Growth and use of metal nanocrystal assemblies on high-density silicon nanowires formed by chemical vapor deposition

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ABSTRACT In this paper, we describe the growth and potential application of metal nanocrystal assemblies on metal-catalyzed, CVD-grown silicon nanowires (SiNWs). The nanowires are decorated by chemical assembly of closely spaced (1–5 nm) Ag (30−100 nm diameter) and Au (5−25 nm diameter) nanocrystals from solutions of AgNO₃ and NaAuCl₄·2H₂O, respectively. The formation and growth of metal nanocrystals is believed to involve the galvanic reduction of metal ions from solution and the subsequent oxidation of available Si-hydride sites on the surfaces of the nanowires. A native oxide layer suppresses formation of metal nanocrystals; adding HF to the ionic solutions significantly increases the density of nanocrystals on the surfaces of the nanowires. The nanocrystals coating the nanowires were characterized by X-ray photoelectron spectroscopy, scanning electron microscopy, and X-ray diffraction. Ag nanocrystals on the nanowires afford sensitive detection of Rhodamine 6G (R6G) molecules in the 100 picomolar–micromolar range by surface enhanced Raman spectroscopy. In addition, Au nanocrystals formed on selected surfaces of a substrate of arbitrary shape can serve as effective nuclei for localized nanowire growth.

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1 Introduction

Interest in semiconducting nanowires (NWs) has accelerated rapidly because of advances in bottom-up and top-down fabrication methods [1–3]. Recent studies have focused on catalyzed silicon nanowires (SiNWs). Their structure [4–6], conductivity [7, 8] and surface reactivity [9–13] have been characterized for potential applications, including nanodevices such as transistors, biological sensors, and integrated logic circuits [14–20]. Our group has recently demonstrated the synthesis of diameter-controlled, self-assembled, thin SiNWs epitaxially grown on single-crystalline silicon substrates [4]. However, before they can become technologically useful, Si-based nanowires require further development in areas including, (1) chemical methods that improve their robust self-assembly for parallel integration and, (2) chemistries that make the surfaces of such nanostructures more sensitive to binding processes. Metal-semiconductor hybrid nanostructures are expected to be useful in a variety of applications, including sensing, because of the large area of the nanowire surface that serves as support for the nanocrystals. Such nanostructures would allow sensing of an analyte by optical or electrochemical detection methods.

To explore the rational design of chemically sensitive semiconducting nanostructures, herein, we report the controlled growth and application of an assembly of metal nanocrystals on SiNWs grown epitaxially on Si substrates using gold-catalyzed chemical vapor deposition (CVD). In the following sections we provide the methods used to nucleate and grow nanocrystals of Ag and Au onto surfaces of SiNWs and discuss the effect of the oxide layer on the nucleation and growth of the nanocrystals. We then demonstrate control of the size and coverage of the metal nanocrystals deposited onto the nanowires using ionic solutions of Ag and Au containing HF. Finally, we demonstrate two potentially beneficial applications of these hybrid nanostructures: (1) optical detection of chemically adsorbed molecules by surface enhanced Raman scattering (SERS) from Ag nanocrystals grown on nanowires, (2) improved nanowire growth for parallel integration by using Au nanocrystals on bulk surfaces as active catalysts for nanowire growth.

2 Experimental procedure

Anchored, gold-catalyzed, p-type silicon nanowires with a typical diameter of ∼25 nm were grown on a p-type (B) Si(111) substrate (0.01−0.02 Ω cm) according to methods previously described [4]. The wafer was subsequently divided into smaller pieces, and each substrate was cleaned in a mixture of H₂SO₄ : H₂O₂ (1 : 1) for 5 min, rinsed with deionized water, and dried with N₂. Each substrate was then immersed into a 1% HF/H₂O solution for 3 min, rinsed for 10−30 s, and dried under a stream of N₂. The dilute HF etch removed the native oxide layer and hydrogen-passivated the nanowire surfaces. Solutions of AgNO₃ (99.999%) and NaAuCl₄·2H₂O (99.9%) were prepared in a range of concentrations from 1 mM to 100 mM. The solutions were kept in the dark to prevent premature reduction of Ag⁺ and Au³⁺ in solution prior to the reaction. Immediately following the HF treatment, SiNWs substrates were spotted with a ∼ 10 μL drop of AgNO₃ or NaAuCl₄ solution that typically spread out to a 5 mm diameter spot over the surface.
To improve the metal coverage, the hydrogen-passivated surfaces of the nanowires were exposed to AgNO₃ or NaAuCl₄ solutions containing HF. In this modified procedure typically ~2 µL of 1% HF solution was added to the already dispensed ~10 µL drop of a 1 mM AgNO₃ or NaAuCl₄ solution, and the mixture was reacted using identical deposition parameters to those used without HF. In an alternate technique a solution of 1% HF was prepared containing 1–100 mM AgNO₃ or NaAuCl₄. Samples were immersed into the solutions for a predetermined duration and subsequently rinsed with purified water filtered to have a TOC < 3 ppb (> 18 MΩ at pH = 5.5, determined by the dissolved CO₂). There was no observable difference between the two methods that used HF-containing solutions. The immersion method was generally used because it produced larger areas on the substrates for surface characterization.

The nanowires were examined using an FEI (model XL30) scanning electron microscope (SEM), typically operating at an accelerating voltage of 20 kV. Raman spectra were acquired using a Joriba-Yvon T64000 micro-Raman system equipped with a 100× plano-achromatic objective and a CCD detector. The excitation wavelength was provided by a 532 nm solid-state laser. The laser power at the sample position was typically 2 mW focused over a 1 µm² area of the substrate. Spectra were recorded over the range of 400–1700 cm⁻¹ and collected in three consecutive traces at 10 cycles per segment (with 1 s/ acquisition), averaged and baseline corrected. Short acquisition times were required in order to minimize photo-bleaching.

In the Raman experiments, diluted solutions of R6G were allowed to bind to the surfaces of the nanowires, which were then analyzed by Raman spectroscopy. In a typical reaction the substrate was immersed into R6G solution, left to incubate for 5 min at room temperature, and then thoroughly rinsed in purified water. The samples were then placed into vials sealed under argon, and analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy within a few hours to minimize interferences from potentially adsorbing surface contaminants.

XPS was performed using a standard X-ray photoelectron spectrometer equipped with an Al Kα X-ray source (1486.6 eV) and a hemispherical analyzer. The main XPS chamber was maintained at a constant base pressure of <3 × 10⁻⁹ Torr during the acquisition period. The samples were introduced through an intermediate pumping stage by using a fast-transfer, mechanical moving rod, a procedure that required a total time of approximately 5 min. All spectra were obtained using identical data-collection parameters. The survey scans (from 0 to 1000 eV) were generally obtained in scanning mode at a spectral resolution of 1 data point/eV, resolution 4 (highest count rate) and were averaged over eight scans. Since the residual adventitious hydrocarbon C 1s peak in the control sample was low (<1%), an external charge neutralizer gun (set to 2 eV) was used during the spectral acquisition to avoid possible surface charging effects.

3 Results and discussion of nanoparticle formation

The nanowires were studied by scanning electron microscopy to examine morphological changes occurring on the surface (Fig. 1a–d). The surface morphologies of the silicon nanowires are not changed by hydrogen passivation prior to reaction with the ionic solutions of AgNO₃ and NaAuCl₄ (Fig. 1a). After exposure to the AgNO₃ solution, nanoparticles are seen on some of the nanowires while other nanowires exhibit just a few or no particles (Fig. 1b–c). In sharp contrast, after exposure to the NaAuCl₄ solution, most nanowires exhibit a higher coverage of nuclei on the surface (Fig. 1d).

These Ag and Au nanoparticles coating the nanowire substrates were confirmed to be crystalline using X-ray diffraction (θ–2θ scans not shown). In addition, the Ag nanocrystals are closely spaced—often separated by only 1–5 nm—and have diameters ranging from 30–100 nm. Au nanocrystals grown for the same duration typically have smaller diameters, ranging from 5–25 nm.

The growth characteristics suggest that the spontaneous deposition of the nano-sized Ag and Au crystals onto the surface occurs through a galvanic displacement mechanism involving transfer of electrons from the zero-valent Si surface to the ions in solution. Si is a known reducing agent in the presence of metal ions [20–23]. In this surface-mediated redox reaction, oxidation of silicon hydride species to Si³⁺ by the aqueous solution provides the reducing equivalents for Ag⁺ and Au³⁺ ions; the electrons flow directly from the Si atoms on the surface to Ag and Au ions that randomly move near the surface.

The difference between the Ag and Au nanocrystal density is consistent with the more positive electrolytic cell standard reduction potential for the half-reaction of Au³⁺/Au (1.498 V) compared to that for Ag⁺/Ag (0.799 V). The more positive reduction potential of Au indicates a larger chemical driving force for the spontaneous displacement of the surface H by reduced Au.

Several parameters, including concentration and time, were varied to assess the nanocrystal growth process in the absence of HF. More concentrated solutions (100 mM) of AgNO₃ or NaAuCl₄ typically resulted in little or no nucleation of metal nanocrystals on the surfaces of the nanowires. Conversely, more dilute solutions (< 10 mM) and shorter deposition times (30–60 s) typically resulted in a higher density of closely spaced Ag and Au nanocrystals (Fig. 1b and d) and eliminated the growth of large, dendritic nanostructures observed after extended deposition times (inset of Fig. 1c). Figure 1b–c shows the effects of changing the duration of the deposition using a 1 mM AgNO₃ solution. After an initial density of Ag nanocrystals form, these nanocrystals grow larger as the exposure continues, and few additional nanocrystals nucleate. A similar trend was observed using NaAuCl₄ solution (images not shown). Even under optimum conditions (1 mM and 30 s deposition) only a marginal number of nanowires were functionalized with a high density of smaller Ag and Au nanocrystals. Similar procedures employed on a plane, hydride-terminated Si(111) surface also yielded a sparse coverage of Ag and Au nuclei. These observations suggest that the lack of nanocrystal nucleation is due to the rapid re-oxidation of the surface Si atoms and the presence of a passivating oxide layer in the absence of HF [13].

This proposed mechanism is consistent with the survey X-ray photoelectron spectra (XPS) shown in Fig. 2a–c.