Nanotechnology

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To cite this article: T Qiu *et al* 2005 *Nanotechnology* **16** 2222

INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY

Nanotechnology **16** (2005) 2222–2226 doi:10.1088/0957-4484/16/10/041

Self-assembled growth and blue emission of a SiO_x-capped (x = 0.5–0.8) silicon nanowire array

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Received 21 May 2005, in final form 28 July 2005
Published 16 August 2005
Online at stacks.iop.org/Nano/16/2222

Abstract
A uniquely structured SiO_x-capped ($x = 0.5$–0.8) Si nanowire array with strong blue emission, like a nanobeacon array, was fabricated using electroless metal (silver) deposition on a water plasma-treated Si wafer. Formation of the nanoscale light source array can be understood on the basis of a self-assembled localized microscopic electrochemical cell model and a diffusion-limited aggregation process. Photoluminescence spectral analysis reveals that the intensity of the broad blue-emitting luminescent band centred at around 435 nm strongly depends upon the irradiation of H_2O^+, HO^+, and O^+ ions, which are present in the water plasma. We attribute the blue PL band to the optical transition of the self-trapped excitons at the surfaces of SiO_x nanocaps.

1. Introduction

In recent years, there has been increasing interest in the fabrication of one-dimensional nanostructures because of their potential utilization in electronic, magnetic, optical, and micromechanical devices [1–3]. Silicon has long been the dominant material in microelectronics, and Si nanowires (SiNWs) have attracted considerable attention due to their unusual physical properties, such as field emission [4], electrical conductivity [5], and visible photoluminescence (PL) caused by quantum confinement effects [6]. On the basis of the vapour–liquid–solid growth mechanism [7], various techniques have been developed for fabricating the SiNWs [8–10]. However, these complicated routes typically yield disordered entanglements of nanowires, which hampers their experimental characterization and applications. Therefore, the fabrication of an ordered Si nanowire array becomes a very important and challenging issue. Recently, we have reported the ultraviolet (UV)-emitting property of Ag-capped SiNWs which can be expected to have favourable applications in optoelectronics such as nanowire UV photodetection [11]. The UV PL is considered to be due to optical transitions in the vacancy defect centres in silver nanocaps on the SiNWs. It has nothing to do with the existence of the SiNWs, because the photoexcited carriers from the SiNWs cannot transfer to the defect states of Ag nanocaps. To reach efficient carrier transfer and meanwhile obtain visible emission, a promising technique is to assemble visible light-emitting semiconductor nanomaterials on the tops of SiNWs. They look like nanobeacons, which will be useful in future nanodevices. However, the relevant work has not been reported so far.

In this work, we present a relatively rapid method of fabricating an SiO_x-capped Si nanowire array via electroless metal (silver) deposition on plasma-treated Si wafers. Electroless metal deposition in ionic metal (silver) HF solution is based on a microelectrochemical redox reaction in which anodic and cathodal processes occur simultaneously at the wafer surface [12]. This is a very simple and low-

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cost fabrication technique and has been widely used in microelectronics and the metal coating industry [13]. Spectral measurements indicate that this kind of SiO$_x$-capped Si nanowire array has strong blue emission centred at 435 nm. On the basis of the experimental results obtained, we discuss the origin of the blue PL.

2. Experimental details

SiO$_x$ films were deposited on p-type, B-doped Si(100) (1–5 Ω cm) wafers using water plasma immersion ion implantation (PIII) [14] as a source of oxygen for achieving a small spread in the oxygen implant profile. The details of the method are described as follows: water vapour was bled into the vacuum chamber to maintain a working pressure of 5×10^{-4} Torr. The PIII parameters were: sample voltage of −30 kV, repetition frequency of 60 Hz and RF power of 1000 W. The water dose was $\sim 5 \times 10^{16}$ cm^{-2}.

After the implantation, one set of samples were etched in a 5.0 mol l^{-1} HF solution containing 0.02 mol l^{-1} silver nitrate at 50 °C for 40 min; this was followed by ultrasound treatment in a water bath for 1 min to clean the surface. The container was a conventional Teflon-lined stainless steel vessel. Then the etched wafers were rinsed with de-ionized water and blown dry in air. The morphology and chemical composition of the samples were characterized with a FEG JSM 6335 field-emission scanning electron microscope (SEM) and a PHI 5600 x-ray photoelectron spectrometer (XPS) with a monochromatic Al Kα source at 14 kV and 350 W. The photoelectron take-off angle was 45°. For PL spectral measurement, a He–Cd laser (325 nm, Kimmon IK series) was used as an excitation source, and the spectrum was collected using a double monochromator (1.4 m Oriel 77225) with a Peltier-cooled photomultiplier detector (Hamamatsu R636-10). The mean dimension of the nanocrystals was examined by means of Raman spectroscopy (on a T64000 triple Raman system from JY Company). The Fourier transform infrared (FTIR) absorption spectrum was obtained on a Nicolet 170SX spectrometer. All the measurements were run at room temperature.

3. Results and discussion

In the oxygen plasma, the coexistence of O$^+$ and O$_2^+$ ions can cause a spread in the oxygen implant depth profile. This will give rise to non-uniformity of the Si oxide formed, in composition and distribution. To overcome the disadvantages, in the present work, water plasma was used as a source of oxygen for achieving a small spread in the oxygen implant profile. H$_2$O$^+$, HO$^+$, and O$^+$ ions, which are present in the water plasma, have comparable masses and therefore will not disperse much in the target silicon at a fixed acceleration voltage [15].

Figure 1(a) shows the cross-section SEM image of the Si-based SiO$_x$ thin film fabricated using PIII. The thickness of the Gaussian-like SiO$_x$ layer [16] can be seen to be about 200 nm and the interface between the buried SiO$_x$ layer and the Si substrate is not smooth. Figures 2(a) and (b) show the cross-section SEM images of the SiO$_x$-coated silicon wafer etched in a mixed HF–AgNO$_3$ solution for 40 min and followed by ultrasound treatment in a water bath for 1 min. It can be clearly seen that the SiNWs formed have almost the same lengths. The as-prepared SiNWs are very much perpendicular to the surface of the Si wafer and have a good distribution on the Si wafer. The diameters of nanowires are in the range of 30–200 nm and the lengths are ∼12 μm. The detailed formation mechanism for the capped Si nanowire array has been reported elsewhere [11]; it can be understood on the basis of a self-assembled localized microscopic electrochemical cell model [17] and a diffusion-limited aggregation process [18].

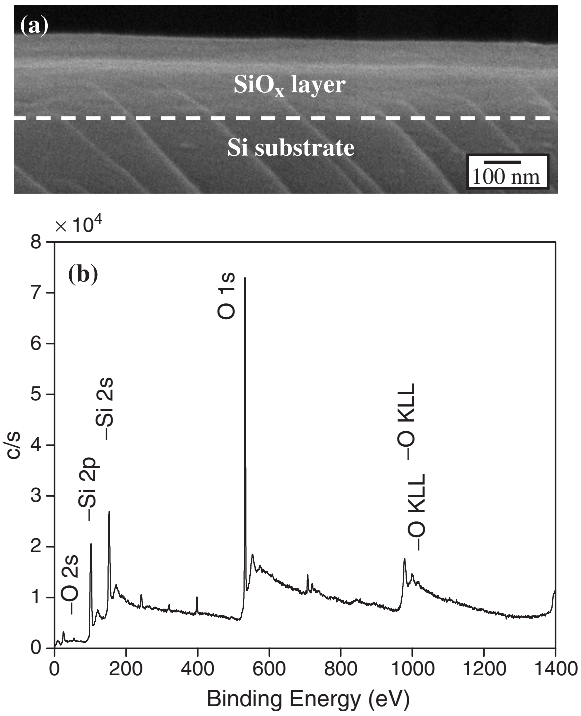

Figure 1. (a) SEM image of SiO$_x$ thin film on the Si wafer. (b) XPS spectrum acquired from SiO$_x$-coated Si wafer at the sputtered depth of ∼10 nm.

To determine the elemental composition and chemical states of the surface nanolayer, we carried out XPS measurements of the water plasma-treated silicon wafers before and after etching. To remove the surface contamination, we used Ar ions to bombard the sample surface for several minutes (removing the surface layer of about 10 nm) and then measured the XPS spectra. The corresponding results are presented in figures 1(b) and 2(c). Obviously, the main elements in the nanolayer of the water plasma-treated silicon wafer before etching are Si and O. The main elements in the nanolayer of the water plasma-treated silicon wafer after etching are still Si and O elements, but there is also a small amount of Ag. Because O element does not exist on the surface of SiNWs produced via the same etching method on pure silicon wafers [19, 20], we conclude that SiO$_x$ nanocaps occur on the tops of SiNWs. Further measurements of Si and O XPS depth profiles prove x to be in the range of 0.5–0.8.

The PL spectrum from the SiO$_x$-capped Si nanowire array is shown in figure 3; it was taken under excitation with the 325 nm line of a He–Cd laser. It can be seen that the nanowire array shows a strong blue emission centred at ∼435 nm

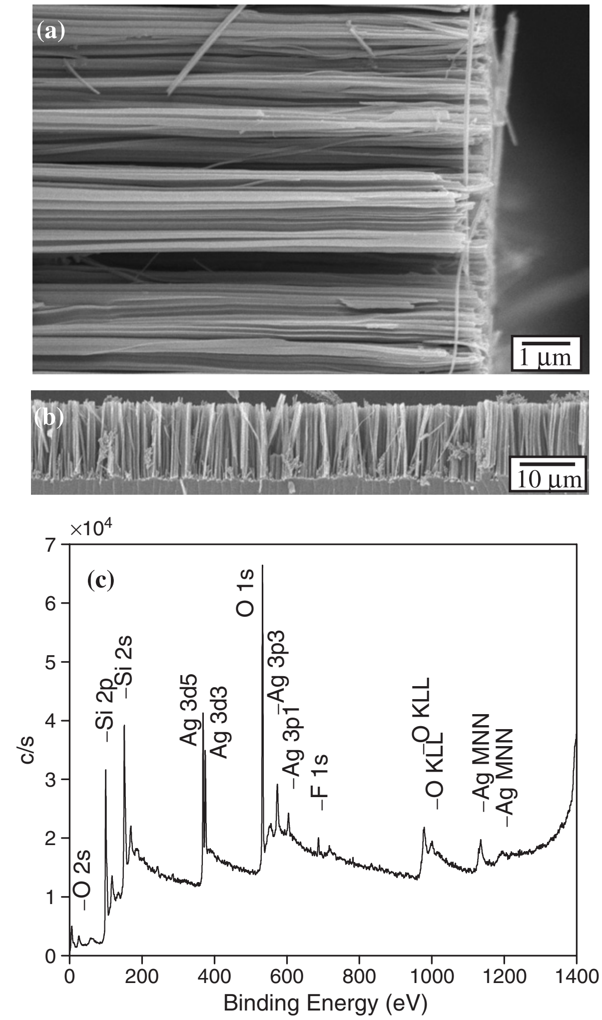

Figure 2. ((a), (b)) SEM images of the SiO_x-capped SiNWs. (c) XPS spectrum acquired from SiO_x-capped SiNWs at the sputtered depth of ∼10 nm.

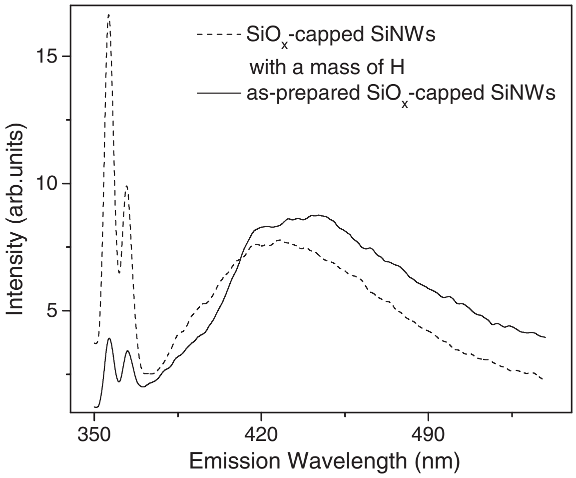

Figure 3. PL spectra of the as-prepared SiO_x-nanocapped SiNWs and SiO_x-capped SiNWs with the mass of H, taken under excitation with the 325 nm line of a He–Cd laser.

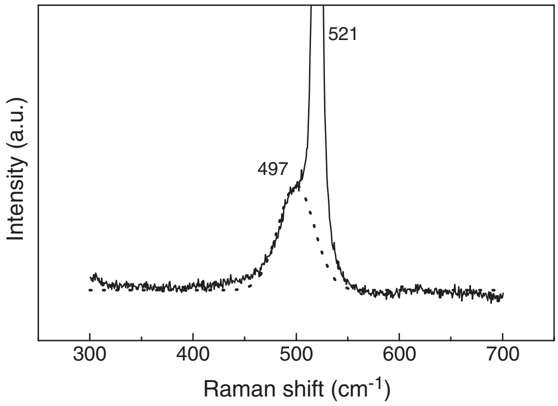

Figure 4. A typical Raman spectrum of the as-prepared SiO_x-capped Si nanowire array.

and two weak ultraviolet (UV) emissions centred at 356 and 364 nm. The two UV emissions have been observed in Si:H:O systems [21] and attributed to optical transitions in H^+-related groups. To give more evidence for the UV PL bands being associated with the H^+-related groups, we examined the PL spectrum of the SiO_x-capped Si nanowire array with a mass of H, which was fabricated on water and H_2 dual-plasma-treated silicon wafer. The corresponding result is also shown in figure 3 (the dashed line). We can see that the intensities of the UV PL from the sample with a mass of H are substantially enhanced. This result indicates that the UV luminescence centres exist in the SiO_x nanocaps and correlate with H^+-related groups. Since the position and intensity of the blue PL band change little, its origin has nothing to do with the H^+-related groups.

To see whether Si nanocrystals with sizes generally less than 10 nm occur in the current nanostructure, we examined the Raman spectrum of the as-prepared SiO_x-capped Si nanowire array. A typical result is presented in figure 4. It can be seen that a Raman peak associated with Si nanocrystals appears at 497 cm^{-1} as a shoulder of the bulk Si TO phonon mode at 521 cm^{-1}. According to the phonon confinement model [22], one can obtain the mean crystallite size as ∼1.8 nm. These small Si nanocrystals should arise from the process of electrochemically etching the Si wafer with the water PIII treatment, because no similar Raman peak appears in the PIII-treated Si wafer without electrochemical etching. To reveal the photoexcition process of carriers, we examined the PL excitation (PLE) spectra by monitoring at different emission wavelengths, and present the corresponding results in figure 5. We can see that a small PLE peak appears in all the PLE spectra (indicated by the arrows). The PLE peak position redshifts with increasing monitored emission wavelength. This result suggests that the PLE peak is from a special excitation in the band with quantum confinement, similar to the situation for porous Si [23]. Since the blue PL peak is relatively broad and shows no Si nanocrystal size dependence, it should not arise from the band-to-band recombination in the quantum confined Si nanocrystals. In addition, according to the quantum confinement theory of Si nanocrystals with sizes of 1.5–2.0 nm, the PL peak position should be at ∼390 nm [24]. Thus, the radiative centres for the blue radiation should be defect/impurity related. From the current samples, radiative

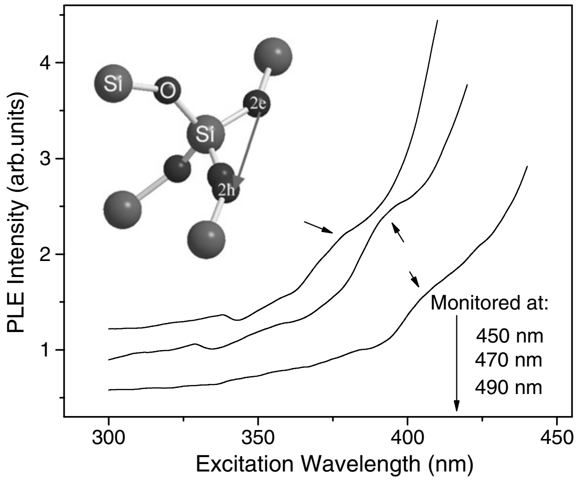

Figure 5. PLE spectra of the SiO_x-capped Si nanowire array, taken under three different monitoring wavelengths. The inset shows a model of the radiative centre which consists of a pair of an oxygen vacancy and an interstitial oxygen. The interstitial oxygen also forms a peroxy linkage with neighbouring lattice oxygen.

recombination of the photoexcited carriers should occur via relaxed electronic states, possibly oxygen-related defect states at the surface of SiO_x nanocaps, while the photoexcited carriers are partially from the Si nanocrystals with sizes of ~1.8 nm.

For amorphous SiO_2, it is known that irradiation with ionizing radiation can produce electron–hole pairs by knock-on, kick-out events, a substantial proportion of which convert to excitons. These excitons become so-called self-trapped excitons [25] when localized by self-induced lattice distortion owing to strong electron–phonon interactions, which is accompanied by defect formation and structural change. Since our present materials are irradiated with H_2O^+, HO^+, and O^+ ions (the PIII treatment), we suggest that the blue PL band originates from optical transitions of the self-trapped excitons at the surfaces of SiO_x nanocaps. A self-trapped exciton is a pair of an oxygen vacancy V_O and an interstitial oxygen I_O that forms a peroxy linkage with a lattice oxygen (with two holes), as shown in the inset of figure 5 [26]. The presence of oxygen vacancies is pronounced in our samples, because x in the SiO_x nanocaps is at 0.5–0.8. To identify the existence of oxygen interstitials, the FTIR spectrum was examined. We found that the main feature in the FTIR spectrum obtained is the same as that observed for Si oxide fabricated using magnetron sputtering of an SiO_2 target [27]. An increased absorption appears in the range of 1100–1200 cm^{-1} at the side of the 1070 cm^{-1} peak. This peak is not the longitudinal optical mode of the Si–O–Si stretching vibration because no increased absorption was observed at the side of the 460 cm^{-1} absorption peak. This is a new infrared absorption peak and can be attributed to interstitial Si–O–Si vibration [23]. Electrochemical etching leads to the appearance of interstitial oxygen at the surfaces of SiO_x nanocaps. Therefore, the blue PL is associated with the existence of both interstitial oxygen and oxygen vacancies. It is the transition transferring of one of the two trapped electrons occupying V_O to the unoccupied O_2 orbit that gives rise to the observed blue emission [23, 28]. The position of the observed PL peak changes with the oxide composition, which determines the local environment of the self-trapped excitons. For a certain SiO_x-nanocapped surface, due to slightly different local structures of self-trapped excitons, the PL band will show a multiple-peak structure. Overlapping of these neighbouring PL peaks causes the observed PL band to have a broad lineshape.

4. Conclusion

In conclusion, a rapid, low-cost method of fabricating a blue-emitting SiO_x-capped ($x = 0.5$–0.8) Si nanowire array has been described on the basis of an electroless metal deposition technique. The blue PL band shows a large intensity and broad lineshape. Micro-Raman examination and FTIR spectral investigation suggest that the blue PL band of the SiO_x-nanocapped Si nanowire array arises from optical transitions of the self-trapped excitons in the SiO_x nanocaps, which are induced by electrochemical etching of the water PIII-treated Si wafer. The alignment of as-prepared SiNWs is important for testing the properties of individual nanowires with existing techniques and effectively incorporating them into nanodevices.

Acknowledgments

This work was supported by Grants (Nos 10225416 and 60476038) from the Natural Science Foundation of China and by Hong Kong Research Grant Council (RGC) Competitive Earmarked Research Grants (CERG) No CityU 1137/03E and CityU 1120/04E, and the City University of Hong Kong Strategic Research Grant (SRG) No 7001642.

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