



Skin dominance of the dielectric–electronic–phononic–photonic attribute of nanoscaled silicon

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Abstract

Nanoscaled or porous silicon (*p-Si*) with and without surface passivation exhibits unusually tunable properties that its parent bulk does never show. Such property tunability amplifies the applicability of Si in the concurrent and upcoming technologies. However, consistent understanding of the fundamental nature of nanoscaled Si remains a high challenge. This article aims to address the recent progress in this regard with focus on reconciling the tunable dielectric, electronic, phononic, and photonic properties of *p-Si* in terms of skin dominance. We show that the skin-depth bond contraction, local quantum entrapment, and electron localization is responsible for the size-induced property tunability. The shorter and stronger bonds between undercoordinated skin atoms result in the local densification and quantum entrapment of the binding energy and the bonding electrons, which in turn polarizes the dangling bond electrons. Such local entrapment modifies the Hamiltonian and associated properties such as the band gap, core level shift, Stokes shift (electron–phonon interaction), phonon and dielectric relaxation. Therefore, given the known trend of one property change, one is expected to be able to predict the variation of the rest based on the notations of the bond order–length–strength correlation and local bond average approach (BOLS-LBA). Furthermore, skin bond reformation due to Al, Cu, and Ti metallization and O and F passivation adds another freedom to enhance or attenuate the size effect. The developed formulations, spectral analytical methods, and importantly, the established database and knowledge could be of use in engineering *p-Si* and beyond for desired functions.

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Keywords: Nanostructures; Silicon; Raman shift; Core level shift; Photoluminescence; Photoabsorption; Stokes shift; Dielectric constant

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Abbreviations: $E_v(0)$, ν the energy level of an isolated atom; $\Delta E_v(z)$, core-level shift of a z -coordinated atom; τ , solid dimensionality; γ_i , Surface-to-volume ratio or the fraction of atoms in the i th atomic layer to that of the solid; BOLS, bond order–length–strength; CN, coordination number; C_z , bond contraction coefficient; E_b , bond energy at equilibrium; E_G , band gap; $e-h$, electron hole pair; $e-p$, electron–phonon; fcc, face-centered cubic; FTIR, Fourier transformation infrared spectroscopy; GFP, Goldschmidt–Feibelman–Pauling; K , dimensionless form of size or number of atoms lined along the radius of a sphere; k_B , Boltzmann constant; LA, longitudinal acoustic phonon; LBA, local bond average; LFR, low-frequency Raman shift; m , bond nature index; NEP, nonbonding electron polarization; PA, photon absorption; PL, photoluminescence; *p-Si*, porous silicon; QC, quantum confinement; RT, room temperature; STM/S, scanning tunneling microscopy/spectroscopy; TA, transverse acoustic phonon; TO, transverse optical phonon; W , Stokes shift; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

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1. Introduction

1.1. Size fascinations

Nanoscaled silicon of various shapes (such as porous structures *p-Si*, nanowires, nanospheres, thin plates, atomic clusters, etc.) with high fraction of undercoordinated atoms exhibits fascinating properties that its parent bulk does never show. The otherwise constant properties for the bulk Si such as the dielectric constant, band gap, lattice vibrational frequencies, etc., remain no longer constant but change simply with the shape and size of the crystal. Fig. 1 shows a comprehensive set of data revealed using the high-energy synchrotron X-ray diffraction coupled to atomic pair distribution function analysis and computer simulations of the oxide-free Si nanoparticles [1]. These data show clearly the particle size dependency of the average first coordination numbers, length of structural coherence, and degree of local bond angle distortions in comparison to the optical properties such as

photoluminescence emission energy, quantum yield, and Raman frequency of nanostructured Si.

In fact, the *p-Si* shares considerable similarities with amorphous Si in the dielectric and optical properties. In contrast to amorphous Si with random loss of bond orders, the performance of *p-Si* is controllable by varying its shape, size, and the extent of surface passivation [2].

The fascinating properties of *p-Si* have come under scrutiny for decades. A dramatic increase of research interest in *p-Si* was initiated in 1990s after its tunable, efficient, room temperature (RT), visible light emission [3]. Not only multi-color photoluminescence (PL , from red to green) [4] but also efficient electroluminescence of visible light were achieved [5–7]. The physical origin of the energy shift in luminescence quickly became a very controversial issue and a plethora of models has been developed [8,9].

The high interest in *p-Si* is for several reasons. Firstly, the *p-Si* could be an efficient light emitter with tunable wavelengths

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