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Annealing effects on the size of Si-nanocrystals embedded in bulk SiO

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1. Introduction Application of silicon nanocrystals (Si-nc) for biological labeling [1] attracts intense attention in recent years, due to their relatively strong luminescence [2] 41 and low toyicity compared

ing [1] attracts intense attention in recent years, due to their relatively strong luminescence [2–4] and low toxicity compared with group II–VI nano-particles [1]. For bio-related applications, it is required to synthesize Si-nc in large quantities effectively. A variety of methods have been proposed and demonstrated, including electrochemical etching of single crystalline silicon [5], gas phase synthesis using CO_2 lasers [6], radio frequency plasma synthesis [7] and thermal annealing of hydrogen silsesquioxane [8], etc.

Recently, annealing of bulk silicon monoxide (SiO) [9] was proposed as a potentially cost-effective method because the fabrication of bulk SiO has been industrialized and simple further annealing treatment is needed. In Ref. [9], infrared light emission was demonstrated on Si-ncs embedded in bulk SiO. In Refs. [10,11], surface modification was carried out on such Si-ncs to achieve visible light emission and high luminescence intensity. However, the formation process and how to control the size of Si-nc by annealing bulk SiO are still unclear. Kapaklis et al. [9,12] reported that the size of Si-nc seemed to be independent of annealing conditions. In contrast, Mamiya et al. [13] found that the size of Si-nc was greatly affected by the annealing temperature while the annealing time was less than 30 min, and short-term saturation was observed with longer annealing time. Moreover,

ABSTRACT

In the process of synthesizing Si-nanocrystals (Si-nc) from bulk SiO, the relationship between Si-nc size distribution and annealing condition (temperature from 800 to 1150 °C and time from 1 to 16 h) is experimentally investigated by X-ray diffraction and high resolution transmission electron microscopy. It is found that the average size of Si-ncs can be tuned through annealing condition from less than 3 nm to ~10 nm, while the size distribution follows a lognormal function with an almost unchanged standard deviation of 0.2. After annealing at even higher temperature (1150 °C), two groups of Si-ncs with very different average sizes exist simultaneously and a double lognormal function should be applied to describe the size distribution.

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detailed information about the size distribution of Si-ncs prepared with this method is still unknown.

In this paper, the relationship between size distributions of Si-ncs and annealing conditions (temperature from 800 to 1150 °C and time from 1 to 16 h) is experimentally investigated by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). It is found that the annealing temperature and time can both affect the average size and size distribution of Si-ncs (especially the former): the average size can be tuned widely from less than 3 to ~10 nm, and the size distribution can be described by a lognormal function with an almost unchanged standard deviation of 0.2. For annealing at even higher temperature (1150 °C), two groups of Si-ncs with very different average sizes exist simultaneously in bulk SiO, and a double lognormal function is needed to describe the size distribution.

2. Experiment

In our experiment, the bulk SiO particles (99.9% purity) are prepared by the reduction of SiO₂ and the diameters are about a few millimeters (purchased from Beijing Founde Star Science and Technology Co., Ltd.) In order to determine the exact stoichiometry, ten particles are cut and polished to obtain a flat plane and then measured with an energy dispersive X-ray spectrometer (EDS, Oxford INCA-300). For annealing treatment, SiO particles are placed in an alumina boat inside a horizontal tube furnace filled with N₂ (99.9%) at a heating rate of 20 °C/min. Various combinations of annealing conditions are applied.

In order to characterize the growth process of Si-nc under different annealing conditions, XRD measurement is carried out

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with Rigaku D/Max 2500PC (CuK α line, 0.154051 nm), and the width of Bragg peak is employed to calculate the average size of Si-ncs. To prepare XRD samples, SiO particles (with a certain annealing condition) are crushed first and then milled. The final powder sizes are about tens of microns, which are determined with an optical microscope. These powders are placed in a 2 cm² square groove on a piece of slide glass and then planished for XRD measurement.

In order to confirm the existence of Si-ncs directly and obtain the size distribution, HRTEM images of some samples are measured with JEOL-2011. Particles are crushed, placed in ethanol and then milled. The suspension is precipitated for about 15 min. A micro-grid is dipped into the top layer of the suspension to absorb some small fragments (most of them are less than 1 μ m). After ethanol evaporates, the micro-grid is used for TEM measurement. To determine Si-nc size from a TEM image, a Si-nc is treated as an ellipse and the lengths of major axis and minor axis are measured.

3. Results

The O/Si ratio of original bulk SiO is found to be 1.02–1.05 and uniform over micron-scale (limited by electron beam size) for all ten measured particles. Fig. 1 shows the XRD spectrum of the original SiO particles (in Fig.1(a) and labeled as "before") as well as those after annealing treatments (labeled with annealing conditions). Five Bragg peaks of Si ranging from 20° to 80° are labeled in the figure for comparison. Fig. 2(a) and (b) shows the HRTEM images of SiO without annealing treatment and those annealed at 1100 °C for 1 h (1100 °C–1 h in short), respectively.



Fig. 1. XRD spectra of SiO before (in part (a), labeled with "before") and after annealing treatment (labeled with their annealing conditions). Five Bragg peaks of Si ranging from 20° to 80° are also labeled for comparison.



Fig. 2. HRTEM images of SiO without (a) and with 1100 °C-1 h annealing (b).

For the original SiO without annealing, two broad peaks around 25° and 50° can be identified in the XRD spectrum. The former is introduced from Si(1 1 1) and α -SiO₂ (which is around 21°) signals, and the latter is from Si(2 2 0) and Si(3 1 1). In the corresponding HRTEM images (Fig.2(a)), there are no nanostructures. These results indicate that the original SiO is a uniform mixture phase of Si and α -SiO₂.

After annealing, Si-ncs emerge from such mixture phase and the process can be revealed by XRD measurements as shown in Fig.1(a)–(d). When the annealing temperature is lower than 800 $^{\circ}$ C and annealing time is shorter than 8 h. no significant change can be found. For 900 °C-1 h annealing, the broad peak around 25° splits into two peaks at 28° and 21°, which are typical responses of Si(1 1 1) and α -SiO₂, respectively. Meanwhile, the peak around 50° also splits into two peaks at 47° and 56° related to Si(2 2 0) and Si(3 1 1), respectively. These phenomena indicate the emergence of crystalline Si, which becomes more profound for annealing treatment stronger than 900 °C-8 h. For higher temperature and/ or longer annealing time, three main Bragg peaks of Si become narrower while other weak signals, such as Si(400) and Si(331), can be observed as well. These trends can be seen very clearly from Fig. 1(b)-(d). HRTEM image of SiO annealed at 1100 °C-1 h is shown in Fig. 2(b), where Si-ncs are clearly observed with the fringe lattice spacing of crystalline Si(1 1 1)-0.31 nm. Under this condition, the average size of Si-ncs is around 5-6 nm.

It is interesting to note that for some strong annealing conditions, such as 1050 °C (longer than 4 h), 1100 °C (longer than 2 h), 1150 °C (longer than 2 h), part of α -SiO₂ begins to crystallize, as shown by the sharp peak at 21° and 36°, which corresponds to the first two strongest peaks of α -cristobalite [14]. Such phenomenon is reasonable because amorphous silica can change into cristobalite with temperatures between 1000 and 1723 °C [15].

4. Discussion

Compared with bulk Si, broad Bragg peaks in XRD spectra of Si-ncs are caused by smaller size. Furthermore, in the process the widths of Bragg peaks become narrower along with stronger annealing condition which corresponds to increasing size of Si-ncs. From Scherrer formula, the diameter of Si-ncs can be extracted from a Bragg peak in the XRD spectrum as

$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where *D* is the diameter of Si-nc, *K* is a constant around 0.9, λ is the wavelength of X-ray, *B* is the full width at half maximum of a Bragg peak, and θ is the Bragg angle. Then, the calculated *D*-values

from the three main peaks $(Si(1 \ 1 \ 1), (2 \ 2 \ 0)$ and $(3 \ 1 \ 1))$ are averaged to represent the average size of Si-ncs. Finally, the average sizes of Si-ncs versus annealing temperature and time are shown in Fig. 3(a) and (b). From Fig.3, one can clearly see that, within the applied range of annealing conditions, the average size of Si-ncs varies from less than 3 nm to about 10 nm, and the effect of annealing temperature is much more significant than that of annealing time.

While the annealing temperatures are 950, 1050 and 1100 °C, the average size of Si-ncs is almost fixed at around 3 nm (annealing time from 1 to 8 h), tunable from 3.5 nm to 4.5 nm (annealing time from 1 to 8 h) and from 5.5 to 8 nm (annealing time from 1 to 16 h), respectively. Under 1150 °C annealing, a much wider tuning range can be achieved within only 4 hours. Generally, the average size of Si-ncs increases gradually along with annealing time. The growth rate is fast within the first 2–4 h and then slows down for longer annealing time. Such a trend of saturation is different from that in Ref. [13], where the growth would stop in less than 30 min.

The growth trend shown above can be explained by Si diffusion controlled growth model [16] or diffusion-limited Ost-wald ripening model [17]. According to these two models, Si-nc size is written as

$$d^2 - d_0^2 \propto texp(-E_a/kT) \tag{2}$$

or

$$d^3 - d_0^3 \propto \frac{t}{T} \exp(-E_a/kT) \tag{3}$$

where *d* is the final size of Si-nc, d_0 is the initial size of Si-nc, *t* is the annealing time, E_a is the diffusion activation energy, *k* is the Boltzmann constant and *T* is the annealing temperature. While the initial size d_0 is ignored, d^2 or d^3 is proportional to annealing time *t*,which would lead to a saturation phenomenon in long-term annealing treatment.

As shown in Fig. 3(b), the effect of annealing temperature on the average size of Si-ncs could be described as an exponentiallike function. This is consistent with the factor $\exp(-E_a/kT)$ predicted by the models mentioned above. With the average sizes of our samples, E_a are found to be 2.1 or ~3.5 eV, which are both similar to the results of Refs. [16,17].

It is to be noted that aside from the annealing conditions, the stoichiometry *x* of SiO_{*x*} can also greatly affect the size of Si-nc. For example, Si-ncs with the size of ~5.5 nm emerge in our samples (x=1) with 1100 °C-1 h annealing, while the size of Si-nc can be only 4.3 and 2–3 nm in x=1.17 [18] and x=1.4 [19] samples with the same annealing condition, respectively.

The width of Bragg peak in XRD spectrum can only reveal the average size of Si-ncs. In order to determine the size distribution



Fig. 3. Annealing time effect (a) and annealing temperature effect (b) on Si-nc sizes.



Fig. 4. Size distribution statistics of SiO annealed with (a) 950 °C-1 h, (b) 1050 °C-1 h, (c) 1100 °C-1 h and (d) 1150 °C-1 h, where gray bars (width=0.5 nm) are counting frequency and solid lines are lognormal distributions whose parameters are labeled in the figures. The TEM images (both large area images and HRTEM images) of each annealing condition are also shown in the corresponding column.

as well as to confirm the calculation results of XRD, statistical treatment was performed on TEM images of some samples. In TEM images, Si-ncs are treated as ellipses and the average size *D* is defined as

$$D = \sqrt{ab} \tag{4}$$

where *a* is the major axis length of the ellipse and *b* is the minor one. The results of SiO annealed with 950 °C–1 h, 1050 °C–1 h, 1100 °C91 h and 1150 °C–1 h are shown in Fig.4(a)–(d), wherein the bars are the counting frequency with each bin of 0.5 nm and the solid lines are calculated with lognormal functions to describe the ideal size distributions. A lognormal distribution is expressed as

$$\rho = A \exp\left(-\frac{(\ln D/D_0)^2}{2\sigma^2}\right) \tag{5}$$

where A is a constant for normalization, D_0 is the average size of Si-ncs and σ is the standard deviation. The corresponding TEM images (both large area images and HRTEM images) are also shown in Fig. 4. Along with the increase of annealing temperature, the increase of size and density of Si-ncs can be seen clearly from these TEM images.

For the annealing temperature lower than 1150 °C, the average sizes of 3, 5.5 and 8 nm (Fig.4(a)–(c)) are consistent with the results of XRD calculations and the standard deviations are all around 0.2. Although the standard deviations are almost unchanged for all samples, the size distribution broadens along with the increasing average size, simply because the full width at half maximum of a lognormal distribution is proportional to D_0 .

It should be noted that a different phenomenon is observed for the samples annealed with 1150 °C–1 h. From the TEM image shown in Fig. 4(d), it can be found that both large (\sim 10 nm) and small (\sim 3 nm) Si-ncs exist at the same time, which is quite different from the other samples. A double lognormal size distribution including 3 nm/0.3 and 10 nm/0.2 is adopted and shown in Fig. 4(d). Such phenomenon may be introduced by further phase separation of SiO under a high temperature. As a result, the size obtained by XRD (\sim 7 nm as shown in Fig. 3) is averaged between two Si-nc groups with sizes of 3 and 10 nm. So for high temperature annealing, one should bear in mind that there is no one-to-one correspondence between XRD spectra and the size of Si-ncs.

Based on the present work, large quantities of free-standing Si-ncs can be synthesized by etching SiO with HF. As an example, 20 mL solution with free-standing Si-ncs is obtained from 50–100 mg SiO annealed with 1100 °C–1 h. Such solution can emit bright red light while irradiated by an ultraviolet pump. Further work is still going on and will be reported elsewhere.

5. Conclusion

In conclusion, Si-ncs in large quantities are prepared by annealing bulk SiO. The relationship between the size distributions of Si-ncs and annealing conditions is experimentally investigated by XRD and HRTEM. It is found that both annealing temperature and time (especially the former) can affect the growth of Si-ncs. Si-ncs with an average size from less than 3 nm to about 10 nm are obtained by proper annealing treatments. While the annealing temperature is not higher than 1100 °C, the size distribution of Si-ncs can be described as lognormal functions with an almost unchanged standard deviation of 0.2. For 1150 °C annealing, a double lognormal function is needed to describe the Si-nc size distribution, while the XRD measurements can only provide the average size value.

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References

- [1] F. Erogbogbo, K.T. Yong, I. Roy, G. Xu, P.N. Prasad, M.T. Swihart, ACS Nano 2 (2008) 873.
- [2] D. Jurbergs, E. Rogojina, L. Mangolini, U. Kortshagen, Appl. Phys. Lett. 88 (2006) 233116.
- [3] M. Ray, K. Jana, N.R. Bandyopadhyay, S.M. Hossain, D. Navarro-Urrios, P.P. Chattyopadhyay, M.A. Green, Solid State Commun. 149 (2009) 352. [4] J.M. Mei, Y.J. Rui, Z.Y. Ma, J. Xu, D. Zhu, L. Yang, X. Li, W. Li, X.F. Huang,
- K.J. Chen, Solid State Commun. 131 (2004) 701.
- [5] V. Lehmann, U. Gosele, Appl. Phys. Lett. 58 (1991) 856.
- [6] X. Li, Y. He, S.S. Talukdar, M.T. Swihart, Langmuir 19 (2003) 8490.
- [7] L. Mangolini, E. Thimsen, U. Kortshagen, Nano Lett. 5 (2005) 655.
- [8] C.M. Hessel, E.J. Henderson, J.G.C. Veinot, J. Phys. Chem. C 111 (2007) 6956.

- [9] V. Kapaklis, C. Politisb, P. Poulopoulos, P. Schweiss, Appl. Phys. Lett. 87 (2005) 123114.
- [10] S. Liu, S. Sato, K. Kimura, Langmuir 21 (2005) 6324.
- [11] S. Sato, M.T. Swihart, Chem. Mater. 18 (2006) 4083.
- [12] V. Kapaklis, C. Politis, P. Poulopoulos, P. Schweiss, Mater. Sci. Eng. B 124-125 (2005) 475.
- [13] M. Mamiya, H. Takei, M. Kikuchi, C. Uyeda, J. Cryst. Growth 229 (2001) 457.
- [14] X.M. Li, X.W. Yin, L.T. Zhang, S.S. He, J. Non-Cryst. Solids 354 (2008) 3254.
- [15] Robert B. Sosman, The Phase of Silica, Rutgers University Press, 1965.
- [16] L.A. Nesbit, Appl. Phys. Lett. 46 (1985) 38.
- [17] C. Bonafos, B. Colombeau, A. Altibelli, M. Carrada, G.B. Assayag, B. Garrido, M. Lopez, A. Perez-Rodriguez, J.R. Morante, A. Claverie, Nucl. Instrum. Methods Phys. Res. B 178 (2001) 17.
- [18] U. Kahler, H. Hofmeister, Opt. Mater. 17 (2001) 83.
- [19] M.C. Kim, Y.M. Park, S.H. Choi, K.J. Kim, J. Korean Phys. Soc. 50 (2007) 1760.