bonding within a semiconductor nanocrystal. As a result, pure hydrogenated silicon clusters that form by self-assembly in a plasma reactor possess optical gaps covering most of the solar spectrum from 1.0 eV to 5.2 eV depending simply on their structure and, in turn, on their degree of electron delocalization. This feature makes them ideal candidates for future bandgap engineering not only for photovoltaics, but also for many nano-electronic devices employing nothing else but silicon and hydrogen atoms.

Cartesian coordinates of the $Si_{19}H_{12}$ isomer D after MP2/6-311++G(d,p) optimization

Si -0.97871 -0.69367 2.72395

Si -2.17782 1.13100 1.78639

Si -0.61780 2.68206 0.93356

Si 1.51409 2.00584 1.74546

Si 1.33704 -0.18319 2.63156

Si -1.32485 -2.55830 1.32264

Si -3.57038 0.47237 0.00455

Si -0.73877 2.61278 -1.44062

Si 2.93131 1.85340 -0.10200

Si 2.49204 -1.64381 1.18345

Si 1.25921 1.40464 -1.67144

Si -1.61599 -1.00391 -2.00989

Si -2.87936 -1.77085 -0.23711

Si 0.68319 -2.64132 0.04600

Si 2.17028 -0.55142 -2.51620

Si 0.43077 -2.21637 -2.31585

Si -2.53680 1.18449 -1.99597

Si 0.10096 -0.38485 -0.50620

Si 3.52404 -0.39623 -0.50944

H -1.38754 -0.88628 4.14259

H -2.99104 1.76157 2.86255

H -0.92234 4.04849 1.44150

H 1.97318 2.95953 2.78942

H 1.89104 -0.19875 4.01389

H -1.67586 -3.83590 1.98672

H -5.01377 0.72842 0.22502

H -0.76928 3.94646 -2.09622

H 3.88748 2.95137 -0.37517

H 3.38993 -2.60644 1.86887

H -3.39099 1.65023 -3.11450

H 4.94823 -0.73343 -0.74300