

## Size-Dependent Donor and Acceptor States in Codoped Si Nanocrystals Studied by Scanning Tunneling Spectroscopy

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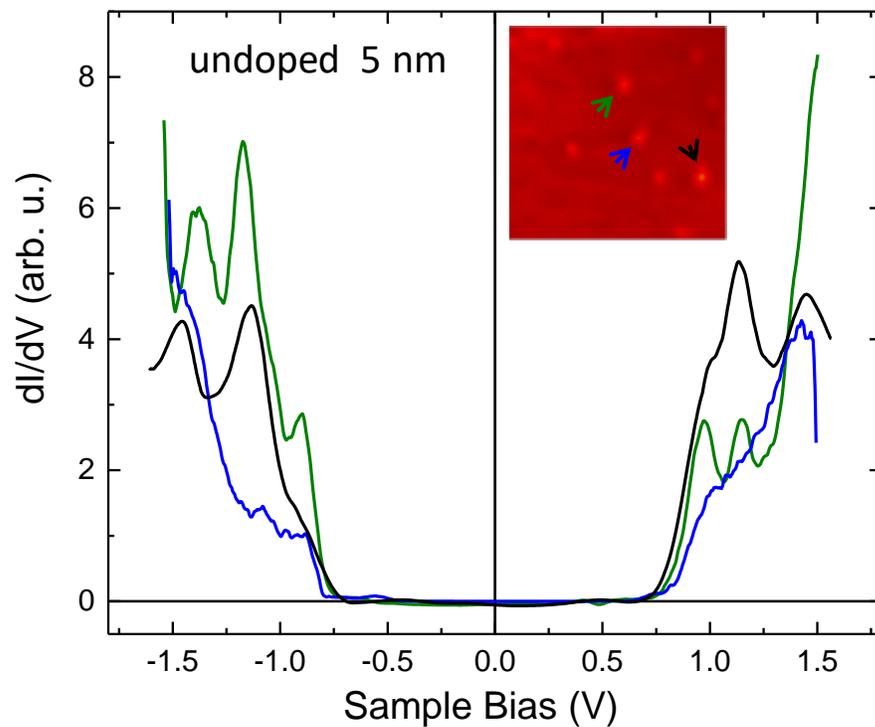
### Supplementary Information

#### Preparation procedure of B and P codoped Si-NCs

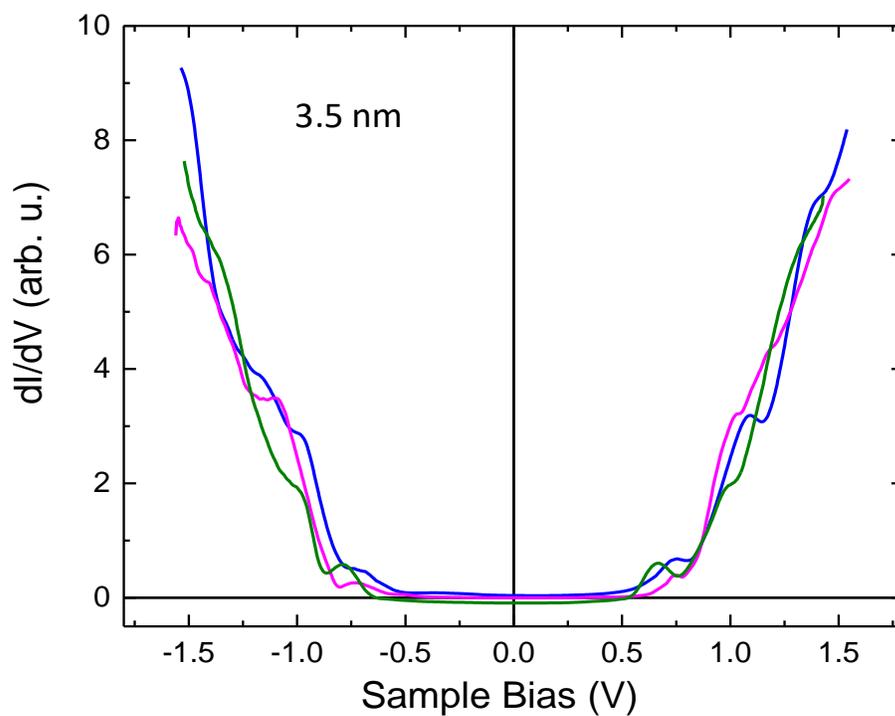
Si-rich borophosphosilicate glass films (~10 μm in thickness) were first deposited on thin stainless steel plates by cosputtering Si, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> in an rf-sputtering apparatus. The films were peeled from the plates and then annealed at 6 different temperatures (1100, 1150, 1175, 1200 and 1250 °C) in a N<sub>2</sub> gas atmosphere for 30 min to grow Si-NCs with different sizes in BPSG matrices. During the growth of Si-NCs, B and P atoms are incorporated into Si-NCs from BPSG matrices. Codoped Si-NCs were liberated from BPSG matrices by etching in HF solutions (46 wt %) for 1 h. Isolated Si-NCs were then transferred to methanol. For the preparation of undoped Si-NCs, Si-rich SiO<sub>2</sub> films were sputter-deposited and then annealed at 1200 °C. Undoped NCs were liberated from the matrices using the same etching process as that of codoped Si-NCs. It should be noted, however, that undoped Si-NCs are not dispersed in methanol and therefore the agglomerates tend to precipitate. All the processes were performed in an ordinary laboratory environment.

#### Additional tunneling spectra

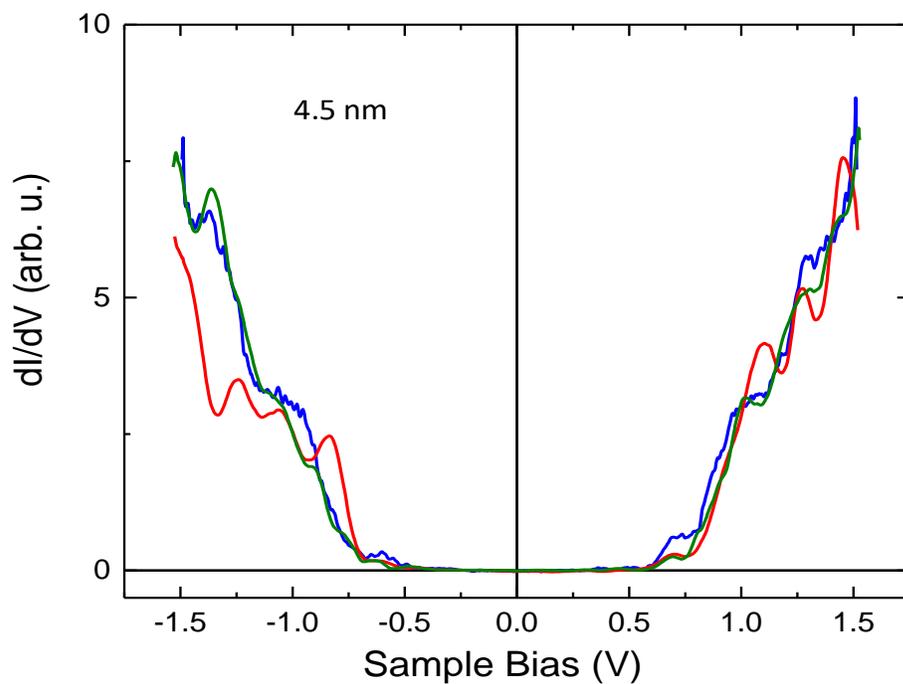
In the following, we present additional tunneling spectra to which we refer in the main text.



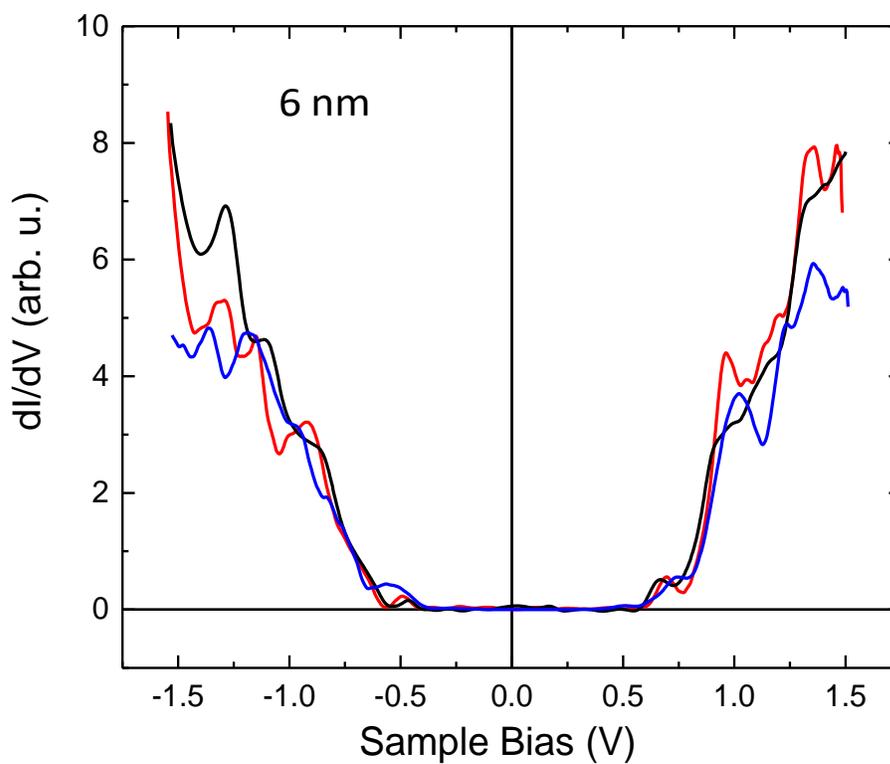
**Fig. S1.** Tunneling spectra measured on 5 nm undoped Si-NCs. The spectra were taken on the NCs marked, with corresponding colors, in the  $75 \times 75 \text{ nm}^2$  topographic (inset).



**Fig. S2.** Tunneling spectra measured on codoped Si-NCs, 3.5 nm in diameter.



**Fig. S3.** Tunneling spectra measured on codoped Si-NCs, 4.5 nm in diameter.



**Fig. S4.** Tunneling spectra measured on codoped Si-NCs, 6. nm in diameter.

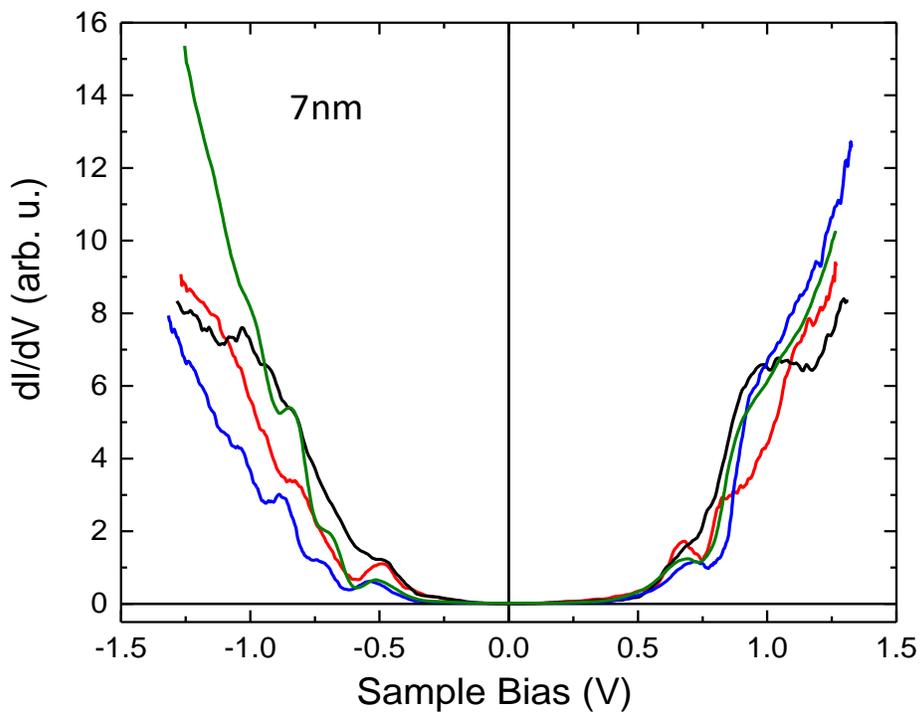


Fig. S5. Tunneling spectra measured on codoped Si-NCs, 7 nm in diameter.

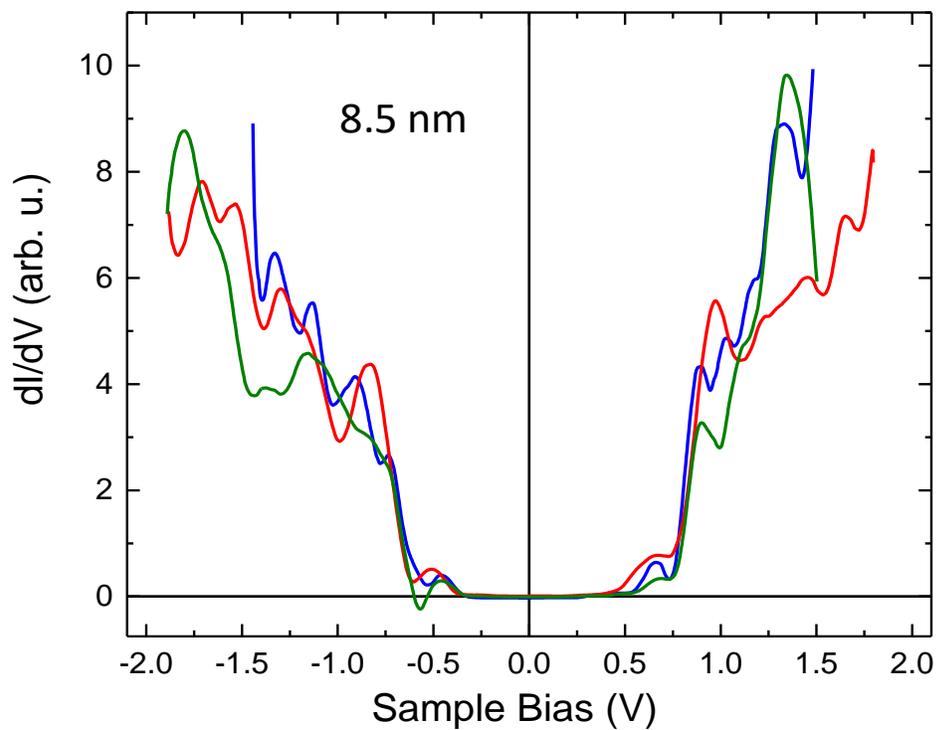


Fig. S6. Tunneling spectra measured on codoped Si-NCs, 8.5 nm in diameter.