Origin of the 745 nm photoluminescence from small diameter silicon nanowires

Y. Xiong a, X.L. Wu b,∗, S.J. Xiong b, Z.Y. Zhang b, G.G. Siu c, Paul K. Chu c

a Nanjing Normal University, School of Science, Nanjing 210016, China
b National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China
c Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

ARTICLE INFO

Article history:
Received 17 June 2008
Received in revised form 15 August 2008
Accepted 21 August 2008 by E.G. Wang
Available online 27 August 2008

A B S T R A C T

A broad photoluminescence band centered at 745 nm was observed from Si nanowires (SiNWs) smaller than 4 nm in diameter with an oxide sheath. This emission band mainly originates from SiNWs grown along the [111] direction and its intensity increases with decreasing diameter and larger length. It becomes unobservable when the crystalline core of the SiNW is completely oxidized. Our theoretical calculations reveal electronic states in the band gap of the small diameter SiNWs when Si–O bands are formed and the results agree with experiments. This result provides insight into the electronic states of small-diameter SiNWs with surface oxide.

© 2008 Elsevier Ltd. All rights reserved.

Recently, Si nanowires (SiNWs) have attracted considerable attention because of their outstanding physical properties and potential applications in many fields such as optoelectronics and chemical and biological sensors, which are partially similar to those of carbon nanotubes. Many techniques such as masking, lithography, metal-catalytic vapor–liquid–solid method, oxide-assisted catalyst-free method, and solution techniques have been developed to fabricate SiNWs [1,2]. These methods yield wires with different orientations and diameters enshrouded by a surface oxide layer. A distinctive feature for thin SiNWs with diameters less than 4 nm is the well-known quantum confinement effect. Similar to the case in the small-diameter Si quantum dots, the quantum confinement on carriers would push the photoluminescence (PL) peaks into the visible range. This makes it useful in optoelectronic integration devices. However, many current fabrication techniques are difficult to obtain the small-diameter SiNWs and therefore the properties of small wires are not very well known.

Theoretical studies on the electronic states of SiNWs have mainly focused on bare or H-terminated SiNWs due to their simple structures [3,4]. However, SiNWs produced experimentally generally have a natural surface oxide [1]. As the wire diameter decreases, strong anisotropy and quantum confinement in the lateral directions will drastically change the structure and bonding states of Si–O–Si bridge bonds on the surface. Hence, theoretical modeling and calculation conducted on ideal SiNW structures without surface oxide cannot be directly compared to experimental data. Moreover, owing to the lack of theoretical studies, the origins of PL from many SiNW structures are unclear or controversial [5–10]. So it is of fundamental and practical importance to investigate the PL characteristics and electronic states of SiNWs with surface oxide.

In the experiments reported here, we observe a broad PL band centered at 745 nm mainly emitted from SiNWs grown along the [111] direction and its intensity increases with decreasing diameter and larger length. It becomes unobservable when the crystalline core of the SiNW is completely oxidized. Our theoretical calculations reveal electronic states in the band gap of the small diameter SiNWs when Si–O bands are formed and the results agree with experiments. This result provides insight into the electronic states of small-diameter SiNWs with surface oxide.

© 2008 Elsevier Ltd. All rights reserved.

The current SiNWs were formed on single crystalline Si wafers placed in an alumina tube inside a furnace. The vapor source consisting of silicon (99.99%) and iron (Fe) (99.9%) powders mixed together with a molar ratio of 10:1 was placed in an alumina crucible and the crucible was placed on the head of an alumina boat. A series of the cleaned Si (100) wafers were placed on the alumina boat at distances from 18 and 24 cm near the alumina
For a SiNW, the surface initially consists of Si–O and Si dangling bonds. With its growth, the contents of the two bonds increase and there are distortions in the Si lattices giving rise to partial breaking of Si–O–Si bonds and formation of some Si=O bonds at the Si/oxide interface due to large stress. This leads to gradual formation of the oxide layer. The samples were characterized using field-emission scanning electron microscopy [SEM, EDAX PV7715/89 ME equipped with an energy dispersive x-ray (EDX) detector] and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 20 S-TWIN TEM). The collected PL and Raman spectra were taken on a T64000 triple Raman system with the Ar line of an Ar+ laser as the excitation source.

Fig. 1(a) shows the SEM image of the as-produced samples. Many nanowires with diameters of 2–15 nm and lengths on the order of a µm can be observed. The EDX result in the lower inset of Fig. 1(a) in the energy range of 0–6.5 keV discloses that the nanowires are mainly composed of Si and O. Fig. 1(b) shows the HRTEM image of another SiNW. The nanowire clearly exhibits that the growth axis of the Si core is along the ⟨111⟩ direction. Such SiNWs with the ⟨111⟩ growth direction can be observed in large amounts in our samples via a series of HRTEM observations. This conclusion was also confirmed through the obtained XRD result, which shows a textured XRD diffraction peak from the ⟨111⟩ reflection of the SiNWs [11]. The thinnest SiNW can be found to have a diameter of smaller than 2.4 nm. In our TEM observations, the SiNWs with other growth directions can also be seen occasionally. Fig. 1(c) depicts the HRTEM image of a nanowire with the ⟨111⟩ surface of the Si core. The nanowire consists of a c-Si core with diameter of about 4.1 nm and an amorphous Si oxide sheath with a thickness of about 1.0 nm. The sheath thickness is about one-fourth of the core diameter. Combining with the selected area electron diffraction pattern, we can infer that the SiNW has the growth axis along the ⟨112⟩ direction. In our experiments, we found that the Fe content and the fabrication temperature are important for the growth of the ⟨111⟩ SiNWs with small diameters. Decreasing the Fe powder content or lowering fabrication temperature is beneficial to the reduction of SiNW diameters.

Fig. 2(a) shows the Raman spectra from different positions of the sample, acquired in the wavenumber region of 400–600 cm⁻¹. The corresponding PL spectra in the wavelength range of 540–920 nm are shown in Fig. 2(b). We can see that when the Raman peak shift exceeds 511 cm⁻¹ (a1–a2), no corresponding PL peak is observed (b1–b2). When the Raman shift is less than 511 cm⁻¹ (a3–a6), the corresponding PL peak appears at ~745 nm (b3–b6) and its position remains unchanged even for smaller Raman shifts. In addition, the smaller the Raman shift, the larger is the PL peak intensity. If we use the phonon confinement theory of a cylindrical nanowire to fit these Raman peaks [12], the average SiNW diameters for lines a3 and a4 are found to be 3.8 and 3.2 nm, respectively. This result implies that the 745 nm PL peak originates from the SiNWs with diameters smaller than 4 nm. In our experiments, we also found that the Raman spectra with peak positions smaller than 498 cm⁻¹ are difficult to be acquired from our samples except for the 480 cm⁻¹ broad amorphous peak. This indicates that the diameters of the nanowires in our samples are more than 1.2 nm [12–14]. Since the 745 nm PL spectra are from the nanowires with diameters less than 4 nm and larger than 1.2 nm, we may obtain the conditions required to observe the PL: the SiNWs have diameters smaller than 4 nm. The PL peak position does not change with the SiNW diameter, so the PL is not due to band to band recombination in the quantum confined SiNW cores. To identify the dependence of the PL peak on the surface oxide, we annealed the samples at 800 °C in O₂ for 20, 60, or 120 min. The corresponding Raman and PL spectra are exhibited in Fig. 2(c) and (d). For the sample with a Raman shift of 502 cm⁻¹, the PL peak still appears at 745 nm (d1). When the Raman shift is at 496 cm⁻¹ (sample annealed for 60 min), the 745 nm peak weakens and becomes a shoulder of the 620 nm PL peak (d2). The Raman spectrum acquired from the samples annealed for 120 min becomes a broad band centered at ~480 cm⁻¹ that is characteristic
of the Raman spectrum of amorphous Si [15], indicating that the SiNW cores have become amorphous. This is understandable because large stress in the interface between the core and oxide during the core oxidation leads to amorphization of the small-sized crystalline core [16]. With further increasing oxidation time, the small-sized amorphous core will be completely oxidized. In this case, the corresponding PL spectrum only shows a strong 620 nm band that is believed to derive from oxygen-related defect states in the Si oxide [17,18]. This result also indicates that the thickness of the oxide sheath increases with annealing time, partially similar to the situation for Si wafer oxidation. The data clearly show that the 745 nm PL peak is closely related to both the Si core and oxygen-related interfacial structures, whereas the thickening of the oxide layer is not beneficial to improvement of the PL intensity. Since the PL was detected in the as-fabricated nanowire with oxide sheath of more than 1 nm, oxidation of the nanowire to produce an amorphous surface layer of >1 nm is necessary in order to observe the 745 nm PL. The fact that the SiNWs grown in high vacuum chamber and passivated by hydrogen do not show similar PL peak supports the postulate [2,3]. For these SiNWs grown in high vacuum chamber and passivated by hydrogen, we may also expect to show the 745 nm PL after they are oxidized to produce a surface oxide layer with enough Si–O–Si bonds. However, such work has not been reported so far and thus we are not able to make a comparison. To rule out Fe-related defects as a possible origin of the 745 nm PL, we used the Si powders to fabricate the SiNWs and found that although the lengths of the [111] SiNWs are short, as shown in the upper inset of Fig. 1(a), the 745 nm PL still occurs even though its intensity diminishes significantly.

It should be noted that the 745 nm PL peak was mainly observed from [111] SiNWs. The peak has barely been detected from [110], [100], or [112] SiNWs because of low density of Si–O bonds in these oriented SiNWs [19], as described below. Based on our experimental results, the following PL mechanism is proposed. The electron-hole pairs in the SiNW core are first excited and then migrate to the interface to recombine radiatively at some oxygen-related states [17,20–22]. The possible interfacial structures that give rise to the observed PL include the Si=O bonds, Si vacancies, and Si–O–Si bridge bonds. We use the method of linear combination of atomic orbital (LCAO) to calculate the electronic states of the SiNWs. In our calculation, we consider the 2s and 2p orbitals of the Si and O atoms. The LCAO approach is used with parameters $ε_{sp}^{Si} = −13.5$ eV, $ε_{sp}^{O} = −7.58$ eV, $ε_{ss}^{Si} = −29.14$ eV, and $ε_{ss}^{O} = −4.13$ eV, where $ε_{sp}^{Si(O)}$ denotes the on-site energy of the s(p) electrons of the Si(O) atoms. The overlap parameters between the nearest neighboring atoms are $V_{ss}^{Si-Si} = −2.08$ eV, $V_{sp}^{Si-St} = 2.48$ eV, $V_{pp}^{Si-Si} = 2.72$ eV, $V_{sp}^{Si-O} = −0.72$ eV, $V_{ss}^{Si-O} = −4.17$ eV, $V_{sp}^{St-O} = 5.48$ eV, $V_{pp}^{O-O} = 9.64$ eV, and $V_{sp}^{O-St} = −2.41$ eV, where $V_{sp}^{A-B}$ denotes the overlap of the s and p states between the A and B atoms, and $σ$ and $π$ stand for the $σ$ and $π$ bondings of the p states, respectively. These parameters are determined by the Slater–Koster overlapping integrals using the Si–Si and Si–O bond lengths, 2.35 and 1.27 Å, respectively [23].

Fig. 3 schematically shows the crystalline structures of the SiNWs which grow along the [111] and [110] directions, respectively. The Si–O–Si bridge bonds are attached to all pairs of nearby Si atoms with one originally impendent bond at the surface. In this model, the Si–Si and Si–O bond lengths are kept to reduce the energy caused by bond distortion. It can be seen that in the [111] direction, all the Si–O–Si bridge bonds are along the wire growth direction, whereas in the [110] direction, the orientations of these bonds are different and deviated from the growth direction. On the other hand, the density of the Si–O–Si bonds in the [111] SiNW is larger than that in the [110] SiNW. For a SiNW with diameter of 1.6 nm and length of 10 nm, we can estimate the ratio of the Si–O–Si bonds to be 2.33. At the same time, the oxygen atoms of the Si=O bonds are attached to Si atoms with two originally impendent bonds at the surface and their orientations are not along the growth direction. Thus, one of the unique features of the [111] SiNW is the existence of dense Si–O–Si bridge bonds along the growth direction on the surface, and this feature becomes more striking in SiNWs with smaller diameters.

Based on the different crystalline structures of SiNWs including [111], [110], and [112] SiNWs with Si–O–Si bridge bonds and Si=O bonds at the surface and with randomly distributed vacancies, we use LCAO to calculate the density of states (DOS). The luminescense intensity is proportional to the average optical matrix square $P^2$ that represents the probability of radiative recombination of the electron-hole pairs in the related states. In all our calculated results, it is found that only the [111] SiNW with Si–O–Si bridge bonds at the surface can give the luminescence spectrum similar to the experimental result shown in Fig. 2. Fig. 4 shows the calculated $P^2$ of the [111] SiNWs with different diameters. We can see that the $P^2$ value mainly appears in the two regions, one being in the range of 1–2.5 eV and the other in the range of 4–6 eV. Since the energy range of 4–6 eV is beyond our experimental measurement value which the spectrometer can reach, we cannot compare the calculated result with the theoretical one. Therefore, we pay our attention to the energy range of 1–2.5 eV. From Fig. 4, it can be seen that a clear broad peak centered at $\sim 1.65$ eV ($\sim 750$ nm) emerges. This peak becomes smaller with larger SiNW diameters and it is consistent with our experimental observation. This may cause a misunderstanding. From Fig. 2(d), we can see that for the oxidized SiNWs, their sizes should be smaller and thus the corresponding PL intensity should also be larger. However, the PL intensity observed in the experiments is lower. Here, we should point out that oxidation of the SiNWs will lead to large reduction of the density of the SiNWs with small sizes which can show the 745 nm PL. Therefore, the PL intensity decrease in the oxidized SiNW samples is reasonable. It does not conflict with our calculation result. The insert in Fig. 4 shows the corresponding DOS. In comparison with the results obtained from bare SiNW, the DOS of the SiNWs with Si–O–Si bonds has several impurity states within the energy gap in the range of $−7.3$ eV, $−5.2$ eV. The energy difference between the closest peak and the conduction band bottom is around 1.6 eV and it gives the corresponding peak in the spectrum. This peak in the gap arises from the Si–O–Si bonds at the surface and is enhanced by decreasing SiNW diameters, also consistent with our experiments. Hence, the Si–O–Si bonds on the surface of the SiNWs are likely the states that give rise to the observed 745 nm peak. Nevertheless, it should be mentioned that this 745 nm peak is quite broad compared to ordinary PL peaks suggesting that it may be due to several levels related to the atom clusters around the bonds as shown in Fig. 4.
For comparison, Fig. 5 shows the results of the LCAO calculations for SiNWs with different lengths grown along the [110] and [111] directions. For the [110] SiNW, the main peak of $P^2$ has moved to 2.0 eV. The remaining shoulder around 1.65 eV indicates that the 750-nm PL peak has much weaker intensity. A similar situation has been observed for the [112] SiNW from our theoretical results and the DOS calculation shown in the inset of Fig. 5 confirms it. By increasing the SiNW length in the calculation, similar to what we have done in the experiment, $P^2$ increases and it can be explained by the increase in the number of Si–O–Si bridge bonds along the SiNW direction. Here we would like to point out that it is difficult to exactly compare the difference between the 745 nm PL intensities from our theory and the experiments because the PL intensity is determined by many factors such as Si–O–Si bond density, Si–O–Si orientation, and $P^2$.

As a summary, we observe a specific red PL at 745 nm in oxide-passivated SiNWs grown in the [111] direction. This peak originates from the Si–O–Si bridge bonds along the wire direction based on our theoretical calculation. By narrowing the wire or by increasing the length, the intensity of this peak is enhanced due to the increase in the density or total number of these bonds. This peak is not observed from other structures such as [110] or [112] SiNWs, implying its dependence on the crystalline configurations. The obtained result is helpful for further investigating the luminescence properties of small-diameter nanowires.

Acknowledgements

This work was supported by the Grant (No. BK2006715) from Jiangsu Natural Science Foundation. Partial support is from the State Key Program for Basic Research of China under Grant No. 2007CB936300 and City University of Hong Kong Strategic Research Grant (SRG) No. 7002138.

References