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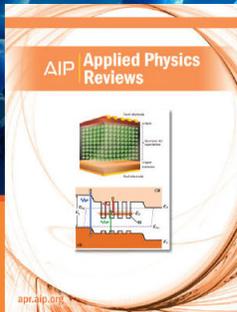
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On the role of spatial position of bridged oxygen atoms as surface passivants on the ground-state gap and photo-absorption spectrum of silicon nano-crystals

Sanaz Nazemi,¹ Mahdi Pourfath,^{1,2,a)} Ebrahim Asl Soleimani,¹ and Hans Kosina²

¹School of Electrical and Computer Engineering, University of Tehran, Tehran 14395-515, Iran

²Institute for Microelectronics, Technische Universität Wien, Gusshausstrasse 27-29/E360, Wien A-1040, Austria

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Silicon nano-crystals (NCs) are potential candidates for enhancing and tuning optical properties of silicon for optoelectronic and photo-voltaic applications. Due to the high surface-to-volume ratio, however, optical properties of NC result from the interplay of quantum confinement and surface effects. In this work, we show that both the spatial position of surface terminants and their relative positions have strong effects on NC properties as well. This is accomplished by investigating the ground-state HOMO-LUMO band-gap, the photo-absorption spectra, and the localization and overlap of HOMO and LUMO orbital densities for prototype ~ 1.2 nm $\text{Si}_{32-x}\text{H}_{42-2x}\text{O}_x$ hydrogenated silicon NC with bridged oxygen atoms as surface terminations. It is demonstrated that the surface passivation geometry significantly alters the localization center and thus the overlap of frontier molecular orbitals, which correspondingly modifies the electronic and optical properties of NC.

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I. INTRODUCTION

The combination of non-toxicity, abundance, low cost, and rather simple processing have made Si as the base-material for semiconductor technology.¹ Crystalline Si is not suitable for optical applications, because of its indirect band-gap. If the size of the system approaches the wavelength of carriers, however, tails of electron and hole wavefunctions partially overlap that give rise to quasi-direct transitions and thus improving optical properties of silicon.² In nano-crystals (NCs) which are smaller than the exciton Bohr radius of the material (~ 5 nm for Si), the optical gap is inversely proportional to the dimension of the structure.³⁻⁵ However, due to the high surface-to-volume ratio in NCs, surface effects become important. Intensive experimental and theoretical studies on parameters that affect optical properties of Si NCs have been performed over the past two decades.⁶⁻¹¹ Chemical nature of the surface including the passivant material and its bonding type have shown to be strongly effective on the optical properties of NC. Using quantum Monte Carlo calculations, Puzder *et al.*⁸ have shown that double bonded surface passivant groups, specifically oxygen atoms, significantly reduce the optical gap of Si NCs, while single bonded groups have a minimal influence. Nurbawono *et al.*⁶ have utilized time dependent density functional tight binding (TDDFTB) model to demonstrate that the absorption spectra of Si NCs can be tuned with small molecule passivations such as methyl, hydroxyl, amino, and fluorine. Effects of passivant species including oxygen,¹² chlorine,^{13,14} fluorine,^{14,15} and nitrogen¹⁶ on the properties of silicon NCs have been studied by various groups. Furthermore, the effect of surface geometry on the optical gap of Si NCs has been discussed in several references:

Puzder *et al.*¹⁷ have demonstrated that highly curved surfaces can dramatically reduce the optical gaps of NCs, Carrier¹⁸ has studied the effects of curvature on band gap for sub-oxide interfaces in planar structures and nano-dots of silicon and has shown that sub-oxides reduce the band-gap in quantum dots, but this trend can be reversed when planar surfaces are formed, Draeger *et al.*¹⁹ have investigated the effect of oxygen on the silicon nano-structures with different surface curvature and angular distortion of the bonds and have reported reconstructions unique to highly curved nano-structures which give evidence for larger optical absorption gaps, and Shu and Levine²⁰ have examined the effect of oxidation state of defects on the oxidized surface of silicon clusters and have demonstrated that conical intersections facilitate the nonradiative recombination.

To the best of our knowledge, a comprehensive study of the effect of the relative position of surface passivants on NC properties is missing. In this work time, (in)dependent density functional theory simulations have been utilized to analyze the role of spatial position of surface passivants on the optical gap of NC. Oxygen is now a well-established and widely used material in the silicon technology,^{21,22} and its effect on optical properties of silicon nano-structures has been extensively studied in recent years.^{8,12,17,23} Moreover, the interaction between oxygen and silicon NC has been employed in novel applications recently, such as photosynthesis of singlet oxygen²¹ and quenching of porous silicon photoluminescence by molecular oxygen for application in storing media.²² Oxygen atom with bridged bonding has been studied for Si-SiO_x interface.^{24,25}

In this work, the effect of bridged oxygen atoms as surface passivants for silicon NCs is comprehensively studied. The paper is organized as follows: Sec. II describes the employed computational method, Sec. III discusses the

^{a)}Electronic addresses: pourfath@ut.ac.ir and pourfath@iue.tuwien.ac.at

size of NC becomes comparable to the Bohr radius, carrier energy gets quantized with a size-dependent trend similar to that of a particle in a box.^{3–5} In strong confinement regime ($r < a_{\text{Bohr}}^*$), the band-gap of NC is inversely proportional to the diameter^{5,36}

$$E_g^{QD}(d) = E_g^{\text{bulk}} + \frac{A}{d^2}, \quad (2)$$

where d is the diameter of NC in nanometer, and A [eV nm^2] is the fitting parameter.⁵ We examined HOMO-LUMO (ground-state) band-gap variations for hydrogen passivated Si NCs with diameters in the range of 1.2–2.2 nm. Fig. 1 clearly shows the inverse proportionality of the band-gap with the NC size. For the given diameter range and $A = 3.57$ (strong confinement regime⁵), Eq. (2) predicts energy gaps in the range of 1.85–3.59 eV, and our numerical analysis indicates bandgaps in the range of ~ 1.5 –3.25 eV which are in good agreement with previous works.^{6,36–38}

Since NC facets have different surface energies, they interact differently with the passivant atoms.³⁹ In addition, dissimilar facet boundaries and the broad range of internuclear distances between the passivant and surface atoms of NC lead to various external potential profiles ($v_{\text{ext}}(r, t)$) for the Kohn-Sham equation, which accordingly result in new eigenstates for the system. Thus, it is anticipated that the position of the surface passivants affects the optical and electrical properties of the NC. First, we examine the effect of a single passivant atom placed at different positions of the surface of a $\text{Si}_{32}\text{H}_{42}$ NC with a diameter of 1.2 nm. A Si atom on a (100) facet is considered, and its two bound hydrogen atoms are replaced with a bridged oxygen followed by the structure relaxation. The calculated HOMO-LUMO band-gaps are presented in Fig. 2 that show a variation of ~ 0.15 eV for various positions of a single oxygen passivant.

The optical responses of the discussed structures are calculated using the TDDFPT method. For single bridged oxygen atom on a (100) facet, TDDFPT predicts an average optical gap of ~ 6.5 eV with variations of the order of ~ 0.55 eV for various passivation position (see Fig. 3). The smaller HOMO-LUMO band-gap in comparison with the optical gap is due to the well-known bandgap underestimation of DFT simulations.^{38,40,41}

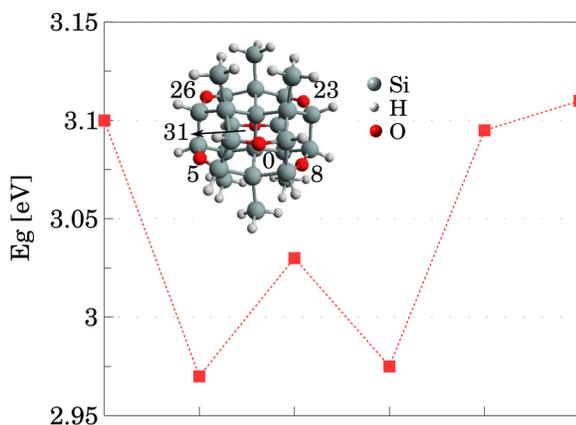


FIG. 2. The HOMO-LUMO band-gaps of $\text{Si}_{31}\text{H}_{40}\text{O}$ NCs with a single bridged oxygen surface passivant at various (100) facets.

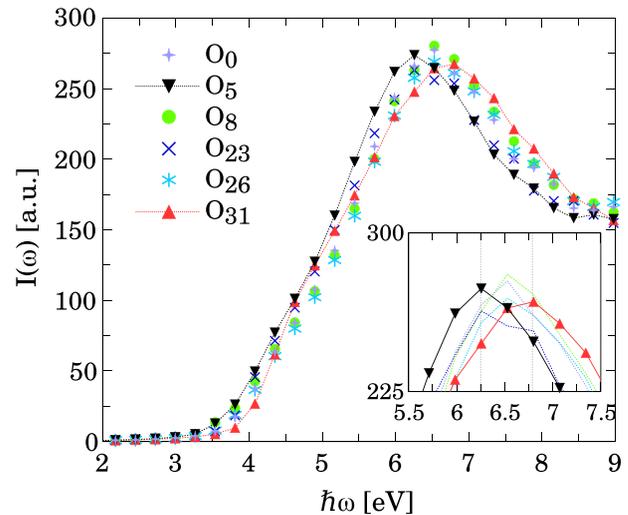


FIG. 3. Optical absorption spectra that are calculated using TDDFPT for $\text{Si}_{31}\text{H}_{40}\text{O}$ NCs with single bridged oxygen passivant atom at various (100) facets. a.u. represents atomic units.

To study the role of relative spatial position of surface passivants, four configurations are considered in which three bridged oxygen atoms with different relative positions are placed on the (100) facets of a $\text{Si}_{32}\text{H}_{42}$ NC, see the first column of Fig. 5. The relative position of terminants in $\text{O}_{0,5,23}$ configuration is symmetric, but with respect to the whole NC structure the surface termination is not symmetric (see subplots 1 and 4 in Fig. 5). The $\text{O}_{0,5,8}$ configuration is similar to the previous structure, but less symmetrical with respect to the relative position of the oxygen atoms (see subplots 16, 17, and 19 in Fig. 5). $\text{O}_{0,5,26}$ and $\text{O}_{0,5,31}$ configurations are similar with respect to the whole NC, while the relative position of passivants is mirrored.

The optical absorption spectra are calculated using TDDFPT simulations (see Fig. 4). As expected, similar to the single-oxygen case, the optical transition energies are different for various surface passivation configurations. In this case, the peak absorption energy varies ~ 0.25 eV between the $\text{O}_{0,5,26}$ and $\text{O}_{0,5,31}$ configurations which show the maximum and minimum absorption peak energy, respectively.

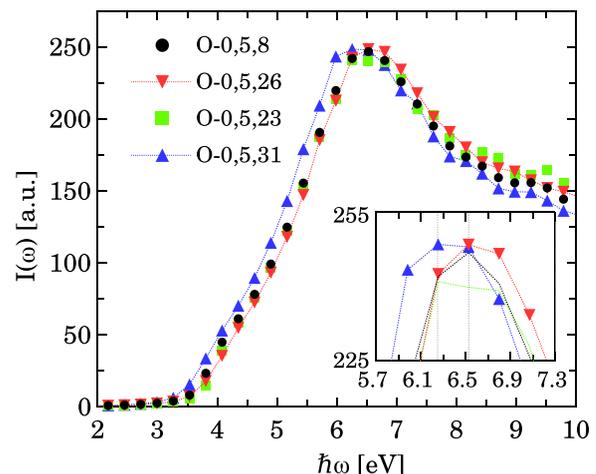


FIG. 4. TDDFPT predicted optical absorption spectra for $\text{Si}_{29}\text{H}_{36}\text{O}_3$ NCs with various relative positions of three bridged oxygen passivants on (100) facets. a.u. represents atomic units.

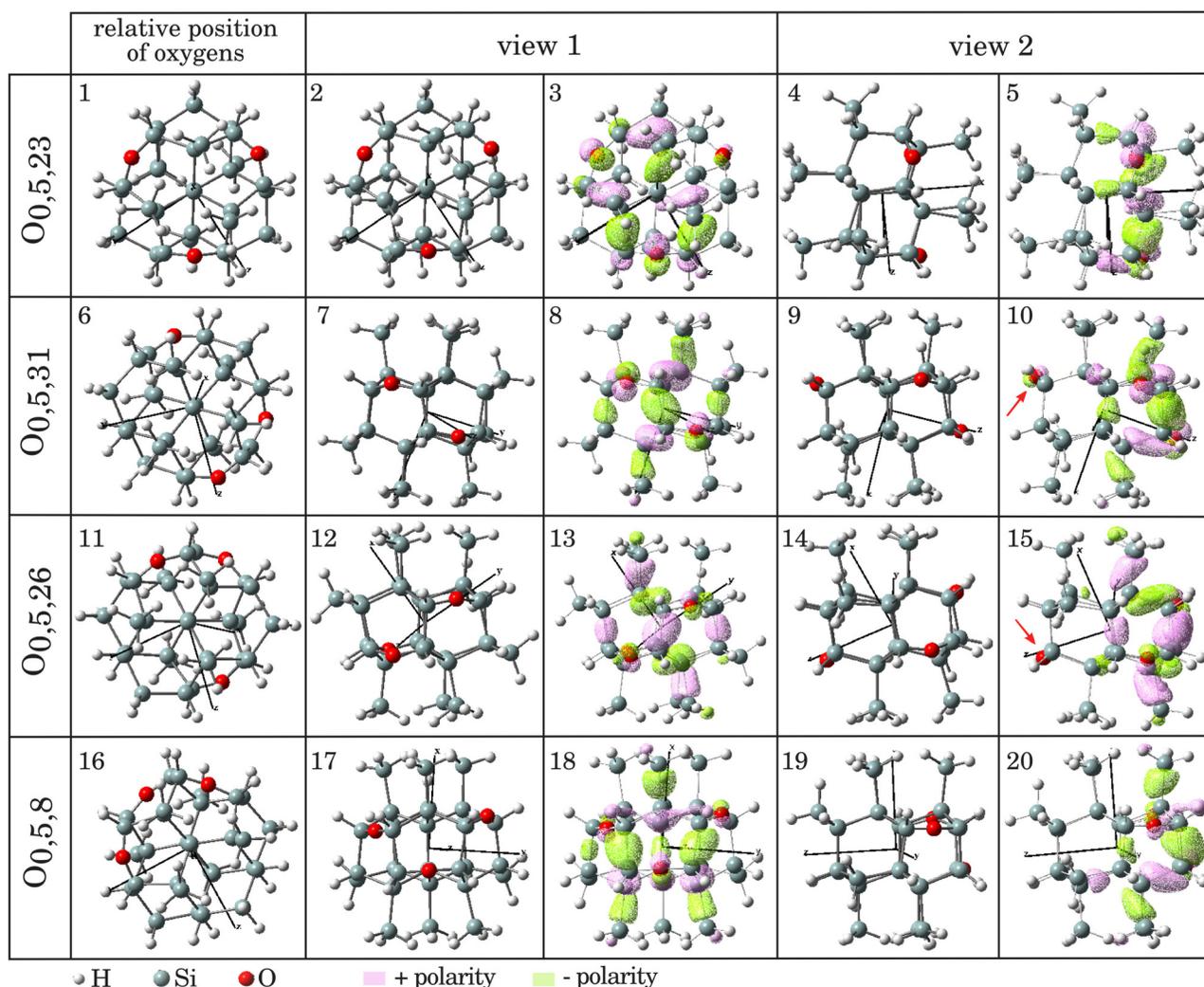


FIG. 5. The first column shows the cross-section of NC in the plane of the three oxygen atoms to represent their relative arrangement. Other columns show the density distribution of HOMO orbital and the corresponding cross-section of the NC. The column “view 1” displays the plane on which the HOMO spreads. The column “view 2” displays the view normal to the “view 1,” representing the plane on which the HOMO is localized. The density iso-surfaces are plotted at $0.033 \text{ electron}/\text{\AA}^3$.

The referred structures are similar, except a mirrored relative position of oxygen atoms. As HOMO is the main electron donor, examining its density distribution can clarify the effect of relative position of passivants. For the four considered configurations, the HOMO iso-surfaces with density iso-value of $0.033 \text{ electron}/\text{\AA}^3$ are plotted in Fig. 5. In the subplots 3 and 8, the relative position of passivants is symmetric, where the HOMO spreads over all oxygen atoms. However, in subplots 10 and 15, which lack symmetric positions for oxygen atoms, the electronic cloud is only localized on the two closer oxygen atoms and the third oxygen atom has not a significant contribution to the HOMO state. It is known that oxygen atom can disturb the *sp* orbital network of a Si NC and results in the localization of the frontier molecular orbitals.^{8,9,12} This is in agreement with our results that the HOMO electron cloud is mainly localized on oxygens. The comparison of subplots 3 and 18 (symmetric arrangement of oxygens) with subplots 8 and 13 (asymmetric arrangement of oxygens) reveals that the localization center of HOMO is mainly determined by the relative position of surface terminants. On the one hand, the localization center

of orbitals determines the overlapping conditions, and on the other hand optical transitions are determined by the overlap of frontier molecular orbitals. Thus, we examined the HOMO/LUMO overlap in more details for the $O_{0,5,26}$ and $O_{0,5,31}$ configurations. The density iso-surfaces of HOMO-3 to LUMO+4 are depicted in Fig. 6.

The HOMO similarly (with opposite polarity) spreads across the two NCs, whereas the UMO distributions are different. As a result, the overlap of HOMO and UMOs and the corresponding coupling strengths are different in the two structures. In $O_{0,5,31}$ configuration, the LUMO, amongst the UMOs, has the most significant overlap with HOMO. The HOMO-1 is localized on top of the NC and has small overlaps with all considered UMOs. In both configurations, HOMO-2 and HOMO-3 are spread almost uniformly over the NC. In $O_{0,5,31}$ configuration, the first strong overlap takes place between HOMO and LUMO, which corresponds to the lowest-energy transition. In $O_{0,5,26}$, HOMO is localized at the bottom of the NC, but LUMO distribution is altered such that it has a small overlap with HOMO. In fact, all considered UMOs are localized at the center of NC and have small

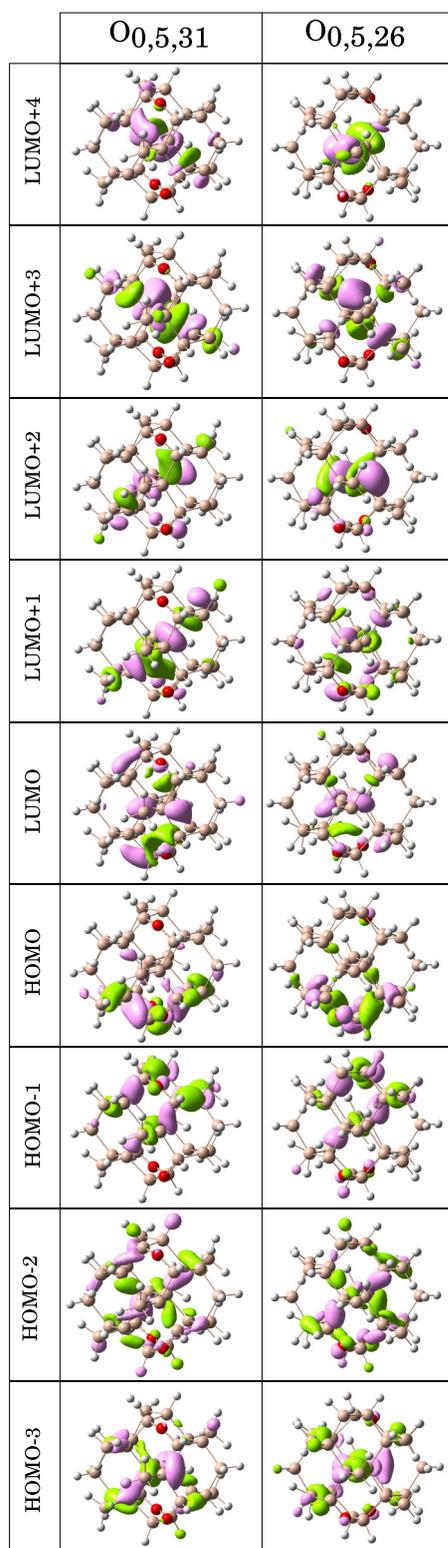


FIG. 6. The density iso-surfaces of HOMO-3 to LUMO+4 states of Si₂₉H₃₆O₃ NCs. The surfaces are plotted at 0.033 electron/Å³. Hydrogen atoms are not displayed for the sake of clarity. The khaki, red, and white colors are used for silicon, oxygen, and hydrogen atoms, respectively.

overlap with the HOMO that prevents the lowest energy transition. In addition, HOMO-1 is localized at the top of NC, and similar to HOMO it has a small overlap with all considered UMOs that prevents the second lowest energy

transition. Thus, the first significant overlap occurs between HOMO-2 and LUMO. As coupling strengths are proportional to the overlap between molecular orbitals, it can be inferred that in the O_{0,5,31} configuration a larger overlap between low-energy frontier MOs leads to a red shift in the photo-absorption spectra compared to the O_{0,5,26} configuration. It is worth-noting that the difference in allowed transitions of O_{0,5,26} and O_{0,5,31} is caused by the changes in the relative position of oxygen surface passivants.

IV. CONCLUSIONS

The effects of the spatial position and the relative position of bridged oxygen passivants on the absorption spectra of hydrogen passivated Si NC are investigated. Examination of the HOMO-LUMO band-gap, optical absorption spectra, and the frontier molecular density distributions demonstrates that the spatial position of each surface passivant and the relative position of passivants can significantly affect the localization center of frontier orbitals, which results in the variation of their overlap and the modification of optical transition energies. Previous studies have focused on chemical nature of surface passivation on NC properties. Our presented results, however, show that the role of spatial position and the geometrical arrangement of surface passivants cannot be neglected.

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- ¹A. Feltrin and A. Freundlich, *Renewable Energy* **33**, 180 (2008).
- ²H. Huff, *Into the Nano Era: Moore's Law Beyond Planar Silicon CMOS*, Springer Series in Material Science (Springer, Berlin, Heidelberg, 2008).
- ³J. Derr, K. Dunn, D. Riabinina, F. Martin, M. Chaker, and F. Rosei, *Physica E* **41**, 668 (2009).
- ⁴V. Kumar, K. Saxena, and A. Shukla, *Micro Nano Lett.* **8**, 311 (2013).
- ⁵E. G. Barbagiovanni, D. J. Lockwood, P. J. Simpson, and L. V. Goncharova, *J. Appl. Phys.* **111**, 034307 (2012).
- ⁶A. Nurbawono, S. Liu, and C. Zhang, *J. Chem. Phys.* **142**, 154705 (2015).
- ⁷G. Seguini, C. Castro, S. Schamm-Chardon, G. BenAssayag, P. Pellegrino, and M. Perego, *Appl. Phys. Lett.* **103**, 023103 (2013).
- ⁸A. Puzder, A. Williamson, J. C. Grossman, and G. Galli, *Phys. Rev. Lett.* **88**, 097401 (2002).
- ⁹A. D. Zdetsis, S. Niaz, and E. N. Koukaras, *Microelectron. Eng.* **112**, 227 (2013).
- ¹⁰Y. Gao, D. Neuhauser, R. Baer, and E. Rabani, *J. Chem. Phys.* **142**, 034106 (2015).
- ¹¹D. Bandyopadhyay, *J. Appl. Phys.* **104**, 084308 (2008).
- ¹²I. Vasiliev, J. R. Chelikowsky, and R. M. Martin, *Phys. Rev. B* **65**, 121302 (2002).
- ¹³Y. Ma, X. Chen, X. Pi, and D. Yang, *J. Phys. Chem. C* **115**, 12822 (2011).
- ¹⁴S. Chopra and B. Rai, *J. Nanostruct. Chem.* **5**, 195 (2015).
- ¹⁵E. Ramos, B. M. Monroy, J. C. Alonso, L. E. Sansores, R. Salcedo, and A. Martinez, *J. Phys. Chem. C* **116**, 3988 (2012).
- ¹⁶S. M. Lee, K. J. Kim, D. W. Moon, and H. Kim, *J. Nanosci. Nanotechnol.* **12**, 5835 (2012).
- ¹⁷A. Puzder, A. Williamson, F. Reboredo, and G. Galli, *Phys. Rev. Lett.* **91**, 157405 (2003).
- ¹⁸P. Carrier, *Phys. Rev. B* **80**, 075319 (2009).
- ¹⁹E. W. Draeger, J. C. Grossman, A. J. Williamson, and G. Galli, *J. Chem. Phys.* **120**, 10807 (2004).

- ²⁰Y. Shu and B. G. Levine, *J. Phys. Chem. C* **119**, 1737 (2015).
- ²¹D. Kovalev and M. Fujii, *Adv. Mater.* **17**, 2531 (2005).
- ²²M. Balaguer and E. Matveeva, *J. Nanopart. Res.* **12**, 2907 (2010).
- ²³A. Puzder, A. Williamson, J. C. Grossman, and G. Galli, *J. Chem. Phys.* **117**, 6721 (2002).
- ²⁴N. B. Nguyen, C. Dufour, and S. Petit, *J. Phys.: Condens. Matter* **20**, 455209 (2008).
- ²⁵K. Seino, F. Bechstedt, and P. Kroll, *Phys. Rev. B* **82**, 085320 (2010).
- ²⁶D. J. Lockwood and L. Tsybeskov, *J. Nanophotonics* **2**, 022501 (2008).
- ²⁷G. H. Lu, M. Huang, M. Cuma, and F. Liu, *Surf. Sci.* **588**, 61 (2005).
- ²⁸J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- ²⁹M. Fuchs and M. Scheffler, *Comput. Phys. Commun.* **119**, 67 (1999).
- ³⁰N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ³¹E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- ³²D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, *J. Chem. Phys.* **128**, 154105 (2008).
- ³³O. B. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni, *Comput. Phys. Commun.* **182**, 1744 (2011).
- ³⁴P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. M. Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ³⁵D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ³⁶L. Brus, *J. Phys. Chem.* **90**, 2555 (1986).
- ³⁷K. Dohnalova, A. N. Poddubny, A. A. Prokofiev, W. D. de Boer, C. P. Umesh, J. M. Paulusse, H. Zuilhof, and T. Gregorkiewicz, *Light: Sci. Appl.* **2**, e47 (2013).
- ³⁸A. J. Williamson, J. C. Grossman, R. Q. Hood, A. Puzder, and G. Galli, *Phys. Rev. Lett.* **89**, 196803 (2002).
- ³⁹H. G. Liao, D. Zherebetsky, H. Xin, C. Czarnik, P. Ercius, H. Elmlund, M. Pan, L. W. Wang, and H. Zheng, *Science* **345**, 916 (2014).
- ⁴⁰V. Kocevski, O. Eriksson, and J. Ruzs, *Phys. Rev. B* **87**, 245401 (2013).
- ⁴¹I. Vasiliev, S. Ögüt, and J. R. Chelikowsky, *Phys. Rev. Lett.* **86**, 1813 (2001).