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# Surface oxidation effects on the optical properties of silicon nanocrystals

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We report first-principles calculations for optical absorption spectra of hydrogenated silicon clusters in the presence of oxygen on the surface. Our computational technique is based on linear-response theory within the time-dependent local-density approximation (TDLDA). The calculated spectra show that oxidation substantially reduces the size of optical gaps in silicon nanocrystals. This result may explain a seeming disagreement between the measured photoluminescence and theoretical predictions based on a quantum confinement model in the limit of small clusters.

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Surface-passivated silicon clusters in the form of spherical quantum dots are frequently used in theoretical studies to simulate the optical properties of porous silicon.[1] According to this model, visible photoluminescence from porous silicon is associated with quantum confinement. Quantum confinement increases the optical gap in silicon nanocrystals and shifts photoluminescence into the visible range.[2,3] However, most calculations for optical absorption and emission in silicon dots do not take into account differences in structure and chemical composition of the dot surface. This creates an ambiguity in the interpretation of experimental data. Almost all *ab initio* and empirical simulations available in literature use silicon dots passivated with hydrogen.[4–6] Other types of surface passivation have not been studied. Only one of the published works[6] presents *ab initio* calculations for optical absorption of two silicon clusters with reconstructed surfaces, $Si_{29}H_{24}$ and $Si_{29}H_{12}$. It appears that no first-principles studies of the optical properties have been conducted for oxidized silicon clusters or clusters with surface defects. On the other hand, porous and nanocrystalline silicon studied in experiments are prepared under a variety of surface conditions determined by the etching technique and external chemical environment. Only a fraction of published experimental data refers to “pure” hydrogenated silicon dots,[7] whereas some measurements are performed on partially oxidized nanocrystals.[8] In many cases, the precise chemical composition of nanocrystalline surfaces is not known.[3,9]

Theoretical calculations[4,5] based on a quantum confinement model show good agreement with experimental measurements[7] for optical absorption in hydrogen-passivated silicon clusters. In contrast, experiments performed on oxidized samples often display photoluminescence with energies significantly below the values of optical gaps predicted by the confinement model for clusters in the same size range.[8] Sometimes, this disagreement could be greater than 1 eV. It has been suggested that the onset of photoluminescence in silicon nanocrystals may be associated with the optical Stokes shift[10] and excitonic exchange splitting.[11] Both of these effects are shown to be significant in small silicon dots. However, it appears that neither the Stokes shift, nor the excitonic exchange splitting alone could explain such a large disagreement between experiment and theory.

Recent experimental data present strong evidence that surface effects produce a very substantial impact on the electronic and optical properties of nanocrystalline silicon. Specifically, Wolkin *et al.* observed a large redshift of photoluminescence in porous silicon after exposure to open air.[12] The study reported a shift of photoluminescence of the order of 1 eV for samples composed of crystallites smaller than 2 nm in size. The observed redshift has been attributed to surface oxidation of silicon nanocrystals. According to the interpretation proposed in Ref. 12, oxygen creates trapped electron and hole states on nanocrystalline surfaces. The trapped surface states reduce the effective size of the optical gap. This mechanism can explain the difference between the energy of the measured photoluminescence and theoretical predictions based on the quantum confinement model.

In this paper we investigate the effects of partial surface oxidation in hydrogenated silicon clusters. The goal of our study is to assess the surface contribution to the optical gap and improve the quality of theoretical models for porous and nanocrystalline silicon.

Our computational approach is based on the finite-difference density-functional pseudopotential method.[5,13] We employ the Kleinman-Bylander form of Troullier-Martins nonlocal pseudopotentials.[14] Calculations are performed on a real-space Cartesian grid, without the use of explicit basis functions. The exchange-correlation potential is approximated by the Ceperley-Alder local-density functional.[15]

Due to a very large number of possible configurations for oxidized silicon clusters, our present study is, for the most part, limited to the case of a single oxygen atom attached to the cluster surface. Oxidized clusters were prepared from regular hydrogen-terminated spherical dots by replacing two hydrogen atoms on the surface with a single atom of oxygen, followed by relaxation of all interatomic forces. Atomic forces were minimized by a variable metric algorithm.[16] This algorithm offers substantial savings in computer time over the standard steepest-descent method. We performed a comprehensive search for low-energy cluster structures. To find the most stable configurations, we tested all possible positions of the oxygen atom on the surface. For each oxidized cluster except for $SiOH_2$, we selected two different geometries with the lowest total energies: one with oxygen attached to a single silicon atom forming a double Si═O bond

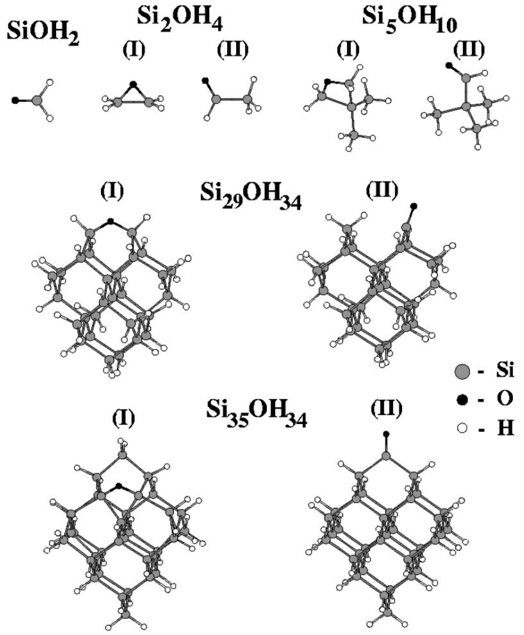

FIG. 1. Structures of $Si_nOH_m$ clusters.

and the other with oxygen connected to two silicon atoms creating Si—O—Si bonds on the surface. Structures of these clusters are shown in Fig. 1.

Absorption spectra and optical gaps were calculated using linear response theory within the time-dependent local-density approximation (TDLDA).[17] The TDLDA method represents a natural extension of the ground-state density-functional formalism and the local-density approximation, designed to include the proper representation of excited states.[18] Compared to other *ab initio* theoretical methods for excited states, TDLDA approach requires less computational efforts and can be used for relatively large clusters. Recently, we have applied this technique to compute optical spectra of hydrogenated silicon dots.[5] Our calculations demonstrated that TDLDA provides good agreement with experiment for optical gaps and low-energy excitations in these systems.

The calculated absorption spectra of oxidized silicon dots are shown in Figs. 2 and 3. In Fig. 2 we compare the spectra of small oxidized and nonoxidized clusters. The comparison indicates that the addition of oxygen creates new absorption bands in the region of lower transition energies. Optical excitations with higher energies are also affected by oxidation, although some intense absorption peaks observed in nonoxidized clusters (such as the peaks at 6.6 and 7.8 eV for $Si_5H_{12}$) appear to be only slightly shifted. Figure 3 shows the calculated spectra of the $Si_{29}OH_{34}$ and $Si_{35}OH_{34}$ clusters. As expected, the overall change in optical absorption caused by the addition of a single oxygen atom becomes less visible for larger clusters. To make the effect of oxidation more evident, we plot in Fig. 3 the differential spectra calculated as the difference in optical absorption of the same cluster before and after oxidation. Positive values of differential photoabsorption correspond to the new absorption peaks that appear only after oxidation. The differential absorption spectra for $Si_{29}OH_{34}$ and $Si_{35}OH_{34}$ clearly show the presence of low-energy optical transitions associated with surface oxygen.

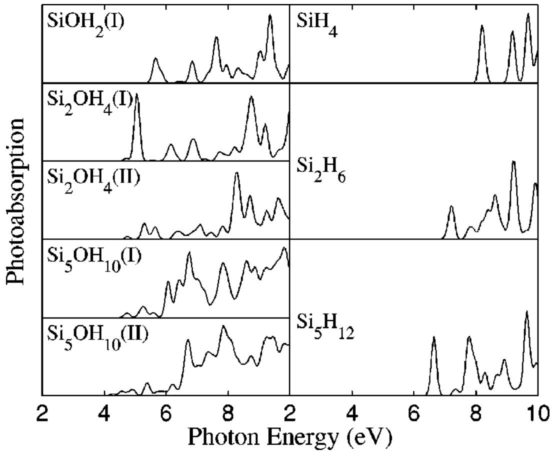

FIG. 2. Left: calculated TDLDA absorption spectra of oxidized hydrogen-terminated silicon clusters. Right: TDLDA spectra of nonoxidized clusters.[5] All spectra are broadened by 0.1 eV using a Gaussian convolution.

The calculated optical absorption gaps in oxidized and nonoxidized silicon dots are compared in Fig. 4. The TDLDA gaps for nonoxidized $Si_nH_m$ clusters are adapted from our previous work.[5] Absorption spectra of large silicon dots are essentially quasicontinuous and exhibit a large number of low-intensity transitions near the absorption edge. Because of that, the gaps reported in Ref. 5 were defined through the integral oscillator strength rather than individual optical transitions. The effective size of optical gaps was evaluated at a very small but nonzero fraction of the complete electronic oscillator strength. The numerical value of this threshold parameter was set at $10^{-4}$ of the total oscillator strength for a cluster. For consistency, in this work we use the same criterion to define the gaps in oxidized silicon clusters. Figure 4 shows that surface oxidation reduces optical gaps in hydrogenated silicon clusters by as much as $1-2$ eV. The change in the size of optical gaps is consistent with the redshift of photoluminescence observed in Ref. 12. As such, we believe that surface effects are primarily respon-

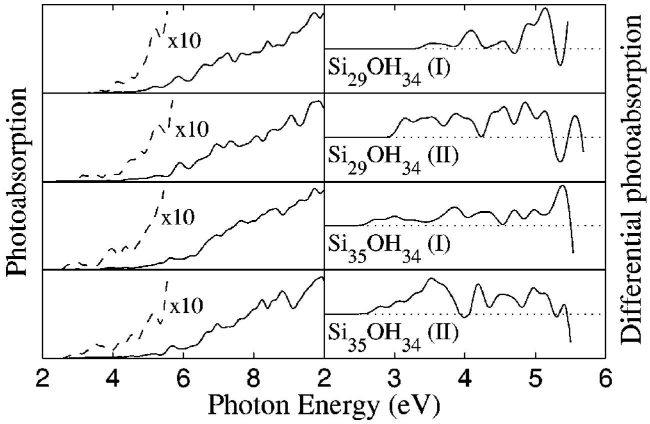

FIG. 3. Left: calculated TDLDA absorption spectra of $Si_{29}OH_{34}$ and $Si_{35}OH_{34}$ clusters. Right: difference in optical absorption between clusters with and without oxygen on the surface. All spectra are broadened by 0.1 eV.

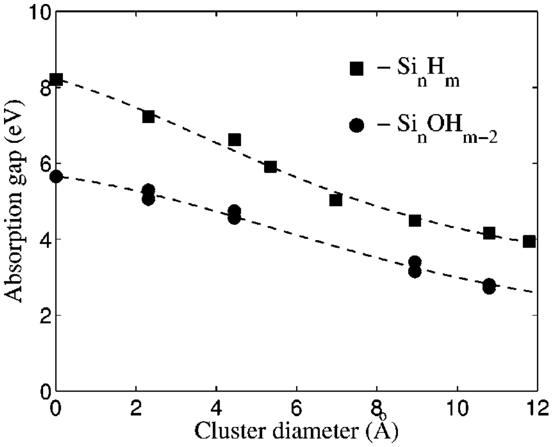

FIG. 4. Comparison between the optical absorption gaps of regular and oxidized hydrogen-terminated silicon clusters. The gaps for $Si_nH_m$ clusters are adapted from Ref. 5. The dashed lines are just a guide to the eye.

sible for the disagreement between experimental photoluminescence from oxidized silicon nanocrystals and theoretical estimates based on the quantum confinement model.

Surprisingly, our calculation shows practically no change in the size of optical gaps between cluster isomers with Si═O and Si—O—Si bonds on the surface. At the same time, Figs. 2 and 3 reveal substantial differences in the shape of optical spectra for these clusters. To understand the mechanisms of the gap formation, we studied electronic excitations in two selected clusters: $Si_{35}OH_{34}$ (I) and (II). The order of electronic levels near the gap is illustrated for both isomers in Figs. 5(a) and 5(b). These diagrams represent simplified schemes that show only the dominant single-electron Kohn-Sham transitions within the TDLDA description and do not account for correlations among individual excitations. The energies of optical transitions shown in Fig. 5 correspond to one-electron singlet TDLDA excitations.[17] As such, they may differ from transition energies of the TDLDA optical spectra shown in Figs. 2 and 3, which correspond to collective electronic excitations. Nevertheless, the single-electron diagrams are useful for the qualitative analysis of optical transitions in oxidized silicon dots.

The authors of Ref. 12 proposed that photoluminescence in small oxidized silicon clusters occurs between the trapped electron and hole states, both of which are associated with the double Si═O bond on the cluster surface. Specifically, the trapped electron state is a *p*-state localized on silicon and the trapped hole state is a *p*-state localized on oxygen. Spatial distributions of electron densities for the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the $Si_{35}OH_{34}$ (II) cluster plotted in Fig. 5(a) confirm that these states are indeed represented by *p*-states mainly localized on the silicon and oxygen atoms. However, the distributions of HOMO and LUMO electron densities for the $Si_{35}OH_{34}$ (I) cluster shown in Fig. 5(b) reveal a different picture. The LUMO state is, for the most part, localized on two silicon atoms that form the Si—O—Si bonds. At the same time, the HOMO state is not localized on the oxygen atom. Instead, this electronic state is spread among the layers of silicon atoms surrounding the Si—O—Si fragment. In both (a) and (b) cases, the direct dipole transitions between the HOMO and LUMO states are forbidden. The absorption edge for $Si_{35}OH_{34}$ (II) is formed mainly by transitions from lower occupied orbitals to the LUMO state. For this cluster, transitions from the HOMO state to higher unoccupied orbitals do not contribute to optical absorption near the gap. For $Si_{35}OH_{34}$ (I), however, both of these types of electronic transitions are involved in the formation of the absorption edge.

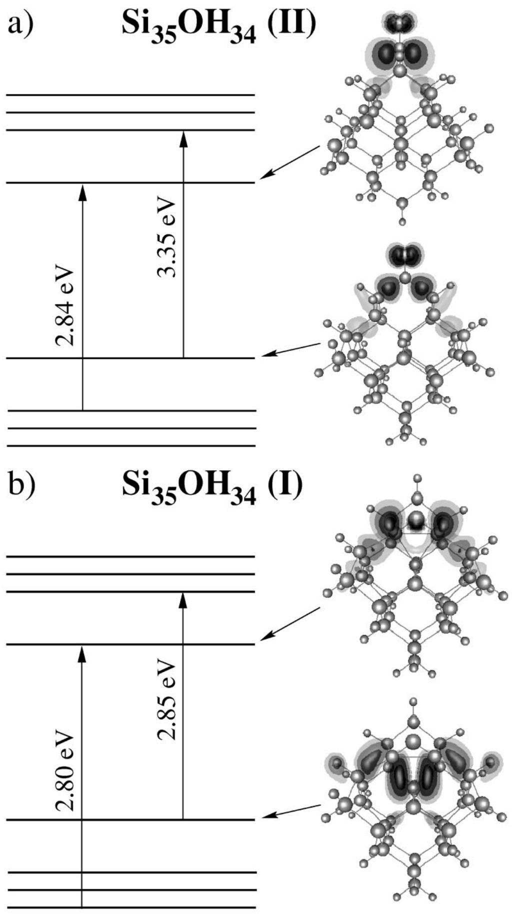

FIG. 5. Schematic representation of electronic levels in the vicinity of the gap for (a) $Si_{35}OH_{34}$ (I) and (b) $Si_{35}OH_{34}$ (II) clusters. In both cases, spatial distributions of electron densities are shown for the HOMO and LUMO states.

Our calculations show that even a low concentration of oxygen on the surface can substantially alter the optical properties of silicon nanoclusters. Experimental studies, however, are not always limited to clusters with low oxygen content. To test how the optical gap would be affected by higher oxygen coverages, we computed the TDLDA absorption spectrum of an ‘‘oxygen-saturated’’ cluster $Si_{35}O_6H_{24}$. This cluster was prepared from the hydrogen-terminated dot $Si_{35}H_{36}$ by replacing 12 outer-shell hydrogen atoms with oxygen to form six double Si═O bonds at the positions symmetrically equivalent to that shown in Fig. 1 for $Si_{35}OH_{34}$ (II). The increase in oxygen coverage caused a further reduction of the absorption gap to 2.4 eV. This value was approximately 0.4 eV lower than the absorption gap for $Si_{35}OH_{34}$ (II), and almost 1.6 eV lower than the gap for the nonoxidized cluster $Si_{35}H_{36}$. We did not see any evidence that the principal mechanism of gap formation for $Si_{35}O_6H_{24}$ was different from that for $Si_{35}OH_{34}$. In our view, the additional reduction of the absorption gap in case of $Si_{35}O_6H_{24}$ could be explained by interactions among oxygen-induced electronic states.

As Fig. 5 indicates, the absorption gap for $Si_{35}OH_{34}$ is reduced by the presence of localized oxygen-induced levels. In the limit of large clusters, the positions of these levels should be essentially independent of the cluster size. Since the gaps in nonoxidized silicon clusters decrease with increasing cluster size as a result of diminishing quantum confinement, at some point the oxygen-induced states are expected to cross over the electronic levels from the body of the cluster. After this point, the oxygen-induced states would no longer be located inside the gap. Using the results of our previous work for hydrogen-terminated silicon dots[5] and assuming that the oxygen-induced states in larger clusters do not change much from those in $Si_{35}OH_{34}$ or $Si_{35}O_6H_{24}$, we can roughly estimate the cluster size at which this crossing would occur. Our calculations suggest that depending on the fraction of oxygen coverage, the oxygen-induced states should not cross over the levels from the body of the cluster for silicon dots up to approximately 20–25 Å in diameter. For larger dots, the overall effect of surface oxidation on the optical properties is likely to be less important.

In summary, we have computed absorption spectra and optical gaps of hydrogenated silicon clusters in the presence of surface oxygen. Our calculations were performed using linear-response theory within the time-dependent local-density approximation. The computed spectra demonstrated that oxidation reduces optical gaps in silicon clusters by as much as $1-2$ eV. The change in the size of optical gaps was consistent with the redshift of photoluminescence observed in oxidized silicon nanocrystals. In contrast to a previously proposed model, we found that the reduction of the gap size is not necessarily associated with the double $Si{=}O$ bond on the cluster surface.

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[1] L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] T. Takagahara and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).
[3] D.J. Lockwood, Solid State Commun. **92**, 101 (1994).
[4] B. Delley and E.F. Steigmeier, Phys. Rev. B **47**, 1397 (1993); J.P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. **61**, 1948 (1992); L.W. Wang and A. Zunger, J. Phys. Chem. **98**, 2158 (1994); J. Chem. Phys. **100**, 2394 (1994); R.J. Baierle, M.J. Caldas, E. Molinari, and S. Ossicini, Solid State Commun. **102**, 545 (1997); N.A. Hill and K.B. Whaley, Phys. Rev. Lett. **75**, 1130 (1995); S. Öğüt, J.R. Chelikowsky, and S.G. Louie, *ibid.* **79**, 1770 (1997); M. Rohlfing and S.G. Louie, *ibid.* **80**, 3320 (1998).
[5] I. Vasiliev, S. Öğüt, and J.R. Chelikowsky, Phys. Rev. Lett. **86**, 1813 (2001).
[6] L. Mitas, J. Therrien, R. Twesten, G. Belomoin, and M.H. Nayfeh, Appl. Phys. Lett. **78**, 1918 (2001).
[7] S. Furukawa and T. Miyasato, Phys. Rev. B **38**, 5726 (1988).
[8] S. Schuppler *et al.*, Phys. Rev. B **52**, 4910 (1995); J. von Behren, T. van Buuren, M. Zacharias, E.H. Chimowitz, and P.M. Fauchet, Solid State Commun. **105**, 317 (1998).
[9] D.J. Lockwood, A. Wang, and B. Bryskiewicz, Solid State Commun. **89**, 587 (1994); Y. Kanemitsu, H. Uto, Y. Masumoto, T. Matsumoto, T. Futagi, and H. Mimura, Phys. Rev. B **48,** 2827 (1993); V. Lehmann and U. Gösele, Appl. Phys. Lett. **58**, 856 (1991).
[10] E. Martin, C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **50**, 18 258 (1994).
[11] T. Takagahara and K. Takeda, Phys. Rev. B **53,** R4205 (1996).
[12] M.V. Wolkin, J. Jorne, P.M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).
[13] J.R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72**, 1240 (1994); J.R. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. B **50**, 11 355 (1994).
[14] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[15] D.M. Ceperley, Phys. Rev. B **18**, 3126 (1978); D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[16] D.F. Shanno and K.H. Phua, Math. Program. **14**, 149 (1978).
[17] I. Vasiliev, S. Öğüt, and J.R. Chelikowsky, Phys. Rev. Lett. **82**, 1919 (1999).
[18] M. E. Casida, in *Recent Advances in Density-Functional Methods*, Part I, edited by D. P. Chong (World Scientific, Singapore, 1995), p. 155; E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory*, edited by R. F. Nalewajski (Springer-Verlag, Berlin, 1996), p. 81.