

Frequency shift in the photoluminescence of nanometric SiO_x : surface bond contraction and oxidation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 L547

(<http://iopscience.iop.org/0953-8984/11/48/104>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.220

The article was downloaded on 15/05/2010 at 18:03

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Frequency shift in the photoluminescence of nanometric SiO_x : surface bond contraction and oxidation

Chang Q Sun[†], X W Sun[‡], H Q Gong[§], H Huang[†], H Ye[†], D Jin[†] and P Hing[†]

[†] Advanced Materials Research Centre, Nanyang Technological University, Singapore 639798

[‡] School of Electric and Electronic Engineering, Nanyang Technological University, Singapore 639798

[§] School of Mechanical Production Engineering, Nanyang Technological University, Singapore 639798

E-mail: cqsun@gintic.gov.sg

Received 20 August 1999

Abstract. The frequency of photoluminescence is determined by the gap between the conduction and valence band. The width of the band gap depends on the crystal field and the chemical reaction, because the crystal field defines the band structure and the reaction repopulates with valence electrons. It is derived that the surface bond contraction and the rise in surface-to-volume ratio enhance the crystal field and determine the trend of frequency change, while oxidation enhances this behaviour by adding a constant.

Investigation of nanocrystalline and porous Si oxide has attracted tremendous interest due to the scientific and technological significance. The nanostructured Si compounds have potential applications in photoluminescence (PL). The frequency of the photon varies over a wide spectral range from the infrared to the ultraviolet, depending on the shape and size of the particles and the chemical treatment process [1]. In addition to the mechanisms of quantum confinement [2], PL centre formation [3] and surface alloying [4], Iwayama, Hole and Boyd (IHB) [5] proposed a mechanism and used it to interpret their interesting findings on the PL of Si nanocrystals embedded in an amorphous SiO_2 matrix—that is, the cluster interaction and the oxidation effect. A knowledge of the functional dependence of the PL frequency on (i) the particle shape and size, (ii) the cluster interaction and (iii) the chemical effect is highly desirable when attempting to achieve an understanding of the nature of this phenomenon. This article presents an approach with this objective.

It is known that the frequency shift of the PL reflects the band-gap change of the system. The band gap originates from the crystal field: a sum of interatomic potentials that depends on the atomic separation and quantity of charge of the neighbouring atoms [6]. A shortened bond length and positively charged ions enhance the crystal field and hence also the band gap. Reaction also enhances the crystal field by weakening the screening effect due to charge transfer. The process of charge transfer further widens the band gap directly by emptying the occupied density of states (DOS) below E_F . It has been shown [7] that electronegative elements such as oxygen and nitrogen possess the special ability to produce or widen the band gap by producing holes below E_F through charge transportation during bond formation.

The particle-size-determined band gap is expressed as [6]

$$\frac{\Delta E_g}{E_g} = \frac{\Delta V(r, nN)}{V(r, nN)} = \sum_{i \leq 3} \gamma_i \frac{\Delta u(d_i)}{u(d)} + \delta = \sum_{i \leq 3} \gamma_i (c_i^{-m} - 1) + \delta \quad (1)$$

where

$$\delta = \frac{nV(D)}{N^2u(d)}$$

where $V(r, nN)$ is the crystal field of n particles where, with each particle, there are N atoms. $u(d)$ is the atomic potential. γ_i is the i th surface-to-volume ratio of a particle and has the form [8]

$$\gamma_i = \frac{N_i}{N} = \frac{n}{k} c_i \left(1 - \frac{i - 0.5}{k}\right)^{n-1} = \gamma'_i c_i \quad (2)$$

where $c_i = d_i/d$ and $c_i < 1.0$ is the coefficient of bond contraction due to the reduction of the coordination number [9] of the surface atoms. i counts from the outermost layer of the particle with dimension $D = 2kd$ and $n = 1, 2, 3$ corresponds to plate, rod, spherical dot, each a nanometre across. γ_i can easily be derived, for a spherical dot example, by dividing the volume of a spherical shell $4\pi[(k - (i - 0.5))d]^2 d_i$ by the volume of the entire dot. Upon bond contraction, the interatomic potential becomes $u(d_i) = c_i^{-m}u(d)$. m is an adjustable parameter that depends on the type of atomic potential. δ describes the contribution of the cluster interaction $V(D)$ to the band-gap enlargement in equation (1). The band-gap expansion of a nanometric system results from the surface bond contraction (c_i) and the rise in surface-to-volume ratio that depends on the shape (n) and size (k) of the particles as well as the type of atomic interaction (m).

Figure 1 simulates the size-dependent PL energy obtained by Schuppler *et al* [10] for SiO_x nanoparticles. Surface bond contractions of 12% and 6% were applied, respectively, to the first two atomic layers of a spherical dot. Such a scale of bond contraction has formed important stages in the O–Cu(100) surface bonding dynamics [11]. It can be seen that the curve for $m = 2$ follows the trend of band-gap expansion. A 27% offset of the curve for $m = 2$ describes the oxidation effect well, with acceptable errors at larger particle size (offset 18%). The error at larger particle size may result from the shape change from spherical dot to columnar rod with increasing particle size. The surface-to-volume ratio of a rod is 2/3 of that of a spherical dot (equation (2)). The cluster interaction seemed not to be apparent in this case. Therefore, the band-gap expansion is dominated by the surface bond contraction and oxidation, which simply adds a constant to the effect of the physical shape and size.

The results support interpretations given by IHB for the Si nanocrystals embedded in an amorphous Si oxide matrix. First, the red-shift of the PL caused by the increase in Si dose (annealing at 1050 °C for eight hours in N_2) can be attributed to the particle size increase [5]. Second, the blue-shift of the PL (after annealing at 1050 °C for eight hours in N_2 and subsequent annealing at 1000 °C for 30–90 min in O_2) can be ascribed as the oxidation effect that widens the band gap. Then, the recovery in the PL energy after re-annealing in N_2 at 1050 °C for one hour may be interpreted as the replacement of oxygen by nitrogen. This phenomenon provides evidence that the effect of nitrogen is weaker than the effect of oxygen on the band-gap enlargement, due to the difference in electronegativity between O (3.5) and N (3.0). The electronegativity difference determines the quantity of charge transfer among the specimens. The intensity change is not covered in the current model but it can be easily understood on the basis of the PL efficiency, particle density and size distribution, as indicated by IHB. Apparently, the band gap is an intrinsic feature of the material and it is independent of the excitation energy. The fact that annealing in N_2 for two hours causes no change in peak position

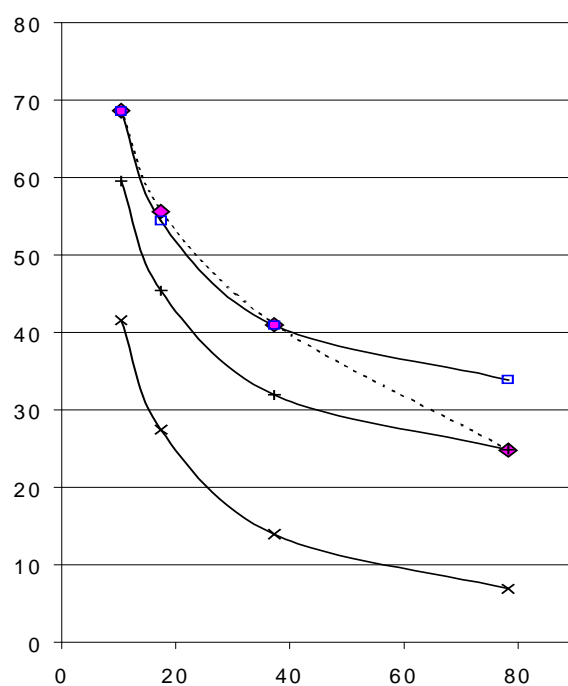


Figure 1. Simulation of the size dependence of the PL shift (broken line) reported in reference [5]. The curve for $m = 2$ makes clear the particle-size (surface bond-contraction) effect and the offset indicates the mixture of cluster interaction and oxidation.

(This figure can be viewed in colour in the electronic version of the article; see www.iop.org)

compared with annealing for eight hours indicates the saturation of the reaction at two hours or less.

Therefore, the overall PL features of nanocompounds can be consistently understood in terms of the crystal field and the chemical reaction. The former defines the band gap; the latter widens it by electron transportation. The frequency of the PL of a nanometric Si compound is determined intrinsically by the surface bond contraction and the rise in surface-to-volume ratio as well as the type of atomic potential. Cluster interaction plays an insignificant role. The trend of the frequency change is dominated by the physical shape and size. Chemical reaction enhances the size and shape effect by adding a constant.

References

- [1] TheiB W 1997 *Surf. Sci. Rep.* **29** 91
- [2] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
- [3] Qin G G and Jia Y Q 1993 *Solid State Commun.* **86** 559
- [4] Koch F, Petrova-Koch V, Muschik T, Nikolov A and Gavrilenko V 1993 *Micrystalline Semiconductors: Materials Science and Devices* vol 283 (Pittsburgh, PA: Materials Research Society) p 197
- [5] Iwayama T S, Hole D E and Boyd I W 1999 *J. Phys.: Condens. Matter* **11** 6595
- [6] Sun C Q, Gong H Q, Hing P and Ye H T 1999 *Surf. Rev. Lett.* **6** L171
- [7] Sun C Q 1998 *Appl. Phys. Lett.* **72** 1706
- [8] Sun C Q 1999 *J. Phys.: Condens. Matter* **11** 4801
- [9] Goldschmidt V M 1927 *Ber. Deutsch. Chem. Ges.* **60** 1270

- [10] Schuppler S, Friedman S L, Marcus M A, Adler D L, Xie Y H, Ross F M, Chabal Y J, Harris T D, Brus L E, Brown W L, Chaban E E, Szajowski P F, Christman S B and Citrin P H 1995 *Phys. Rev. B* **52** 4910
- [11] Sun C Q 1997 *Vacuum* **48** 535