Si nanowires sheathed with thin diamondlike carbon films

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Via electroless metal deposition and industrial plasma technology, we have successfully synthesized unique composite silicon nanowire structures with diamondlike carbon (DLC) sheaths acting as inorganic passivation layers. We have also discussed their growth mechanism in terms of a self-organization process. The thickness of the DLC sheaths were quantified with Raman spectroscopy. The Raman analytical result is in good agreement with direct microstructure observations. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2207155]

I. INTRODUCTION

In the past several years, silicon nanowires have attracted considerable attention due to their potential applications in interconnection uses and basic components for future nanoelectronic and especially optoelectronic devices.[1,2] Major efforts have been placed on methodology development for silicon nanowire synthesis, assembly, and property elucidation. In general, semiconductor nanowires need to have an inorganic passivation layer because an unprotected surface may alter their optical and electrical properties.[3] However, a significant bottleneck in the field is the lack of a general approach to the synthesis of nanowire building blocks composed of complex functional materials. Though surface coating of nanowires and nanofibers has been attempted by the direct deposition of sol-gel coatings,[4] polymeric films,[5] or various metallic coatings such as gold,[6] nickel, and copper,[7,8] it is generally difficult to control thickness and uniformity by liquid-based methods and the resulting coatings are usually rough with particulate texture. Vapor-phase processing has shown more promising results with respect to the versatility of substrate/film combinations and thickness control. Here we report a versatile approach to the synthesis of composite silicon nanowire structures with diamondlike carbon (DLC) sheaths acting as inorganic passivation layers using industrial plasma technology, where the compositional limitation is no longer an issue.

II. SAMPLES AND EXPERIMENTS

Cleaned *p*-type, B-doped silicon (100) (1–5 Ω cm) wafers were etched in a 5.0 mol/l solution containing 0.02 mol/l silver nitrate at 50 °C for 60 min, followed in an ultrasonic water bath for 1 min to clean the surface. The container was a conventional Teflon-lined stainless steel vessel. The silicon wafers were then rinsed with de-ionized water and blown dry in air. During selective chemical etching, silver-capped silicon nanowires were fabricated on the silicon wafers via electroless metal deposition. These fresh silicon nanowires were then coated with DLC sheaths using acetylene plasma deposition at room temperature. The details of the deposition method are described as follows. The samples were first cleaned by argon sputtering prior to film deposition. A mixture of acetylene [20 SCCM (SCCM denotes cubic centimeter per minute at STP)] and argon (5 SCCM) was subsequently introduced into the vacuum chamber. A 500 W radio-frequency source ignited the C_2H_2 plasma, and the samples were pulsed biased to −100 V with a pulse duration of 100 μs and a pulse frequency of 50 Hz. The deposition time was 2 h.

The morphology of the samples was characterized with a FEG JSM 6335 field-emission scanning electron microscope (SEM) and a JEOL JEM-200CX transmission electron microscopy (TEM). The structure and bonding configuration in the DLC sheaths were investigated in terms of Raman spectroscopy (a Jobin-Yvon T64000 triple Raman system). The used excitation source is the 514 nm line of Ar^+ laser. All the measurements were run at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 1 shows a SEM image of the as-prepared dense oriented Si nanowires with DLC sheaths. Due to a spatially nonuniform etching rate of Si wafer during the Si nanowire formation and the Van der Waals attraction between individual nanowires, the observed nanowires exist in the form of bundles.

Detailed formation mechanism of the Si nanowires as cores can be understood on the basis of self-assembled localized microscopic electrochemical cell model.[9] For silver/

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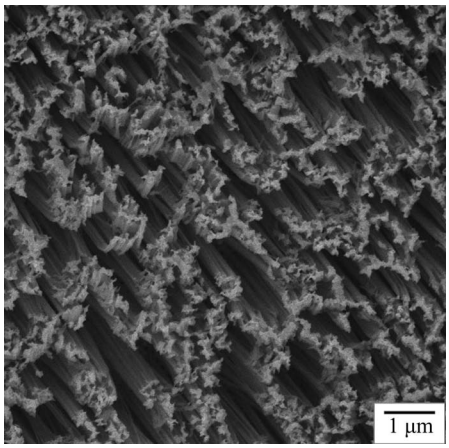

FIG. 1. SEM image of dense oriented Si nanowires with DLC sheaths.

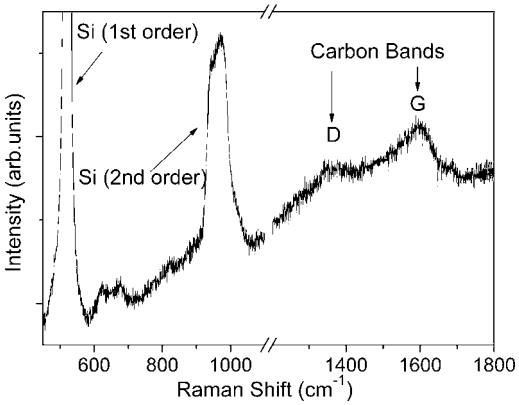

FIG. 3. Raman spectrum from the composite Si nanostructure.

silver ion couple with highly positive equilibrium potential $[E^{o}(Ag^{+}/Ag)=0.7996\ V]$,[10] the energy states of the silver ion overlap with the valence band of silicon and silver deposition can occur in the dark through injection of holes from the silver ion in solution, both on *p*-type and on *n*-type silicon.[11–14] The injected holes are consumed via oxidation of the silicon surface so that substrate atoms are replaced by silver atoms (displacement plating). The formation processes are as follows. At the start, the silicon etching and silver deposition occur simultaneously at the silicon surface. The deposited silver atoms first form nuclei and then form nanoclusters which are uniformly distributed on the surface of the silicon wafer [see Fig. 2(a)]. Many small flat honeycombs form around one tiny deposited silver nanocluster, that is, to say, numerous nanosized honeycomblike anodes and one silver nanocluster acting as a local cathode form an electrochemical cell. These cells self-assemble on the surface of the silicon wafer. Honeycombs around the silver nanoclusters are etched larger and deeper. Many of them incorporate to form one nanopore. If the silicon wall between two nanopores has not yet been etched completely [that is, the nanopore boundary still consists of a thin silicon wall, as shown in Fig. 2(b)], the undetached Si nanotube forms.[15]

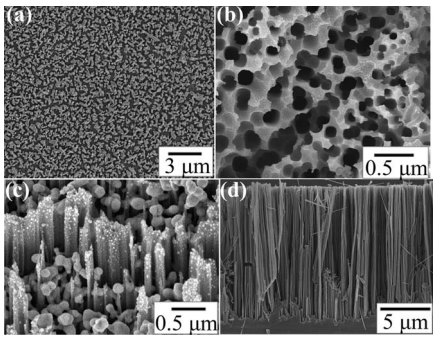

FIG. 2. SEM images of (a) silver nanoclusters distributed on the silicon wafer at the initial stage, (b) nanopores at the intermediate stage, and (c) surface morphology of the silicon wafer etched for 10 min, showing silver nanoclusters embedded in Si nanowire arrays and tiny silver nanocrystals attached on the apexes and walls of Si nanowires. (d) Cross sectional SEM image of silicon nanowires formed during 60 min etching in the end.

Further etching of intermediate undetached Si nanotubes will lead to the formation of specially shaped Si nanowires. Figure 2(c) shows the SEM image of the as-grown Si nanowires. The damaged tube walls (thin layers) can be seen attaching to the nanowires, indicating that they are the residual walls at triple points between the cell grains. The residual tube walls result in the observation of large span of Si nanowire diameters (30–300 nm) in the SEM images. According to our previous work,[9] after 60 min etching the lengths of silicon nanowires are $\sim 15\ \mu$m which can also been verified in Fig. 2(d).

In the process of silicon nanowire preparation, the etched silicon wafer was always covered with a layer of thick silver film, which is rather loose and could be easily detached from the surface of silicon wafer.[9] Though the surfaces were ultrasonically cleaned, nanometer-sized silver nuclei, encapsulated during the DLC deposition, may still distribute on the tips of the composite nanowires (see Fig. 1).

Raman spectroscopy has become one of the most important tools for analyzing carbon-based films. It has widely been used as an analytical chemical tool to fingerprint signatures of various forms of carbon such as graphite, diamond, and DLC coatings.[16,17] In sp^2-containing carbon films, Raman analysis can be performed on films as thin as 1 nm with visible light excitation because the Raman intensities can be enhanced by 10^3–10^4 via the resonant Raman effect.[18,19] The Raman spectrum acquired from the composite Si nanostructures is shown in Fig. 3. The following Raman bands were observed: a Si (first order) band centered at 521 cm^{-1}, a Si (second order) band at 970 cm^{-1}, a carbon *D* (disorder) band at 1350 cm^{-1} which indicates the presence of nanoscale graphitic domains, and a carbon *G* (graphitic) band at 1600 cm^{-1} which was identified in previous studies to reflect C sp^2 vibrations.[20]

Raman analysis has recently also been used to assess the thickness of very thin DLC coatings. Taking advantage of its enhanced sensitivity, researchers have shown that Raman intensities correlate very well with thickness.[18,21,22] Based on Beer's law for quantifying the thickness of thin Raman ac-

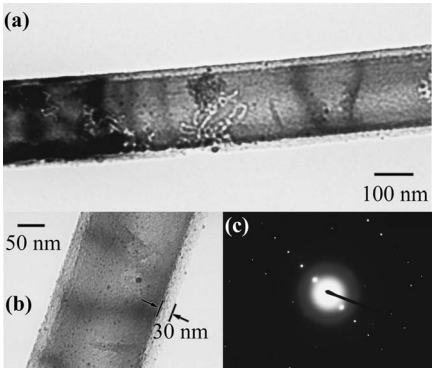

FIG. 4. (a) TEM image of a composite Si nanowire. (b) High-resolution TEM image of another composite Si nanowire. (c) The selected area diffraction pattern of the composite nanowire shown in (b).

tive coatings on Raman active substrates, Scharf and Singer[23] have given a model to quantify the thickness of thin DLC coating layers ranging from 10 nm to 2 μm, using systematic variations in the Raman carbon (G band) and Si (first order) peak intensities versus thickness. The integrated intensity ratio of Si (first order) and carbon (G band) curves (I_{Si}/I_C) is noteworthy in the model. According to their model, the thickness of the current DLC coating layer was calculated to be less than 50 nm. The Raman result indicates that the DLC thin films have successfully been deposited on the surfaces of silicon nanowires.

To give direct experimental proof for the formation of Si nanowires sheathed with thin DLC films, we carried out TEM observations on the samples. Figure 4(a) shows a long Si nanowire sheathed with a thin DLC film. The diameters ($\sim$200 nm) of the coated Si nanowires are relatively homogeneous. The high-resolution TEM image of another Si nanowire is shown in Fig. 4(b). It can be seen that the thickness of DLC layer is approximately 30 nm, in good agreement with the Raman analytical result. The corresponding selected area diffraction pattern is shown in Fig. 4(c), which indicates that the composite Si nanowire structure has a crystalline core and a surrounding amorphous layer.[24]

IV. CONCLUSION

In summary, a rapid, inexpensive method of fabricating the Si nanowires with DLC sheaths has been described on the basis of self-assembled localized microscopic electrochemical cell model and industrial plasma technology. This is a general approach to the synthesis of nanowire building blocks composed of inorganic passivation layer. The thickness of the DLC sheath was quantified with Raman spectroscopy. The Raman analytical result is in good agreement with direct TEM observations.

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