

Available online at www.sciencedirect.com



Solid State Communications 133 (2005) 151-155

solid state communications

www.elsevier.com/locate/ssc

Catalytic and non-catalytic growth of amorphous silica nanowires and their photoluminescence properties

Soumitra Kar, Subhadra Chaudhuri*

Department of Materials Science, Indian Association for the cultivation of Science, Jadavpur, Kolkata 700 032, India

Received 4 September 2004; accepted 6 October 2004 by C.N.R. Rao

Available online 3 November 2004

Abstract

A simple method based on the thermal oxidation of Si wafers in presence of a mixture of MgO and graphite powder was developed for large-scale synthesis of very long amorphous silica nanowires. The synthesis was done with and without gold as the catalyst. Almost aligned uniform nanowires with diameters within 60–90 nm and length up to few hundred micrometers were obtained using gold as the catalyst while bicycle chain like nanowires were obtained in absence of the catalyst. The growth sequence of the nanowires was observed through scanning electron microscope. Both forms of the nanowires emitted blue lights at 414 nm (3 eV) under excitation at 250 nm.

© 2004 Elsevier Ltd. All rights reserved.

PACS: 61.46.+w; 68.37.Hk; 68.37.Hp; 78.55.-m

Keywords: A. Nanowire; B. Silica; C. Scanning and tunneling electron microscopy; D. Photoluminescence

1. Introduction

In recent years, 1D nanomaterials have attracted considerable attention because of their potential application in nanoscale optics, magnetics, electronics and optoelectronics etc. [1–3]. There is an excellent review article on 'Inorganic nanowires' by Rao et al. [4] packed with huge information about the synthesis and characterization of various types of one-dimensional nanostructures. Nano-scale optical wires are of scientific and technological interest in the fields of localization of light, low dimensional wave-guide and scanning near-field optical microscopy (SNOM) [5]. Silica (SiO₂), an important photoluminescence (PL) material, has been actively studied for a long time. The PL band of bulk SiO₂ or SiO₂ films have peaks around 1.9-4.3 eV [6,7]. SiO₂ nanowires have been prepared by several methods [5,8–13]. Excimer laser ablation method had been adapted by Yu et al. [5] to synthesize amorphous SiO_2 nanowires and they have also reported intense blue light emission from the nanowires. Conventional VLS mechanism was modified by Pan et al. [8] to grow SiO₂ nanowires by using molten gallium (low melting point material) as catalyst placed on Si wafer heated at temperature 1150 °C for 5 h. Tin (Sn) was also used [9] as the catalyst on Si wafer to grow SiO2 nanowires. Carbothermal reduction process [10], electrochemically induced sol-gel route [11] and CVD process [12] were also employed to generate one-dimensional silica nanostructures. Lee at el. [13] has produced silica nanowires by direct solid-state transformation from silica films on TiN/Ni/SiO2/Si substrates during annealing in H₂ and H₂:CH₄ mixture at 1050 °C. Recently, Deepak et al. [14] has reported the formation of crystalline silica nanowires by heating a mixture of fumed silica and activated carbon at 1300 °C for 5 h in flowing Ar atmosphere. All these processes required either very high temperature or long deposition time or additional Si source other than Si substrates or some reducing gas to synthesize silica nanowires.

^{*} Corresponding author. Tel.: +91 33 2473 4971; fax: +91 33 2473 2805.

E-mail address: mssc2@mahendra.iacs.res.in (S. Chaudhuri).

^{0038-1098/\$ -} see front matter © 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.ssc.2004.10.026

In this letter, we report the production of large quantity of amorphous silica nanowires by direct oxidation of Si wafers in presence of MgO powder and graphite powder in equal weight ratio using moderate temperature and short deposition time. The effect of Au catalyst on the growth morphology of the nanowires and the photoluminescence (PL) property of the nanowires were investigated.

2. Experimental

For the synthesis of silica nanowires conventional horizontal tube furnace was used. Synthesis was done with and without gold as the catalyst. In order to prepare amorphous silica nanowires a mixture of MgO powder and graphite powder in the weight ratio of 1:1 was loaded into a quartz boat. An n-type Si (100) wafer, ultrasonically cleaned in acetone for 30 min, was clipped over the quartz boat 2 mm above the MgO and graphite powder mixture and the total system was positioned inside a quartz tube. The quartz tube was connected to a rotary vacuum system along with an argon gas cylinder to maintain the argon flow (at $\sim 500 \text{ cm}^3/\text{min})$ in the tube throughout the deposition period. The inlet of the argon gas as well as that of the rotary outlet was in the same side of the quartz tube. The whole quartz tube was inserted inside the preheated furnace with a set temperature of 1100 °C and it was kept at that temperature for a desired time period. For the catalytic growth, cleaned Si wafers were coated with a thin (~ 25 A) layer of gold (Au) by using simple sputtering technique and keeping the other parameters unchanged, the deposition temperature was reduced to 1000 °C.

The products were characterized using Seifert 3000 P Xray diffractometer with Cu K_{α} radiation and the compositional analysis was done by EDAX (Kevex, Delta Class I). Microstructures of the nanoforms were obtained by scanning electron microscopy (Hitachi S-3200). High-resolution transmission electron microscopic (HRTEM) image and the typical selected area electron diffraction (SAED) pattern of SiO₂ structures were taken with JEOL HRTEM (JEM 3000 F). Photoluminescence (PL) measurements were carried out at room temperature using 250 nm as the excitation wavelength using a luminescence spectrometer (Perkin– Elmer, LS50B).

3. Results and discussion

3.1. Microstructural analysis

The growth sequence and morphology of the silica nanowires were revealed through the SEM and TEM (Figs. 1 and 2). For the SEM investigations, the as deposited products were directly transferred to the SEM chamber without disturbing the original nature of the products.

3.1.1. Non-catalytic growth

To study the non-catalytic growth process several cleaned Si wafers (substrates) were placed in the deposition chamber and were heated for different periods in 1100 °C. Fig. 1(a) shows the general morphology of the Si wafer heated for 15 min, revealing the initial nucleation stage of the silica nanowire. At this temperature the Si wafer may have been reacted with the oxygen present in the deposition system to give numerous SiO₂ nanoparticles partially covering the wafer to give the unique pattern shown in Fig. 1(a). Fig. 1(b) shows the Si wafer heated for 25 min, revealing the intermediate stage of the silica nanowire growth. A large quantity of silica nanowires was found lying over the Si wafer between the growth centers. This figure has established our view that the silica nanoparticles assembly was the origin of the silica nanowire. Fig. 1(c) shows the general morphology of the products deposited on the Si substrate heated for 45 min. The figure reveals that the thick white layer on the Si wafer was consisted of large quantities of silica nanowires with a unique bi-cycle chain like morphology. This unique morphology is also revealed through the TEM study (Fig. 1(d)). The diameters of these nanowires were found to vary within 60-120 nm and their length goes up to several micrometers.

3.1.2. Catalytic growth

To observe the different growth stage for the catalytic growth of the silica nanowires, several Si wafer coated with 25 Å thick Au film were heated at 1000 °C for different time periods. Fig. 2(a) shows the SEM image of the Au deposited Si wafer, heated for 10 min. At this stage the Au film on the Si wafer breaks up and nanoparticles with diameters in the range 10-80 nm were formed on the Si surface. These nanoparticles act as the nucleation site for the growth of SiO₂ nanowires. EDAX spectra (shown in the inset of Fig. 2(a)) taken from these nanoparticles revealed the presence of gold, silicon and oxygen, indicating these nanoparticles to be Au/silica nanocomposite particles. Fig. 2(b) shows the Si wafer, after 15 min of heating, which reveals the early stage of the catalytic growth of the silica nanowires. This figure reveals that the silica nanowires start from these nano composite particles. Fig. 2(c) shows bundles of silica nanowires were formed on Si wafer, oriented along the Ar flow path when heated for 30 min. The nanowires were found to have diameters within the range 60-90 nm and length up to several micrometers. Fig. 2(d) shows the TEM of these nanowires revealing their smooth and uniform morphology.

3.2. Phase and compositional analysis

The XRD patterns (not shown here) of the products revealed their amorphous nature. The amorphous natures of the nanowires were further confirmed by the HRTEM (Fig. 3(a)) and the SAED pattern (inset of Fig. 3(a)) taken from a single nanowire. The HRTEM also showed the smooth nature of the nanowires. EDAX spectra of the nanowires



Fig. 1. SEM images showing the non-catalytic growth sequence of silica nanowires with deposition time (a) 15 min, (b) 25 min and (c) 45 min. Unique bi-cycle chain like morphology of the nanowires is revealed in (c) along with its magnified image in the inset and the TEM image shown in (d).

were taken to confirm their phase and elemental composition. EDAX spectrum taken from both form of the nanowires were perfectly identical. Fig. 3(b) shows the spectrum taken from a single nanowire, which revealed the presence of only Si and oxygen with atomic ratio approximately 1:2 (33.6:66.4) confirming the products to be silica nanowires. The EDAX spectra also indicated compositional purity of the nanowires.



Fig. 2. The catalytic growth sequence: (a) SEM image of Au/silica nanocomposite particles with EDAX spectrum in the inset, (b) SEM image of the initial stage of silica nanowire formation from the Au/silica nanocomposite particles and (c) SEM image of long uniform oriented silica nanowires. The TEM image (d) shows bundles of smooth SiO_2 nanowires. The magnified image of a single nanowire is shown in the inset of (d) revealing the cross-section of the nanowires to be circular.



Fig. 3. (a) HRTEM image of a single nanowire with corresponding SAED pattern in the inset revealing the amorphous nature of the nanowires. The EDAX spectrum (b) recorded from a single nanowire confirms its composition.

3.3. Photoluminescence

The photoluminescence (PL) spectra (Fig. 4) of the as synthesized silica nanowires were measured at room temperature with 250 nm excitation. A strong blue luminescence was observed with the peak position at 414 nm (3 eV). Another shoulder peak at 445 nm (2.8 eV) was also observed. As shown in the figure the PL spectra for both forms of the nanowires were almost identical in nature. This indicated that the luminescence of the silica nanowires were independent of their morphology. Several other groups [5, 10,13,15] working on silica nanowires have also reported similar type of blue luminescence from the nanowires. Nishikawa et al. [6] observed different luminescence bands with peak positions lying within 1.9-4.3 eV for pure silica glasses. They have attributed the 2.7 eV (459 nm) band to neutral oxygen vacancy (≡Si–Si≡) and the 3 eV (413.3 nm) band to some intrinsic diamagnetic defect centers, such as the twofold coordinated silicon lone pair centers. These defects were due to oxygen deficiency in the sample. In fact, oxygen vacancies in the silica nanowires originated during



Fig. 4. Room temperature photoluminescence spectra of the silica nanowires recorded with excitation at 250 nm.

the sample preparation, gives rise to the structural defect centers, which are responsible for the blue emission.

3.4. Growth mechanism

In order to understand the role of MgO and graphite powder mixture in the mechanism of silica nanowire growth, we have performed the same experiments without MgO and graphite mixture and we have also compared our work with the work of other groups, who have employed similar approach to produce silica nanowires. In the case non-catalytic growth, the Si wafer reacts with the oxygen present in the deposition chamber to give large quantities of silica nanoparticles. This oxygen might have come from (i) absorbed oxygen in the substrates, (ii) some leakage through the vacuum system, (ii) some oxygen contamination in the Ar gas or (iv) by decomposition of any sort of moisture present in the Ar gas. These nanoparticles acts as the nucleation center for the unique bi-cycle chain like nanowires. Hu et al. [16] have also reported the growth of silica nanowires by directly heating bare silicon substrates in two steps: first at 850 °C for 30 min followed by heating at 1300 °C for 5 h. They have observed silica nanoparticle assemblies after 1 h of heating whereas silica nanowires were obtained after additional 5 h of heating. But we have obtained the silica nanowires by heating the bare substrates at 1100 °C for 45 min only. When we have performed the same experiment without using the MgO and graphite mixture, no such nanowire formation was observed. This shows that in presence of the mixture of MgO and graphite powder, the silica naowires grow very rapidly compared to the other reported methods.

The catalytic growth of the silica nanowires on the Au deposited Si wafer was governed the conventional VLS mechanism. In the early part of the reaction the Au film on the Si wafer breaks up and liquid nano-droplets were formed. These liquid Au droplets at high temperature might have etched the Si surface to generate some Si vapor surrounding the substrates, after which the Au nanodroplets absorbs Si vapor and oxygen from the surrounding atmosphere to form Au/silica nanocomposites. With time silica nanowires originates from these nanodroplets according to the VLS mechanism. Liu et al. [15] have obtained Au/ silica nanocomposite particles by heating Au coated Si wafer in vacuum at 850 °C for 30 min. But they have obtained silica nanowires only after introducing silane as the additional Si source along with He at 850 °C for 1 h. We have achieved Au catalyzed aligned silica nanowires by heating the Au deposited Si wafer in flowing Ar atmosphere at 1000 °C for only 30 min without introducing any additional Si source. The bundles of silica nanowires were found to be aligned along the Ar flow direction over the Si surface. The reason behind the alignment of the nanowires might be the high Ar flow rate. In addition to this, the overcrowding effect [17] might be another reason behind the alignment. But, no such nanowire formation was observed when the total synthesis procedure was repeated without introducing the MgO and carbon mixture.

The above discussions indicate that, the MgO and carbon mixture might have some positive influence on the nanowire growth. Ma et al. [18] have reported the formation of silica nanowire by subliming In₂O₃ powder to a Si wafer coated with nickel nanoparticles under N₂/NH₃ atmosphere at a relatively low temperature. They have observed the formation of In-Ni alloy microballs, which acts as the nucleation center for the nanowires. They have proposed that the In₂O₃ powder acts as the necessary oxygen source for the nanowire growth. But in our case, the EDAX analysis failed to show the presence of elementary Mg even in minute quantity within the nanowire samples. So the only other possibility remaining open is that, the MgO and graphite powder mixture might have supplied some additional active oxygen along with the other known oxygen sources present in the deposition chamber (discussed earlier). But the exact mechanism behind the roleplayed by the MgO powder and graphite mixture in enhancing the silica nanowire growth is not clear and need further investigation.

4. Conclusions

We have synthesized amorphous silica nanowires by simply heating the Si wafers in presence of mixture containing MgO and active carbon powder in equal weight ratio. The morphologies of the nanowires were controlled by the presence of Au catalyst over the Si wafer. Nanowires grown with Au catalyst were smooth, ultra long and their diameter varied within 40–90 nm. On the other hand, nanowires grown without any Au catalyst possessed a unique bicycle chain like morphology. The nanowires were aligned along the flow direction of the Ar gas in the deposition chamber. High intensity blue light emission was observed from the silica nanowires. The nature of emission was found to be independent of the morphology.

Acknowledgements

The authors like to express their sincere gratitude for financial assistance by the Department of Science and Technology (DST), government of India under the programme 'nanomaterials Science and Technology Initiative (NSTI)—phase-II'.

References

- Y. Li, J. Wang, Zh. Deng, Y. Wu, X. Sun, D. Yu, P. yang, J. Am. Chem. Soc. 123 (2001) 9904.
- [2] M. Huang, S. Mao, H. Feick, H. Yan, Y. Yu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
- [3] J. Han, S. Fan, Q. Li, Y. Hu, Science 277 (1997) 1287.
- [4] C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, Prog. Solid State Chem. 31 (2003) 5.
- [5] D.P. Yu, Q.L. Hang, Y. Ding, Z.H. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, S.Q. Feng, Appl. Phys. Lett. 73 (1998) 3076.
- [6] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohki, Phys. Rev. B 45 (1996) 586.
- [7] L.S. Liao, X.M. Bao, X.Q. Zheng, N.S. Li, N.B. Min, Appl. Phys. Lett. 68 (1996) 850.
- [8] Z.W. Pan, Z.R. Dai, C. Ma, Z.L. Wang, J. Am. Chem. Soc. 124 (2002) 1887.
- [9] S.H. Sun, G.W. Meng, M.G. Zhang, Y.T. Tian, T. Xie, L.D. Zhang, Solid State Commun. 128 (2003) 287.
- [10] X.C. Wu, W.H. Song, K.Y. Wang, T. Hu, B. Zhau, Y.P. Sun, J.J. Du, Chem. Phys. Lett. 336 (2001) 53.
- [11] D. Xu, Y. Yu, M. Zheng, G. Guo, Y. Tang, Electrochem. Commun. 5 (2003) 673.
- [12] B. Zheng, Y. Wu, P. Wang, J. Liu, Adv. Mater. 14 (2002) 122.
- [13] K.H. Lee, H.S. Yang, K.H. Baik, J. Bang, R.R. Vanfleet, W. Sigmund, Chem. Phys. Lett. 383 (2004) 380.
- [14] F.L. Deepak, G. Gundiah, M.M. Seikh, A. Govindaraj, C.N.R. Rao, J. Mater. Res. 19 (2004) 2216.
- [15] Z.Q. Liu, S.S. Xie, L.F. Sun, D.S. Tang, W.Y. Zhou, C.Y. Wang, W. Liu, Y.B. Li, X.P. Zou, G. Wang, J. Mater. Res. 16 (2001) 683.
- [16] J.Q. Hu, Y. Jiang, X.M. Meng, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 367 (2003) 339.
- [17] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
- [18] R. Ma, Y. Bando, Chem. Phys. Lett. 377 (2003) 177.