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Spectroscopic Investigation of well aligned Silicon Nano wires Fabricated by Metal Induced Etching

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Abstract

Well aligned Silicon nano-wires (SiNWs) were fabricated by metal induced etching (MIE). Scanning electron microscopy has been employed to study the surface morphology and cross sectional view for confirming the nano-wire like structures in our samples. Presence of electronic continuum and quantum confinement effect in the SiNWs- samples has been revealed from Raman and photoluminescence (PL) spectroscopy. Blue emission is achieved from SiNWs sample. Moreover, the effect of etching time on fabrication of SiNWs and associated PL spectra are studied here. We found with increasing etching time, pores are broader resulting in smaller size nano-wires. With further increasing in etching time, these NWs broke from the top, resulted in a blunt top surface leading to large size NWs. After a certain etching time, upper part of SiNWs is being broken, which is also reflected in PL spectra. Raman Spectroscopy shows the phonon confinement and is used to estimate the particle size. A detailed results and discussions have been presented here

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1. Introduction

Silicon nano-structures has attracted lots of attention in the field of research due to its unique properties and its potential to be used for various applications such as in solar cell¹, optoelectronics^{2,3}, field emission⁴, sensor⁵ etc. Si nano-wires (NWs) are two-dimensional confined systems. The quantum confinement effect in such type of materials offers flexible wide range application due their tuneable optical, electrical, thermal, and chemical properties for desired applications⁴. The one of most important property, which makes Si nano-structures, as a smart material is its luminescence property⁶. The origin of PL has been matter of debate for a long time. The PL mechanism from Si nano structures (NS) has been studied by various model^{6,7,8,9,10}. Si NS/NWs can be fabricated by many methods such as laser induced etching¹¹, ion beam irradiation¹², Metal Induced Etching (MIE)^{13,14}. Among these methods MIE has many advantages over other methods. MIE is the simple and low cost method to fabricate porous Si or Si NWs. In this method, firstly metal nano particles (M NPs) like Ag, Au, Pt etc. are grown on clean Si wafer then it is dipped into etching solution for fixed time. In the present work, we have adopted MIE for fabrication of Si NWs and Silver nano particles (Ag NPs) are used as M NPs. Raman spectroscopy is one of the versatile technique to characterize nano materials^{4,15} and study the damage if present in the system. This is possible because the intensity, half-width and peak shift of the zone center phonon peak are very sensitive to structural disorder, damage and stress in the lattice. In addition to this, using the bond polarizability model (BPM), Raman Spectroscopy provides a tool to estimate the size of NCs in case they are present in the system. In the case of crystalline Si (c-Si), the first-order Raman scattering probes the optical phonon frequency at the Γ -point in the Brillouin-zone due to the $q = 0$ selection rule. This leaves a Raman active mode at 521 cm^{-1} , which gives a single line with a line-width of $\sim 4\text{ cm}^{-1}$. At nano-scale, this selection rule is relaxed due to constraints imposed by the uncertainty principle. There is a softening and broadening of the first-order phonon mode resulting in a shift of the Raman line towards lower wavenumber together with a broadening in the line-shape. Compared to this, in a-Si, due to loss in long range order, the q selection rule does not apply. As a result, all the phonons are optically allowed and the Raman scattering results in a broad hump at 480 cm^{-1} . In the present work, we have fabricated Si NWs using MIE technique and study its morphology and optical properties using SEM, Raman scattering and Photoluminescence Spectroscopy.

2. Experimental

Si (100), n-type with resistivity 1-20 Ω -cm samples were used as a substrate for fabrication of Si NWs. We have adopted MIE technique. First, Si wafers were cleaned in acetone and ethanol to remove impurities prior to starting the porosification process. The cleaned wafers were immersed in HF solution to remove thin native oxide layer formed at surface. After removal of oxide layer, wafers were dipped in solution containing 4.8 M HF and 0.005M AgNO_3 for one minute at room temperature to deposit Ag nano particles (Ag NPs). The Ag NPs deposited samples were then kept for etching in an etching solution containing 4.6 M HF and 0.5 M H_2O_2 for 45 minutes (sample A), 60 minutes (sample B) and 75 minutes (sample C). To dissolve remaining Ag metal from the samples, these prepared samples were transferred in HNO_3 acid. Finally, the samples were dipped into HF solution to remove oxide layer induced by nitric acid used in above step. Samples were kept at room temperature in air atmosphere. These etched samples were characterized using Scanning electron microscopy (SEM), Raman scattering and Photoluminescence spectroscopy. Morphological study has been done by SEM using supra55 Zeiss and Carl Zeiss. The PL from the etched samples was recorded using TRIAX 550 spectrometer, at an excitation wavelength of 325 nm using a He-Cd laser. Raman Scattering measurements were carried out using Horiba high resolution micro Raman Spectrometer at an excitation wavelength of 632.8 nm (air cooled He-Ne laser).

3. Result and Discussion

The morphology of the etched samples at different etching time has been studied using SEM measurements, both planar and cross-sectional. Figure 1 shows the cross-sectional SEM images of etched samples at different etching time, (a) – (c) are the images as obtained from sample A, sample B and sample C respectively. It is interesting to see that samples etched for 45 minutes shows dense and vertically well aligned Si nano-wires¹³.

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