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# Communication: Visualization and Spectroscopy of Defects Induced by Dehydrogenation in Individual Silicon Nanocrystals

Dmitry A. Kislitsyn  
*University of Oregon*


Jon M. Mills  
*University of Oregon*

Vancho Kocevski  
*Uppsala University*

Sheng-Kuei Chiu  
*Portland State University*

William J.I. DeBenedetti  
*Portland State University*

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## Authors

Dmitry A. Kislitsyn, Jon M. Mills, Vancho Kocevski, Sheng-Kuei Chiu, William J.I. DeBenedetti, Christian F. Gervasi, Benjamin N. Taber, Ariel E. Rosenfield, Olle Eriksson, Ján Ruzs, Andrea Mitchell Goforth, and George V. Nazin

## Communication: Visualization and spectroscopy of defects induced by dehydrogenation in individual silicon nanocrystals

Dmitry A. Kislitsyn,<sup>1</sup> Jon M. Mills,<sup>1</sup> Vancho Kocevski,<sup>2,a)</sup> Sheng-Kuei Chiu,<sup>3</sup> William J. I. DeBenedetti,<sup>3,b)</sup> Christian F. Gervasi,<sup>1</sup> Benjamin N. Taber,<sup>1</sup> Ariel E. Rosenfield,<sup>1</sup> Olle Eriksson,<sup>2</sup> Ján Ruzs,<sup>2</sup> Andrea M. Goforth,<sup>3</sup> and George V. Nazin<sup>1,c)</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Materials Science Institute, Oregon Center for Optical, Molecular and Quantum Science, University of Oregon, 1253 University of Oregon, Eugene, Oregon 97403, USA

<sup>2</sup>Department of Physics and Astronomy, Uppsala University, P.O. Box 516, SE-751 20 Uppsala, Sweden

<sup>3</sup>Department of Chemistry, Portland State University, Portland, Oregon 97201, USA

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We present results of a scanning tunneling spectroscopy (STS) study of the impact of dehydrogenation on the electronic structures of hydrogen-passivated silicon nanocrystals (SiNCs) supported on the Au(111) surface. Gradual dehydrogenation is achieved by injecting high-energy electrons into individual SiNCs, which results, initially, in reduction of the electronic bandgap, and eventually produces midgap electronic states. We use theoretical calculations to show that the STS spectra of midgap states are consistent with the presence of silicon dangling bonds, which are found in different charge states. Our calculations also suggest that the observed initial reduction of the electronic bandgap is attributable to the SiNC surface reconstruction induced by conversion of surface dihydrides to monohydrides due to hydrogen desorption. Our results thus provide the first visualization of the SiNC electronic structure evolution induced by dehydrogenation and provide direct evidence for the existence of diverse dangling bond states on the SiNC surfaces. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4954833>]

Silicon nanocrystals (SiNCs) have recently attracted a great deal of attention as a promising photophysical material with applications in photovoltaics,<sup>1–4</sup> light-emitting devices,<sup>5,6</sup> and biological tagging.<sup>7,8</sup> SiNCs offer the advantages of low toxicity and robust surface passivation involving, for example, formation of covalent Si–C bonds.<sup>9,10</sup> Importantly, the optical properties of SiNCs are strongly dependent on their dimensions, with a dramatic brightening of radiative transitions observed for sufficiently small SiNCs,<sup>11–14</sup> a consequence of changes in the electronic structure leading to the relaxation of the momentum conservation rules known to suppress radiative transitions in bulk silicon.<sup>15–17</sup> While the ultra-small size of SiNCs is essential for optical applications, the resulting large surface to volume ratio means that SiNCs are very susceptible to their chemical environment and the presence of defects on their surfaces.

A wide variety of approaches for controlling the SiNC surface chemistry have been developed, including passivation with organic molecules<sup>18–20</sup> as well as oxidation.<sup>21–23</sup> One of the most common defects found at SiNC surfaces, regardless of the surface passivation technique, is the silicon dangling bond (DB). For example, DBs exist at Si–SiO<sub>2</sub> interfaces<sup>24,25</sup> and at the surfaces of alkyl-passivated SiNCs.<sup>26</sup> DBs can also be produced by mild oxidation of hydrogenated SiNCs<sup>27</sup> and by exposure to ultra-violet radiation.<sup>28,29</sup> DBs

are known to act as non-radiative recombination centers leading to de-excitation of electronically excited states.<sup>30</sup> In contrast, charged DBs have been found to serve as radiative recombination centers in SiNCs with sufficiently large gap energies.<sup>31</sup> Further, depending on their charge and local stress, DBs at the surface of oxidized SiNCs were predicted to be capable of inducing intermittency in the SiNC photoluminescence.<sup>32</sup> However, the varied impact of the different DB charge states on SiNC photophysics, especially in the context of the different possible surface passivations, remains to be fully addressed.

While the DB-induced electronic states in SiNCs have received a great deal of attention,<sup>33,34</sup> conventional experimental techniques are often limited to ensemble-level measurements, where the variations in DBs structures and local environments are averaged out.<sup>32</sup> A promising approach for addressing individual defects on SiNC surfaces is scanning tunneling microscopy (STM), which has proven to be uniquely suited for studies of individual DBs on silicon single-crystal surfaces.<sup>35–38</sup> Further, STM enables scanning tunneling spectroscopy (STS),<sup>39</sup> a technique that has been used to visualize the electronic structures of individual DBs,<sup>36</sup> as well as complex structures composed of many DBs.<sup>38,40–42</sup> However, until now, no STM/STS results describing DBs on SiNC surfaces have been reported, even though STS has been used to study quantum-confined,<sup>43</sup> as well as defect-induced,<sup>44</sup> electronic states in individual SiNCs.

In this report, we describe, for the first time, spatially resolved STS mapping of charged and neutral DB defects created by current-induced dehydrogenation of individual hydrogen-terminated SiNCs. SiNCs were sprayed onto an

<sup>a)</sup>Present address: Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA.

<sup>b)</sup>Present address: Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA.

<sup>c)</sup>Author to whom correspondence should be addressed. Electronic mail: [gnazin@uoregon.edu](mailto:gnazin@uoregon.edu)

Au(111) substrate held in high-vacuum conditions and studied using an ultra-high vacuum (UHV) cryogenic scanning tunneling microscope (STM)<sup>45</sup> (see the supplementary material for further experimental details).<sup>46</sup> The deposited SiNCs formed a near-monolayer film on Au(111), with individual SiNCs appearing as protrusions with lateral dimensions of 2–4 nm, as shown in Fig. 1(a). To characterize the electronic structures of individual SiNCs, we recorded the differential tunneling conductance (dI/dV) as a function of the

applied bias voltage and location. Thus produced dI/dV (STS) spectra are interpreted as energy-dependent local density of states (LDOSs) spectra with the bias voltage giving the energy scale.<sup>46</sup> Thirty individual SiNCs were studied in this fashion, as detailed in the following for one representative SiNC [Fig. 1(b)].

STM-induced dehydrogenation of single-crystal silicon surfaces has been studied in detail in the past two decades, with significant insights achieved into the physical mechanisms of hydrogen desorption<sup>47</sup> and the electronic structures of dehydrogenated areas.<sup>48,49</sup> Generally, elevated bias voltages are required, with the exact magnitude of the bias voltage and tunneling current strongly affecting the mode of desorption, which can involve either direct electronic or multiple-vibrational excitation of the Si–H bond via tunneling electrons.<sup>50</sup> This process is thus referred to as electron-stimulated desorption (ESD).<sup>51</sup> Depending on the chosen parameters of the voltage pulse, hydrogen desorption can either occur one atom at a time or involve several atoms.<sup>52</sup> In our experiments, in order to induce desorption of hydrogen, we applied voltages in the range of ~2.5–3 V, chosen to be sufficiently low to prevent extensive changes to the SiNC surfaces. For single-crystal silicon surfaces, the desorption of hydrogen at such bias voltages was previously attributed to multiple vibrational excitation via electrons tunneling through the  $\sigma^*$  (Si–H) unoccupied orbital.<sup>47,50,53</sup>

Before ESD was induced by STM, LDOS spectra measured at different locations on “pristine” SiNCs showed progressions of electronic states with electronic bandgaps closely matching those predicted by theoretical calculations.<sup>44</sup> For example, in the case of the chosen representative SiNC from Fig. 1(b), the apparent bandgap of ~2.5 eV was found, formed by an occupied state  $H_1^{A1}$  and an unoccupied state  $E_1^{A1}$  in curve  $A_1$  of Fig. 1(c) [we define the bandgap as the voltage difference between the onsets of conduction]. This bandgap value is expected to be larger than the real bandgap due to the finite bias voltage drop inside the NC: in a biased tunnel junction involving a NC, a finite voltage drop occurs across the NC volume shifting the energy of all electronic states by  $\alpha eV_B$  (where  $V_B$  is the bias voltage, and  $\alpha < 1$  is a function of the NC dimensions and dielectric susceptibility). This means that the voltage corresponding to the onset of tunneling for a state with energy  $E_S$  (this energy is measured with respect to the Fermi level of the sample and can be positive or negative) can be then calculated as  $E_S/(1 - \alpha)$ .<sup>54,55</sup> Here, we roughly estimate  $\alpha$  to be ~0.2 (as explained further in the supplementary material, Figs. S1 and S2),<sup>46</sup> which gives a real bandgap of  $2.5 \text{ eV} \times 0.8 = 2 \text{ eV}$ . This value is consistent with that obtained from density functional theory calculations,<sup>56</sup> as illustrated by the LDOS spectrum FH in Fig. 1(e),<sup>16</sup> calculated (taking into account the finite value of  $\alpha$ ) for a model hydrogen-passivated SiNC shown in Fig. 1(d). (The diameter of this SiNC is ~2.2 nm, which matches that extracted from Fig. 1(b) after correcting for the tip convolution effects, as explained in Ref. 44.) Our calculations show that each one of the LDOS peaks is comprised of several quantum-confined electronic states formed from Bloch states associated with different electronic valleys in the Brillouin zone of bulk silicon.<sup>16,17,44</sup> Due to their close energy spacing,

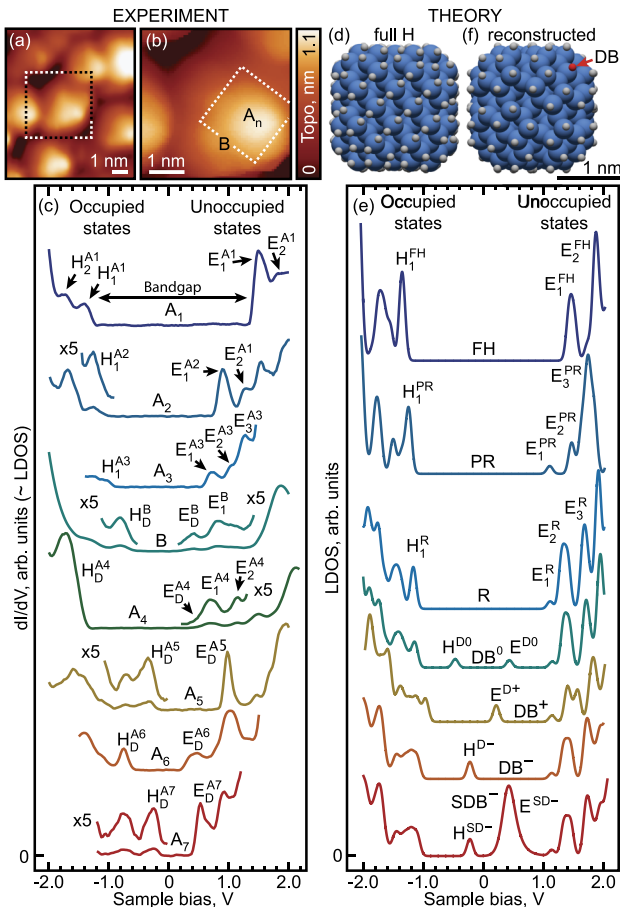


FIG. 1. STM/STS characterization and theoretical modeling of SiNCs. (a) Topography of an area showing several SiNCs. (b) Enlarged topography corresponding to the dashed square in (a). (c) STS spectra measured at locations A and B marked in (b). Curves  $A_1$ – $A_7$  show transformations of the LDOS spectra in location A with successive application of bias voltage pulses (see text for details). States marked “H” and “E” correspond to occupied and unoccupied states, respectively, except for features caused by “reverse” tunneling, as described in the text. Spectra are offset for clarity. (d) Model of fully hydrogen-passivated SiNC (composition  $H_{172}Si_{239}$ ). (e) Theoretical LDOS spectra averaged over the entire NC surface. Spectra FH and R correspond to the fully hydrogen-passivated SiNC in (d), and to the completely reconstructed SiNC in (f), respectively. Spectrum PR corresponds to a partially reconstructed version of SiNC from (d), with 33% of dihydrides converted to monohydride dimers.  $DB^0$ ,  $DB^+$ , and  $DB^-$  are spectra of the completely reconstructed model with an additional DB and charges 0,  $+e$ , and  $-e$ , correspondingly. Spectrum  $SDB^-$  illustrates the effect of “bipolar” tunneling on STS of electronic states with LDOS described by curve  $DB^-$ . Spectra were Gaussian-broadened by 100 mV, with onsets corresponding to the discrete energy levels obtained from DFT calculations. All spectra were modeled assuming a finite bias voltage drop inside the SiNC (see text). (f) Model of a monohydride-passivated SiNC (composition  $H_{100}Si_{239}$ ) with  $2 \times 1:H$  surface reconstruction and silicon core identical to that of (d). Location of the DB is also indicated. For further details of the measurements including spatial drift estimates, see the supplementary material.<sup>46</sup>

these states are not completely resolved in our LDOS spectra, where electronic peaks are significantly broadened (typical peak width of  $\sim 200$  mV) by coupling of tunneling electrons to vibrational excitations.<sup>57</sup>

For each “pristine” SiNC, after recording LDOS spectra at several representative locations, we attempted to induce ESD by applying higher bias voltages (2.5–3 V) and quantified the results at each step by detailed mapping of LDOS in order to establish the presence of DBs. For the SiNC from Fig. 1(b), application of higher bias voltages resulted in the formation of new peaks  $H_n^{A2}$  and  $E_n^{A2}$  [curve  $A_2$  of Fig. 1(c)], and a notable reduction in the apparent bandgap. Importantly, peaks  $H_n^{A2}$  and  $E_n^{A2}$  are delocalized over the entire SiNC surface (Fig. S3)<sup>46</sup> suggesting that they do not correspond to localized defects. This behaviour can be explained by reconstruction of the SiNC surface induced by the hydrogen desorption. Specifically, while a significant portion of Si surface atoms in the as-synthesized SiNCs are passivated with dihydride groups (Fig. S4),<sup>46</sup> hydrogen desorption from neighbouring  $\text{SiH}_2$  can lead to their dimerization analogous to the  $2 \times 1$ :H reconstruction observed on the Si(100) surfaces [see Fig. 1(f) for a model of a fully reconstructed monohydride-only SiNC with the same Si core as in Fig. 1(d)]. The DBs at the neighbouring Si atoms form  $\pi$ -electronic bonds producing delocalized states with an electronic bandgap reduced by an amount dependent on the extent of surface reconstruction, as shown by curves PR and R in Fig. 1(e) for the partially and fully reconstructed models of the SiNC. Indeed, curve  $A_2$  of Fig. 1(c) likely corresponds to a partially reconstructed SiNC because further ESD pulses on this SiNC resulted in additional reduction of the bandgap [curve  $A_3$  of Fig. 1(c)], with electronic peaks  $H_n^{A3}$  and  $E_n^{A3}$  delocalized across the SiNC surface (Fig. 2).

With additional ESD pulses, however, spatially localized midgap LDOS features, attributable to defects, appear on the SiNC surface, with three representative examples demonstrated by curves B,  $A_4$ , and  $A_5$  in Fig. 1(c). Specifically, curves B and  $A_5$  show pairs of midgap peaks ( $H_D^B$  and  $E_D^B$ , as well as  $H_D^{A5}$  and  $E_D^{A5}$ , respectively), while curve  $A_4$  shows only one midgap peak  $E_D^{A4}$ . Intriguingly, we found that inter-conversion between the different defect types was possible. In particular, defects B and  $A_4$  in Fig. 1(c) could be spontaneously converted to defects of type  $A_5$  under typical tunneling conditions (bias voltage  $\sim 2$  V). For example, curve  $A_5$  was recorded at the same location as  $A_4$  immediately

after a positive bias voltage of 2.4 V was applied. Further transformation could be induced by applying voltages of  $\sim -1.5$  V with the resulting LDOS spectrum corresponding to curve  $A_6$ , which is very similar to that of defect B measured earlier at location B [Fig. 1(b), and curve B in Fig. 1(c)]. Finally, the local spectrum at location A was converted from  $A_6$  to  $A_7$  [Fig. 1(c)] showing a shape qualitatively similar to that of  $A_5$  (the origin of peak shifts in curve  $A_7$  versus  $A_5$  is explained in the following).

The spectral characteristics of the observed midgap states, as well as the possibility for their inter-conversion, can be explained in the most straightforward manner by attributing these midgap states to DB defects, as discussed further below. Some of the described peaks, however, are produced by different tunneling processes rather than distinctly different electronic states, as can be seen from the dramatically different spatial behaviours of these peaks. For example, for curve  $A_7$  in Fig. 1(c), peak  $E_D^{A7}$  shows substantial onset voltage variations across the NC, while peak  $H_D^{A7}$  and other unoccupied states appear at nearly the same voltages in all locations, as illustrated in Fig. 3(b). This is despite the fact that peaks  $E_D^{A7}$  and  $H_D^{A7}$  are closely co-localized in the vicinity of location A [Fig. 1(b)], as shown by LDOS maps of Figs. 3(b), 3(d), and 3(e) and should therefore correspond to the same defect. The described asymmetry in onset voltage variations is analogous to those reported for the “bipolar” tunneling investigated previously for a variety of molecular systems.<sup>54,55,58</sup> Bipolar tunneling is a consequence of the fact that in a biased tunnel junction involving a NC, a finite voltage drop occurs across the NC volume, which, in addition to the “direct” type of tunneling described earlier [Fig. S1(a)]<sup>46</sup> with the onset voltage of  $E_S/(1 - \alpha)$ , also leads to “reverse” tunneling [Fig. S1(b)]<sup>46</sup> with the onset voltage of  $-E_S/\alpha$  (where  $E_S$  and  $\alpha$  were defined previously).<sup>54,55</sup> Voltage onsets for both “direct” and “reverse” tunneling (at opposite bias polarities) vary with tip position on the NC surface due to the sensitivity of  $\alpha$  to the geometry of the junction,<sup>54</sup> as shown in Fig. S2.<sup>46</sup> Nevertheless, because  $\alpha$  is typically small [ $\alpha \approx 0.2$  for peaks  $E_D^{A7}$  and  $H_D^{A7}$ ], expression  $E_S/(1 - \alpha)$  varies significantly less than  $E_S/\alpha$ , which explains the differences in the onset voltage variations for peaks  $E_D^{A7}$  and  $H_D^{A7}$  in Fig. 3(b). In addition, the spectral lineshapes of the two types of bipolar peaks are affected by the asymmetry in the tip-NC and NC-substrate tunneling rates (the former is lower than the latter), which tends to produce notably more intense and sharper peaks at the onset of conduction for the “reverse” tunneling process.<sup>54,59</sup> This is indeed observed for peak  $E_D^{A7}$ , which, together with its spatial voltage onset variations, suggests that this peak corresponds to the “reverse” tunneling process, while peak  $H_D^{A7}$  corresponds to “direct” tunneling. The effect of “bipolar” tunneling on the  $dI/dV$  curves is illustrated by curve  $\text{SDB}^-$  in Fig. 1(e) [obtained from curve  $\text{DB}^-$  by assuming  $\alpha \approx 0.2$ , and a finite rate for tunneling between SiNC and substrate], where peaks  $E_D^{\text{SDB}^-}$  and  $H_D^{\text{SDB}^-}$  correspond to the “reverse” and “direct” tunneling processes, respectively, analogously to peaks  $E_D^{A7}$  and  $H_D^{A7}$  (we note that the overtone structures of peaks  $E_D^{A7}$  and  $H_D^{A7}$  were not included in the modelling).

Analysis similar to that presented above for peaks  $E_D^{A7}$  and  $H_D^{A7}$ , when applied to the rest of the spectra in Fig. 1(c),

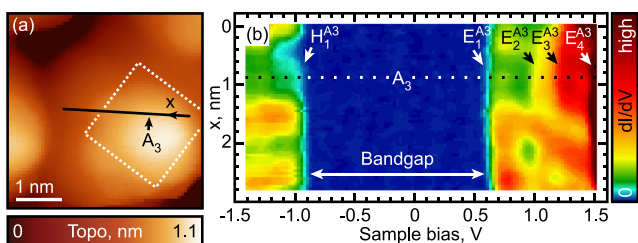


FIG. 2. Spatial mapping of LDOS for the SiNC from Fig. 1(b) after (partial) dehydrogenation, but before DBs were generated. (a) Topography of the SiNC. (b) LDOS as a function of the bias voltage and position  $x$  along the path (solid line) shown in (a).

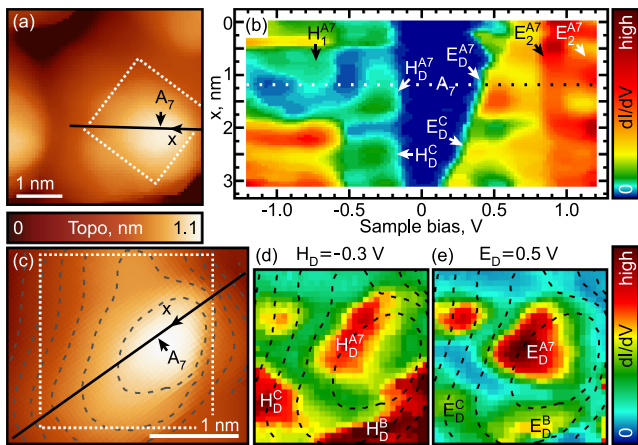


FIG. 3. Spatial mapping of LDOS for the SiNC from Fig. 1(b) after DBs were generated. ((a) and (c)) STM topographic images of the SiNC. (b) LDOS as a function of the bias voltage and position  $x$  along the path (solid line) shown in (a) and (c). ((d) and (e)) 2-D LDOS maps for voltages corresponding to  $H_D$ ,  $E_D$  LDOS peaks marked in (b). Mapping area corresponds to the dotted squares in (a) and (c). Dashed lines are topographic contours from (c).

suggests that peaks  $E_D^B$ ,  $E_D^{A4}$ ,  $H_D^{A5}$ ,  $E_D^{A6}$ , and  $H_D^{A7}$  are all produced by “direct” tunneling, while peaks  $H_D^B$ ,  $H_D^{A4}$ ,  $E_D^{A5}$ ,  $H_D^{A6}$ , and  $E_D^{A7}$  should correspond to “reverse” tunneling. This assignment results in a clear distinction between the curves B,  $A_4$ , and  $A_6$  versus the curves  $A_5$  and  $A_7$ : while only unoccupied midgap states are distinguishable in curves B,  $A_4$ , and  $A_6$ , in curves  $A_5$  and  $A_7$ , only occupied midgap states are clearly observable. This assignment offers an explanation for the inter-conversion between the different types of spectra in Fig. 1(c). For example, the transitions from spectrum  $A_4$  to spectrum  $A_5$  and spectrum  $A_6$  to spectrum  $A_7$  were induced with positive voltages (this corresponds to electrons being added to the SiNC), and resulted in disappearance of unoccupied midgap states  $E_D^{A4}$  and  $E_D^{A6}$ , as well as appearance of occupied midgap states  $H_D^{A5}$  and  $H_D^{A7}$ . Similar spectral transformations in individual atoms<sup>60</sup> and molecules<sup>61</sup> have been attributed to electron trapping. This suggests that individual electrons are likely being trapped in states  $E_D^{A4}$  and  $E_D^{A6}$ , which results in appearance of trap states  $H_D^{A5}$  and  $H_D^{A7}$ . On the other hand, transition from  $A_5$  to  $A_6$  occurred when negative voltage was applied, and the corresponding spectral changes may be attributed to extraction of an electron from state  $H_D^{A5}$ , which is thereby converted to state  $E_D^{A6}$ , similarly to the de-trapping process described for molecules.<sup>61</sup>

The local charging of SiNC described above is consistent with the presence of DBs, which have been shown to exist in different charge states on silicon surfaces,<sup>36,38,62</sup> and is also consistent with the expectation that desorption of hydrogen atoms should lead to the creation of DBs. In addition, DBs appear deep in the silicon electronic bandgap, similarly to the states appearing near zero bias in Fig. 1(c). This similarity is illustrated by the theoretically calculated LDOS for DBs in different charge states on the surfaces of model SiNCs [curves DB,<sup>0</sup> DB<sup>+</sup>, and DB<sup>-</sup> in Fig. 1(e)]. For example, curve  $A_4$  only shows an unoccupied midgap state, consistent with curve DB<sup>+</sup>, while curve  $A_5$  only shows an occupied state, consistent with curve DB<sup>-</sup>. Assignment of spectra B,  $A_6$ , and  $A_7$  is less certain because the “reverse” tunneling LDOS features

seen in these curves may be obscuring “direct” tunneling features that would be expected for the neutral DB (curve DB<sup>0</sup>). The similarity of spectra  $A_5$  and  $A_7$ , however, suggests that  $A_7$  may also be associated with DB<sup>-</sup>. Curves B and  $A_6$  are relatively similar and, given their distinct spectral shapes, may be attributed to a neutral state, even though they may also be variants of  $A_4$  (DB<sup>+</sup> state) corresponding to slightly different local surface structures. We note that similar spectral features attributable to charged and neutral DBs were found in other studied SiNCs (Fig. S5).<sup>46</sup>

In conclusion, our work shows that when sufficiently high-energy electrons are injected into SiNCs, dramatic changes in the SiNC electronic structures are observed: gradual shrinking of the SiNC electronic bandgap occurs initially and is eventually followed by the appearance of localized states deep in the electronic bandgap. We find that these midgap states can exist in different inter-convertible charge configurations. These observations are consistent with the hypothesis that high-energy electron injection can lead to dehydrogenation of the SiNC surfaces, resulting in surface reconstruction driven by conversion of surface dihydride species to monohydride groups, and creation of dangling bonds in different charge states. These findings provide a direct visualization of possible scenarios for defect generation in SiNC-based optical and opto-electronic applications, where photo-generated charge carriers with sufficient energies could induce creation of surface defects.

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