Comment on "Quantum Confinement and Electronic Properties of Silicon Nanowires"

In a recent Letter, Zhao *et al.* [1] investigated the electronic properties of isolated silicon nanowires by means of *ab initio* calculations based on, and going beyond, density functional theory. One important conclusion of their work concerns the anisotropy of the dielectric response of these systems that is claimed to vanish for wires with diameters as small as 2 nm. We believe that this conclusion has only a very limited meaning, as the authors completely neglect depolarization effects, which dramatically change the anisotropy. In the following, we will illustrate this fact, both by *ab initio* calculations and by using the effective medium theory (EMT).

Zhao *et al.* calculated absorption spectra using Fermi's golden rule in the independent-particle transition picture. This scheme leads to a macroscopic dielectric function in the form of the spatial average of the dielectric matrix, hence neglecting the effects due to the nonhomogeneity of space. This approximation is not sufficient to predict or even to interpret anisotropies in the spectra of nanostructured materials [2]. In fact, in these systems it is important to take into account the microscopic components arising in the response to a perturbing macroscopic field. In particular, the induced microscopic variations of the Hartree potential, the so-called depolarization or local-field effects (LFE), suppress absorption at lower energies when the polarization of the light is perpendicular to a surface. Although further contributions arise from quasiparticle and excitonic effects, the LFE are the key ingredients for the discussion of strong anisotropies in nanostructured systems [3].

In order to assess the importance of LFE for Si nanowires, we performed response calculations [4] within the random phase approximation (RPA) for the largest wire considered in Ref. [1], the $d = 2.2$ nm [110] wire, in the same supercell geometry as in Ref. [1], but using a larger interwire distance ($\approx$2.5 nm). This is necessary as LFE (and the calculation of any excited states quantity, like also *GW* corrections) depend much more on the distance between wires than a ground state calculation. By neglecting LFE we reproduce the spectra of Ref. [1] for both the component of the imaginary part of the dielectric function along the wire axis $\varepsilon_2^{\parallel}$ and the one perpendicular to the wire axis $\varepsilon_2^{\perp}$ (Fig. 1, solid and dotted lines). Our spectra are rigidly redshifted with respect to Ref. [1], as we do not include *GW* corrections (this does not influence the conclusions). When LFE are included, no significant changes in $\varepsilon_2^{\parallel}$ (dashed line) are observed. However, it turns out that $\varepsilon_2^{\perp}$ (dash-dotted line) is extremely sensitive to LFE: the absorption is shifted to higher energies and the nanowires become transparent up to 6–7 eV. Hence, we prove that the anisotropic contribution to the spectra due to LFE does not disappear for $d > 2$ nm. This result can be better understood if we use the fact that, for large wires, the *ab initio* calculations tend to reproduce the classical limit given by the EMT [5]. The gray lines in Fig. 1 show the results of the EMT, using the RPA bulk silicon dielectric function. The agreement between the model and the *ab initio* calculations is extremely good for both polarization directions. This shows that the observed anisotropy can be explained almost entirely by classical effects (that are contained in the *ab initio* calculations when LFE are included), and that one can use the EMT to estimate anisotropies for larger diameters. In view of our conclusions, the results of Zhao *et al.* imply that only the contribution to the anisotropy due to band structure vanishes for $d > 2$ nm. Their results do not allow one to estimate, even approximately, the anisotropy that might be actually measured.

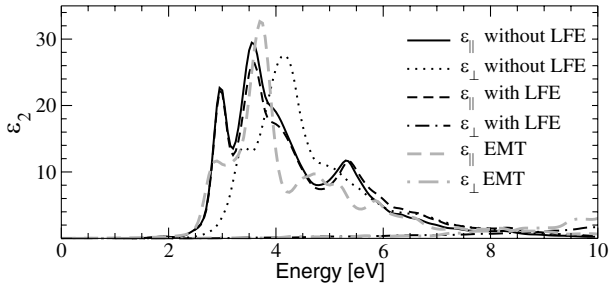

FIG. 1. Imaginary part of the dielectric functions for [110] $d =$ 2.2 nm nanowires, calculated within the RPA.

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