

Theoretical absorption spectra of silicon carbide nanocrystals

S.L. Shi^a, S.J. Xu^{a,*}, X.J. Wang^b, G.H. Chen^b

^a Department of Physics and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

^b Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

Available online 19 September 2005

Abstract

In this article, we report on theoretical absorption spectra of 3C–SiC nanocrystals with different sizes and different surface termination foreign atoms using the semiempirical PM3 localized-density-matrix method. Pronounced size dependence of the absorption spectra is clearly demonstrated. Besides size effect, the influence of the surface configurations on the optical property of SiC nanocrystals is also studied. The absorption spectra of 3C–SiC nanocrystals terminated with OH or NH₂ species are calculated. Compared with H-terminated case, the absorption edge of OH-terminated or NH₂-terminated 3C–SiC exhibits a significant red shift. It is also found that there are some fine structures appearing at the lower energy side of the dominant absorption peak (~4.4 eV) for OH-terminated 3C–SiC nanocrystals.

© 2005 Elsevier B.V. All rights reserved.

PACS: 78.67.Bf; 73.22.-f

Keywords: Silicon carbide; Nanostructures; Surface and interface states; Optical properties

1. Introduction

Silicon carbide (SiC) is a wide gap semiconductor with many outstanding physical and chemical properties and has important applications in high-temperature electronics [1–5]. Currently, its nanostructures are attracting a considerable interest since they are expected to exhibit novel physical properties such as enhanced luminescence efficiency [6–9]. Stable and efficient light emission may make SiC nanostructure to be a promising material for optoelectronic applications [10].

Due to huge surface-to-volume ratio, the surface states have been recognized to play a key role in determining physical and chemical properties of semiconductor nanocrystals. Available studies show that the green/blue luminescence which is found in oxidized nanocrystalline and “porous” silicon is associated with the presence of OH groups adsorbed on structural defects in SiO₂ network [11]. Similarly, optical properties of SiC nanostructures are expected to be sensitively dependent on their surface states. In this work, we investigate theoretically the optical absorption of the SiC nanocrystals with different sizes and different surface adsorbents using localized-density-matrix PM3 (LDM-PM3) method [12,13]. The LDM-PM3

method has been developed to calculate the ground- and excited-state properties of very large systems containing thousands of atoms. It is based on the truncation of reduced single electron density matrix and thus its computation time cost reduces substantially. The method has been successfully employed to calculate the absorption spectra of polymer [13,14] and carbon nanotubes [15].

2. Method

It is known that SiC has many polytypes. In this study, 3C–SiC nanocrystals are considered. Fig. 1 shows the tetragonal bonding of a central C atom and 4 nearest Si atoms. The

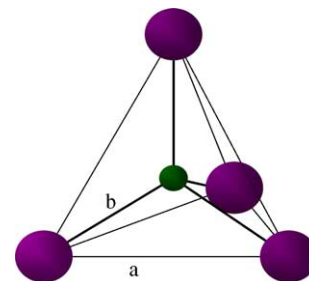


Fig. 1. The tetragonal bonding of a carbon atom with the four nearest silicon neighbors.

* Corresponding author.

E-mail address: sjxu@hkuc.hku.hk (S.J. Xu).

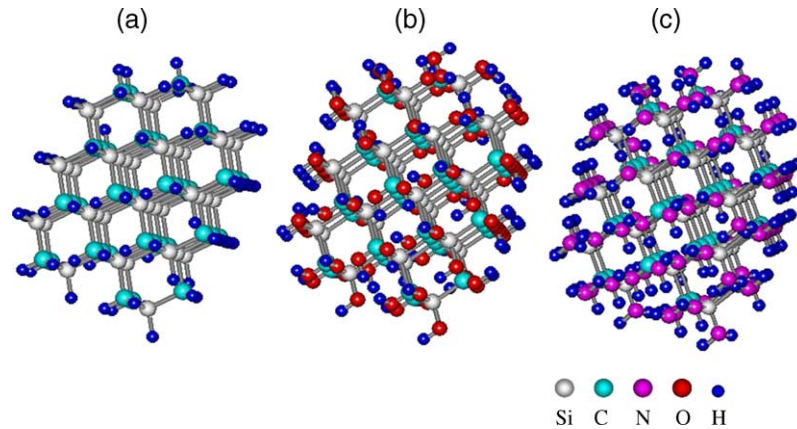


Fig. 2. Geometric structures of the 3C-SiC nanocrystals with 81 C and Si atoms used in the calculations: (a) terminated by -H; (b) terminated by -OH; (c) terminated by -NH₂.

distances, a and b , are approximately 3.08 Å and 1.89 Å for 3C-SiC, respectively. The LDM-PM3 method adopted in the present calculations has been previously described elsewhere in detail [12,13], which is successfully used to calculate the excited-state properties of very large electronic system [14,15]. Here we employ this method to compute the absorption spectra of 3C-SiC nanocrystals in the radiation field with the electric field along with the [100] crystal direction of the nanocrystals. The geometry optimization is performed by Molecular Mechanics method force field. The geometric structures of SiC nanocrystals with 81 atoms and three kinds of surface-terminating species used in the calculation are shown in Fig. 2.

3. Results and discussion

To investigate the size effect, the absorption spectra of the 3C-SiC nanocrystals with 51, 81, 111 and 201 atoms were calculated. The surfaces of the four nanocrystals are terminated with H atoms. The calculated absorption spectra are depicted in Fig. 3. From Fig. 3, it can be seen that there are three main structures, denoted by a, b, and c, in the absorption spectra. As the nanocrystal size increases, red shift of the three absorption peaks can be observed, which is a typical quantum size effect expected. It is also found that an additional peak labeled by “d”

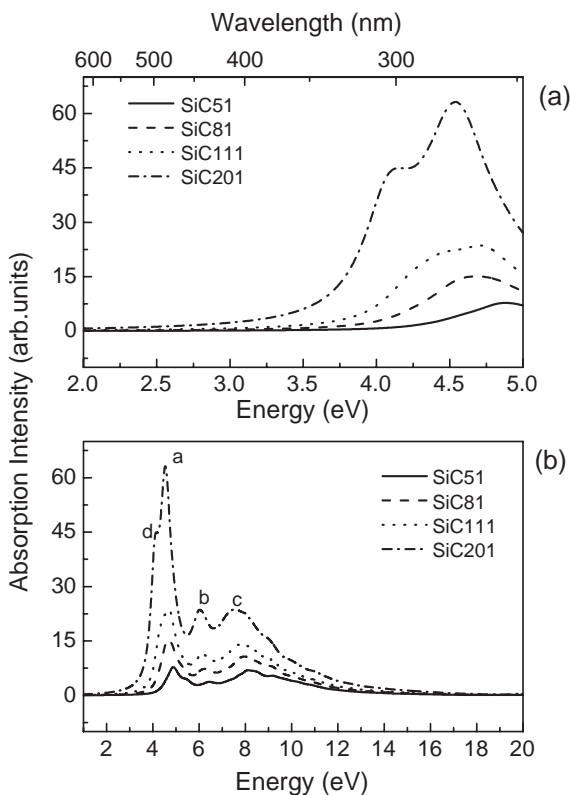


Fig. 3. (a) Enlarged lower energy parts of the absorption spectra shown in (b). (b) Calculated absorption spectra of SiC nanocrystals consisting of different numbers of atoms.

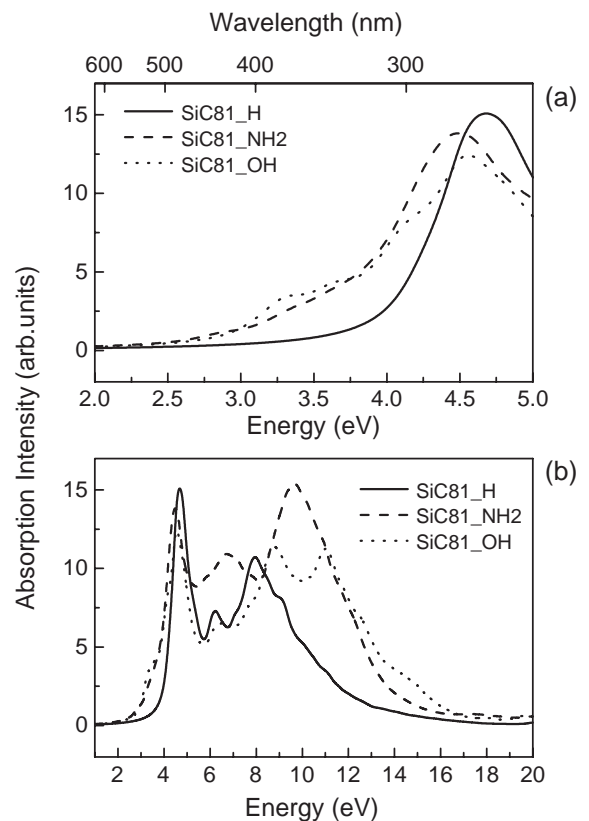


Fig. 4. (a) Enlarged lower energy parts of the absorption spectra shown in (b). (b) The absorption spectra of 81-atom SiC nanocrystals terminated by H, OH and NH₂ species.

develops at the lower energy side of the peak *a* as the nanocrystal size increases.

Calculations on the H-, OH-, and NH₂-terminated SiC nanocrystals with 81 atoms of C and Si were performed, respectively, in order to investigate the surface effect. The results are shown in Fig. 4b. As expected, the absorption spectra of 3C-SiC nanocrystals depend strongly on their surface terminating configurations. It comes from the strong variation of electron structures of the SiC nanocrystals terminated by different foreign atoms. We are particularly interested in the shift of the lowest absorption peak and the absorption edge because they are closely related to the luminescence. Enlarged lower energy parts of the absorption spectra in Fig. 4b are shown in Fig. 4a. Compared with the spectrum of the H-terminated SiC nanocrystal, the absorption edge and the lowest absorption peak of the OH- and NH₂-terminated SiC nanocrystals exhibit a large red shift. Moreover, two additional structures located at ~4.1 and 3.3 eV appear for the OH-terminated case. The red shift of the lowest absorption peaks and the appearance of the new structures in the lower energy side of the lowest absorption peak originate from the substantial change in electronic structures of the SiC nanocrystals terminated with different species. It is found that the number of these foreign atoms “covering” SiC nanocrystals is comparable with that of Si or C atoms which chemically combine into the nanocrystals. It is not difficult for one to imagine that the electronic structure of the tiny nanocrystal is significantly modified when its surface atoms absorb many foreign atoms. The exact physical origin causing the red shift of the absorption edge for the OH- and NH₂-terminated SiC nanocrystals are not clear at present. Solving the problem requires further investigations.

4. Conclusions

We have applied the semiempirical PM3 localized-density-matrix method to evaluate the absorption spectra of 3C-SiC

nanocrystals with different sizes and different surface states. The results show that the optical properties of SiC nanocrystals depend strongly on their surface configurations or adsorbents. Modification of SiC nanocrystal surfaces may be a useful way to tune their optical properties.

Acknowledgements

The work was supported by HK RGC-CERG grant under Contact No. HKU 7049/04P.

References

- [1] B. Dely, E.F. Steigmeier, *Phys. Rev. B* 47 (1993) 1397.
- [2] L. Tsykeskov, J.V. Vandyshev, P.M. Fauchet, *Phys. Rev. B* 49 (1994) 7821.
- [3] G.L. Harris, *Properties of Silicon Carbide*, INSPEC, London, UK, 1995.
- [4] Robert P. Devaty, Wolfgang J. Choyke, S.G. Sridhara, L.L. Clemen, D.G. Nizhner, David J. Larkin, T. Troffer, Gerhard Pensl, Tsunenobu Kimoto, H.S. Kong, in: G. Pensl, H. Morkoc, B. Monemar, E. Janzen (Eds.), *Silicon Carbide, -Nitrides and Related Materials*, Stockholm, Sweden, 31 Aug.–5 Sept. 1997, *Mater. Sci. Forum*, vols. 264–268, 1998, p. 455.
- [5] D. Engemann, R. Fischer, J. Knecht, *Appl. Phys. Lett.* 32 (1978) 567.
- [6] K.S. Min, K.V. Sheglov, C.M. Yang, H.A. Atwater, M.L. Brongersma, A. Polman, *Appl. Phys. Lett.* 69 (1996) 2033.
- [7] Y. Kannemitsu, *Phys. Rev. B* 48 (1993) 4883.
- [8] S. Furukawa, T. Miyasato, *Jpn. J. Appl. Phys., Part 2* 27 (1988) L2207.
- [9] S.J. Xu, M.B. Yu, Rusli, S.F. Yoon, C.M. Che, *Appl. Phys. Lett.* 76 (2000) 2550.
- [10] L. Hoffman, G. Ziegler, D. Theis, C. Weyrich, *J. Appl. Phys.* 53 (1982) 6962.
- [11] H. Tamura, M. Ruckschloss, Thomas Wirschem, Stan Veprek, *Appl. Phys. Lett.* 65 (1994) 1537.
- [12] S. Yokojima, G.H. Chen, *Chem. Phys. Lett.* 292 (1998) 397.
- [13] C.Y. Yam, S. Yokojima, G.H. Chen, *Phys. Rev. B* 68 (2003) 153105.
- [14] M.-F. Ng, Y. Zhao, G.H. Chen, *J. Phys. Chem. B* 107 (2003) 9589.
- [15] W.Z. Liang, X.J. Wang, S. Yokojima, G.H. Chen, *J. Am. Chem. Soc.* 122 (2001) 11129.