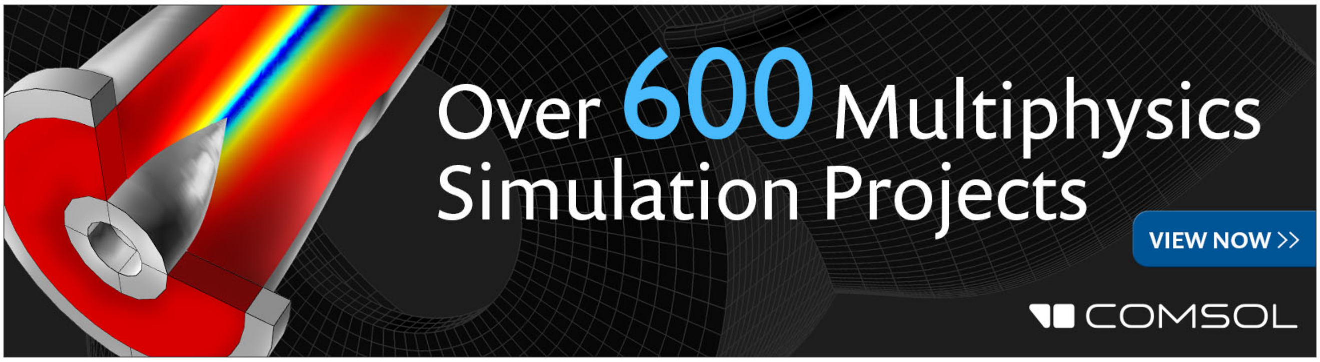
AIP Applied Physics Letters

Electronic states and curved surface effect of silicon quantum dots

Wei-Qi Huang, Zhong-Mei Huang, Han-Qiong Cheng, Xin-Jian Miao, Qin Shu, Shi-Rong Liu, and Chao-Jian Qin

Citation: Applied Physics Letters **101**, 171601 (2012); doi: 10.1063/1.4761945
View online: http://dx.doi.org/10.1063/1.4761945
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/101/17?ver=pdfcov
Published by the AIP Publishing



Electronic states and curved surface effect of silicon quantum dots

Wei-Qi Huang,[1,a)] Zhong-Mei Huang,[1] Han-Qiong Cheng,[1] Xin-Jian Miao,[1]
Qin Shu,[1] Shi-Rong Liu,[2,b)] and Chao-Jian Qin[2]
[1]*Institute of Nanophotonic Physics, Key Laboratory of Photoelectron Technology and Application, Guizhou University, Guiyang 550025, China*
[2]*State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550003, China*

(Received 7 June 2012; accepted 8 October 2012; published online 22 October 2012)

The calculation results show that the bonding energy and electronic states of silicon quantum dots (Si QDs) are different on various curved surfaces (CS), for example, a Si-O-Si bridge bond on curved surface provides the localized levels in band gap and its bonding energy is shallower than that on facet. Curved surface breaks symmetrical shape of silicon quantum dots on which some bonds can produce localized electronic states in band gap. The red-shifting of photoluminescence spectra on smaller silicon quantum dots can be explained by CS effect. In CS effect, surface curvature is determined by the shape of Si QDs or silicon nanostructures, which is independent of their sizes. The CS effect has the interesting fundamental physical properties in nanophysics as that of quantum confinement effect. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4761945]

The investigation of silicon quantum dots (Si QDs) is a very active field of research because it has the interesting fundamental physical properties of these mesoscale objects and promising applications in advanced electronic devices and optoelectronic devices.[1–6] Si QDs provide nanoscale electronic confinement resulting in opening of bandgap and occurring of quasi-direct gap, which pushes their photoluminescence (PL) emission in blue-shifting with decreasing of crystallite sizes. But the wavelength of PL emission stands at some fixed positions for smaller Si QDs prepared in oxygen, nitrogen, or air atmospheres.[7,8] Numerous models have been proposed to explain the change of the PL, Wolkin *et al.* indicated that the disappearing of the blue-shifting is related to the trapping of an electron by Si = O bond that produces localized levels in the bandgap of nanocrystals smaller than 3 nm, which was argued because no any Si = O bond has been detected in FTIR transmission spectra.[9] Hadjisavvas *et al.* found that the shape of larger nanocrystals is often observed to be faceted, while that of smaller ones is always found to be spherical.[10]

The central questions which arise are why some bonds on the surface of smaller QDs can produce localized states in gap to break the quantum confinement (QC) effect and what relation it is between the localized levels and the shape of QDs. Our calculation results show that the localized levels can be produced in bandgap by Si-O-Si bridge bond on the curved surface (CS) of smaller Si QDs, but no any localized state occurs in gap for Si-O-Si bridge bond on the facet. Therefore, besides size, shape of Si QDs is more essential for producing localized electronic state in bandgap. This may be called curved surface effect for smaller Si QDs. The analysis of PL spectra on curved surface can show the character of the type-II emission due to the curved surface effect.

We have chosen some models in order to simulate various kinds of surface structures of Si QDs prepared in different atmospheres. The models based on supercells have advantages that are simple and emphasize the quantum confinement effect and deformation of the surface structure. The electronic behavior is investigated by an *ab initio* non-relativistic quantum mechanical analysis in this work. The DFT calculation was carried out by using the local density approximation (LDA) and gradient-corrected exchange-correlation function (GGA) for the self-consistent total energy calculation.

For comparing their bonding energy and density of states, some special structures including a facet and a curviform surface are built on Si QDs. An opened bandgap and a quasi-direct gap structure are obtained for a good passivation of Si-H bonds. Figure 1(b) shows a structure and a density distribution of states that have localized levels obviously in gap by a Si-O-Si bridge bond on curved surface. And Figure 1(a) shows structure of Si-O-Si bridge bond on facet and its density of states in which no any localized state is found in gap. It is found that the bonding energy on the facet (Fig. 1(d)) is deeper than that on the curved surface (Fig. 1(c)) for a Si-O-Si bridge bond. But for a Si = O bond, everything is almost same, as shown in Fig. 2, bonding energy and density of states have little change from facet (b) to curved surface (a).

The quantum dots were fabricated by plasma produced from the interaction between silicon and pulse laser. We prepared the Si QDs by using a pulse laser (wavelength: 1064 nm, pulse width (FWHM): 60–80 ns, repetition rate: 1000–3000/s).[11] A wafer of P-type silicon with room temperature resistivity of 20 Ω cm was used as starting material, which was cleaned in a Summa cleaner for 20 min. The nanosecond pulse of laser was normally focused on the silicon sample placed in oxygen or other atmospheres. The intensity of the laser pulse was about $5 \times 10^8\ \mathrm{W\,cm^{-2}}$ on silicon, which was sufficient to produce the plasma on sample. After irradiation, a lot of silicon quantum dots are prepared by plasma, which distribute on the wall of the cavity hit by laser beam. In plasma, the dangling bonds are formed

---

[a)] Electronic mail: WQHuang2001@yahoo.com.
[b)] Electronic mail: SRLiu@yahoo.com.

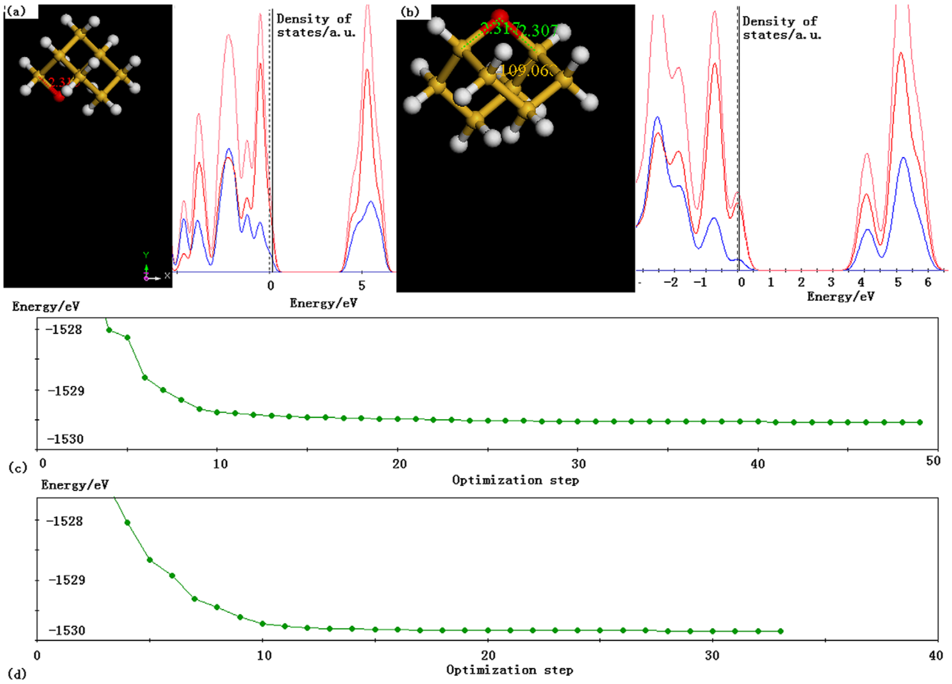


FIG. 1. (a) Si-O-Si bridge bond on facet of Si QDs and its density of states. (b) Si-O-Si bridge bond on curved surface of Si QDs and its density of states. (c) Bonding energy of Si-O-Si bridge bond on curved surface of Si QDs. (d) Bonding energy of Si-O-Si bridge bond on facet of Si QDs.

on the surface of Si QDs. Passivation of the dangling bonds on surface could be obtained by different gas atoms in different atmospheres. Some surface bonds may not provide a good passivation in smaller crystallites, which provide the localized states in bandgap. After annealing, the range of QDs sizes becomes narrower and the defect states decrease so that the emission from some localized levels becomes stronger.

By using RENISHAW Micro-Raman Systems, PL spectra of the samples were measured under the 514 nm excitation. Figure 3(a) shows the PL spectra and their deconvoluted fit peaks on the sample prepared by nanosecond pulse laser in oxygen atmosphere, in which the fit peak A is related to an emission band due to the quantum confinement effect (QDs scale: 2 nm–4 nm), the fit peaks C and D are the emission of the localized states from some surface bonds, respectively. After rapidly annealing for 5 min, the peaks C and D related to the localized states occur, whose center is near 700 nm or 600 nm, respectively, as shown in Fig. 3(b). After suitable annealing, the peaks C and D related to narrower range of the localized states become sharper and narrower because of decreasing defect states and arrangement of QDs sizes, and the narrowest width (FWHM) of the peaks reaches to 0.4 nm, as shown in Fig. 4(a).

Figure 4(b) shows a physics process of emission on Si QDs. In Fig. 4, the right side shows the opening band structure produced by QC effect, in which the type-I emission from near 800 nm to the ultraviolet is related to the electron jumping back to valence band in QDs with different sizes. This kind of emission forms a weaker and wider emission band produced by direct-recombination of electron-hole between conduction band opened and valence band. In another way, the electron is pumped to the conduction band opened, and it tunnels into the localized states with different levels related to different surface bonds to form active centers. The lifetime of the states on bottom of conduction band

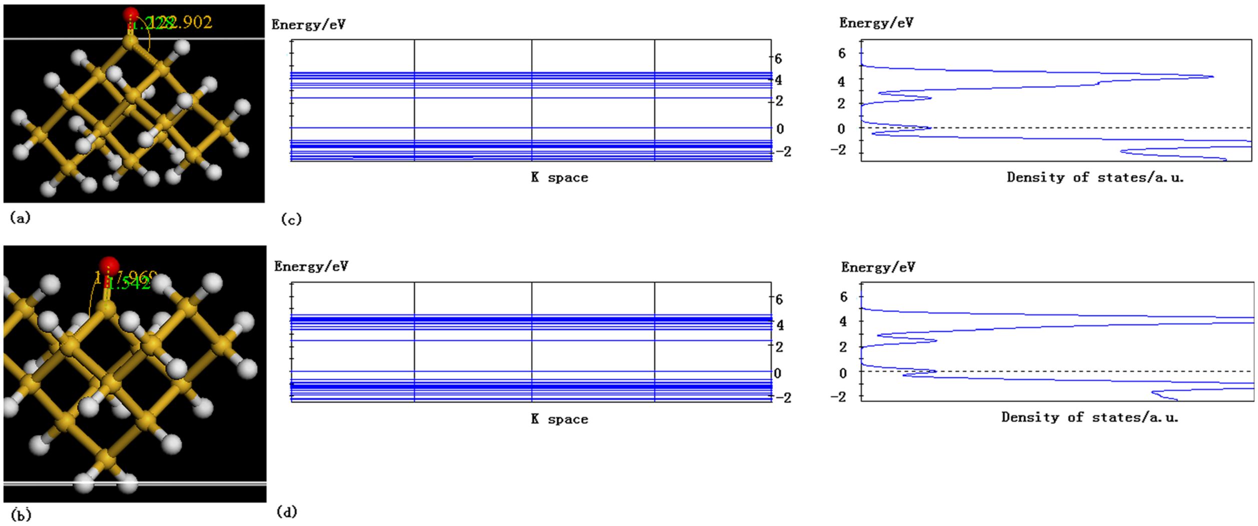


FIG. 2. Si = O bond structures on curved surface (a) and on facet of Si QDs (b), and their density of states.

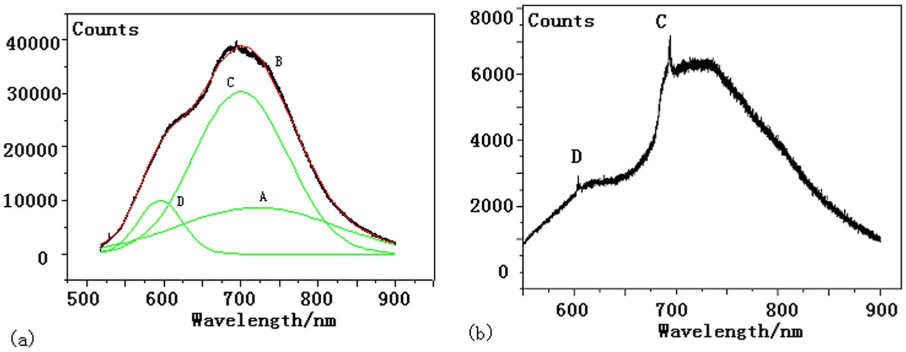


FIG. 3. (a) PL spectra on Si QDs prepared in oxygen atmosphere, in which peak A relates to type-I emission band, peaks C and D relate to type-II emission due to localized levels, respectively. (b) PL spectra on Si QDs prepared in oxygen atmosphere after rapidly annealing for 5 min, in which the peaks C and D related to the localized states occur, whose center is near 700 nm or 600 nm, respectively.

opened is shorter, which is suitable for pumping. Here, it is important that some bonds on curved surface of smaller QDs can provide the localized states, for example, the localized state of 1.78 eV and the localized state of 2.03 eV in gap. The population inversion could be formed between the valence band and the localized levels for stimulated emission, which belongs to the emission of type-II.[12] The annealing is an important step in activation for emission. The suitable annealing can decrease the arrangement of sizes of Si QDs to improve the emission of type-II.

The calculation results indicate that curviform surface breaks the symmetrical shape of silicon quantum dots on which some bonds can provide localized states in bandgap. The electronic behavior is investigated by an *ab initio* nonrelativistic quantum mechanical analysis in this work. By combining the simulation with the results of experiments, we propose some forms to describe the CS effect of QDs. At first, a curviform bonding factor A is defined as shown in the following form, which will affect the bonding energy and the localized states in gap,

$$A = B^{1/(1+d)}/R. \tag{1}$$

In the formula, R is the curvature radius of surface and B is the bonding cover factor on surface whose index d is cover dimension, such as d = 0 for Si = O bond, d = 1 for Si-O-Si bond, and d = 2 for Si-N bond. They relate to point, line, and face forms of bonding cover, respectively. It is clear that the bonding cover of lower dimension has more asymmetrical properties so that it is easy to form localized states in gap. The energy E_L of localized levels on Si QDs with the CS effect can be stated by the following form

$$E_L = C/r^m - \beta A, \tag{2}$$

where β is the bond coefficient, r is the radius of QD, and C is the coefficient of QC effect in which the index m is about 2 for Si QDs embedded in oxide. In formula (2), the first term relates to the QC effect and the second term presents the CS effect on smaller Si QDs, which provide localized levels lower than the bottom of conduction band. Here, it is

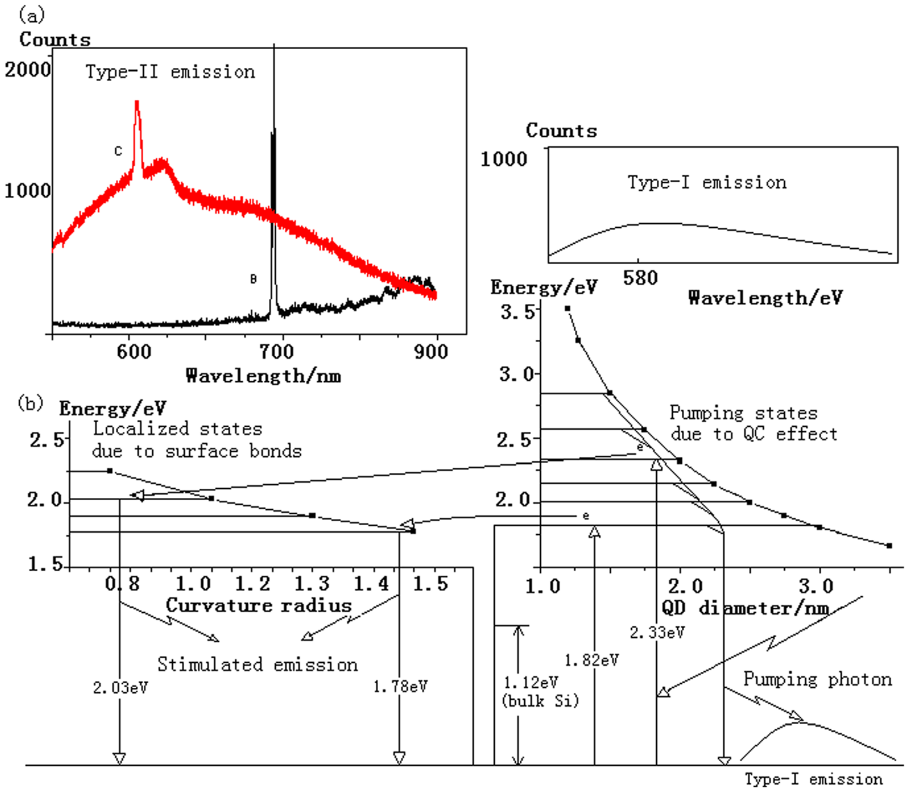


FIG. 4. (a) Type-II emission after suitable annealing and type-I emission on Si QDs before annealing; (b) physics model and proceeding of emission on Si QDs.

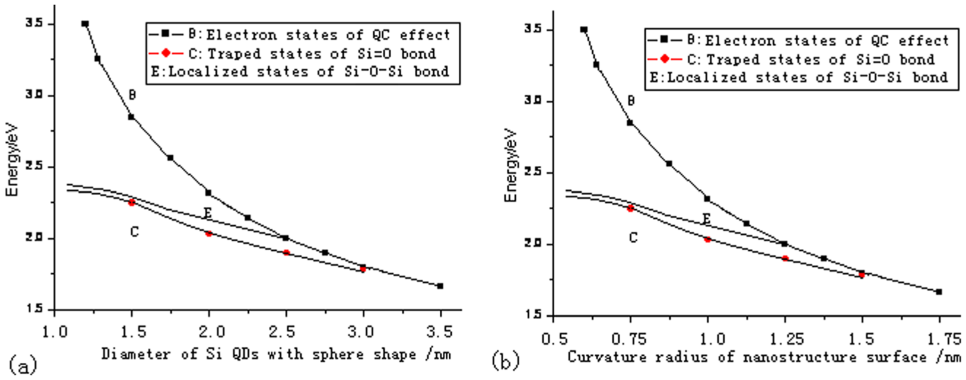


FIG. 5. (a) Level evolution of the localized states affected with the diameter of Si QDs with sphere shape. (b) Level evolution of the localized states affected with the curvature radius of Si QDs with sphere shape, which shows CS effect.

clear that the term βA relates to the red-shifting in the emission with QC effect.

A curviform energy factor A′ can be defined as shown in the following form:

$$A' = B^{(1+d)}/R. \tag{3}$$

While the bonding energy E_B with the CS effect can be described by A′,

$$E_B = -E_{B0} + \zeta A', \tag{4}$$

where ζ is the bonding coefficient and E_{B0} is the bonding energy for some bond on facet of Si QDs. Here, the bond of higher dimension d has a bigger change of bonding energy. The bonding energy is deeper on facet and its bond is more stable for Si QDs with larger sizes (>3–4 nm). For smaller Si QDs (<2–3 nm), facet on surface disappears and some bonds on curved surface begin to produce the localized states in bandgap. Therefore, the CS effect on smaller QDs is the most important factor for forming the localized levels in gap. The CS effect can explain the reason why the red-shifting of PL spectra occurs on smaller Si QDs (<3 nm) oxidized. The coefficients ζ and β in the above formulas could be modulated according to the results of experiment.

Figure 5 shows the CS effect on smaller QDs, such as along with curve E, in which the localized levels due to Si-O-Si bond on curved surface begins to form in bandgap, when the diameter of Si QDs is smaller than 2.5 nm. The sizes of Si QDs are not important; the most essential factor is the curvature of surface bonded. We look at the evolution of the curve C or curve E as if the diameter of Si QDs with sphere shape affects the levels of the localized states as shown in Fig. 5(a), but in fact, it is the curvature radius of Si QDs with sphere shape which plays a main role for providing the localized states in bandgap as shown in Fig. 5(b).

In conclusion, the results of calculation and experiment demonstrate the CS effect on smaller Si QDs, from which two problems are solved. The first one is that some bonds, such as Si-O-Si bridge bond, on curved surface of smaller Si QDs provide the localized levels in bandgap to form emission center which breaks the blue-shifting of PL spectra with the QC effect. Therefore, the CS effect plays an important role for PL emission of smaller Si QDs prepared in oxygen or other atmospheres. The second one is that the facet distributes on bigger Si QDs on which it is difficult for Si-O-Si bridge bond of surface to produce the localized states, so the QC effect plays a main role for the PL spectra of bigger Si QDs. In CS effect, it is the most important factor that the surface curvature of Si QDs or silicon nanostructures is larger, on which the Si-O-Si bridge bond or some other bond can provide the localized states in band gap. This kind of surface curvature is determined by the shape of Si QDs or silicon nanostructures, which is independent of their sizes. It can be understood why the enhancement and the red-shift of PL occur on curved surface of various Si nanostructures passivated by oxide or nitride, such as on porous silicon oxidized or hole-net silicon oxidized even on surface with larger curvature in silicon microstructures oxidized. Experiments demonstrate that silicon quantum dots are activated for emission due to the localized levels provided in CS effect.

Support from the National Natural Science Foundation of China (Grant Nos. 60966002 and 11264007) and from the National Key Laboratory of Surface Physics in Fudan University is gratefully acknowledged.

[1] A. Fowler, Phys. Today **50**(10), 50 (1997).

[2] K. D. Hirschman, L. Tsybeskov, S. P. Duttagupta, and P. M. Fauchet, Nature (London) **384**, 338 (1996).

[3] P. M. Fauchet, J. Ruan, H. Chen, L. Pavesi, L. Dal Negro, M. Cazzaneli, R. G. Elliman, N. Smith, M. Smoc, and B. Luther-Davies, Opt. Mater. **27**, 745 (2005).

[4] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, and F. Priolo, Nature (London) **408**, 440 (2000).

[5] S. Chen, B. Qian, K. J. Chen, X. G. Zhang, J. Xu, Z. Y. Ma, W. Li, and X. F. Huang, Appl. Phys. Lett. **90**, 174101 (2007).

[6] Y. Yang, C. Wang, R. D. Yang, L. Li, F. Xiong, and J. M. Bao, Chin. Phys. B **18**, 4906–4911 (2009).

[7] W. Q. Huang, F. Jin, H. X. Wang, L. Xu, K. Y. Wu, S. R. Liu, and C. J. Qin, Appl. Phys. Lett. **92**, 221910 (2008).

[8] G. Faraci, S. Gibilisco, A. R. Pennisi, G. Franzo, S. L. Rosa, and L. Lozzi, Phys. Rev. B **78**, 245425 (2008).

[9] M. V. Wolkin, J. Jorne, and P. M. Fauchet, Phys. Rev. Lett. **82**, 197 (1999).

[10] G. Hadjisavvas, I. N. Remediakis, and P. C. Kelires. Phys. Rev. B **74**, 165419 (2006).

[11] W. Q. Huang, L. Xu, and K. Y. Wu, J. Appl. Phys. **102**, 053517 (2007).

[12] W. Q. Huang, R. T. Zhang, H. X. Wang, F. Jin, L. Xu, S. J. Qin, K. Y. Wu, S. R. Liu, and C. J. Qin, Opt. Commun. **281**, 5229 (2008).