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Fabrication of Cobalt Silicide Nanowire Contacts to Silicon Nanowires

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A novel method to fabricate cobalt silicide nanowire contacts to silicon nanowires is described. Nanoporous anodized alumina membranes were used to define the wires' dimensions. Cobalt was deposited electrochemically within the pores of the membranes. On top of the cobalt, gold was deposited electrochemically to catalyze the growth of the silicon nanowires. The well-known vapor-liquid-solid mechanism was used to grow the silicon nanowires. During the growth of silicon, cobalt reacts with the growing silicon nanowire, forming cobalt silicide, and under certain conditions, all of the Au used to catalyze the growth of the silicon nanowire travels along the tip of the growing wire, away from the cobalt silicide/Si interface. We also discuss the influence of the amount of Au catalyst on the structural quality of the wires.

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Semiconductor nanowires have generated tremendous interest in recent years due to their potential applications in nanoelectronic and nanoelectromechanical devices.[1-3] Considerable interest has been devoted to the fabrication and characterization of silicon nanowires (SiNWs), and researchers have synthesized SiNWs using various methods including electron beam lithography,[4-6] reactive ion etching,[1,4,6-8] laser ablation[9-13] (which may be oxide[9,10] or metal[11,13] assisted), and the classical metal catalyzed vapor-liquid-solid (VLS) growth mechanism introduced by Wagner and Ellis[14-16] and described in detail by Givargizov and co-workers.[17,18] In this method, a catalyst such as Au, Zn, Ga, or Pt is usually deposited on a silicon wafer. Subsequently, the wafer is placed in a furnace at a temperature high enough to form a liquid alloy droplet between the catalyst and silicon. When a silicon-containing gas such as $SiCl_4$ or SiH_4 is introduced, the liquid droplet catalyzes the decomposition of the silicon-containing gas, and silicon is released. The released silicon subsequently diffuses into the liquid droplet until it becomes saturated with silicon. After saturation, excess silicon precipitates from the liquid droplet. Using the VLS growth mechanism, large numbers of SiNWs with high aspect ratios have been synthesized.[19-21] However, not all of these efforts have produced long, thin, straight nanowires.

A new approach in which the SiNWs were grown on gold-coated, mesa-shaped silicon projections was reported by Okajima *et al.*[22] in an effort to position the wires without fusing or kinking on a Si wafer. This technique yielded wires over 500 μm long; however, the wire diameter was still large (∼20 μm). Westwater *et al.* conducted a similar study aimed at controlling the size and position of the SiNWs grown on a silicon wafer.[23,24] They patterned an oxide-coated silicon wafer using photolithography to create an array of circular holes. Gold was then deposited on top of the silicon within the holes, and VLS growth was conducted. The diameter and the position of the wires were controlled by the diameter and the position of the holes, which may be useful for studying individual wires, but the yield of SiNWs is low.

Recently, a novel method combining VLS growth with an anodized alumina nanoporous membrane as an initial template was developed.[25,26] In this method, the pores of the alumina membrane are used to define the size of the wires. Consequently, precise control of the wire diameter can be achieved by growing within nanoporous templates. Using this method, a high yield of uniform SiNWs can be synthesized. This approach also provides a controlled method for contact formation.

For nanoelectronic devices to reach their potential, ohmic contacts to the SiNWs are required. In microelectronics, the silicide $CoSi_2$ has emerged as a leading choice as a contact material due to its low resistivity, stability on Si, and small lattice mismatch (−1.2%) with silicon.[27] Furthermore, the low mutual solubility of Co and Au[28] protects cobalt from mixing extensively with the Au catalyst during the VLS growth. Therefore, we were motivated to incorporate Co in the SiNW fabrication scheme reported by Lew *et al.*[26] Interestingly, Li *et al.*[29] have attempted another method to fabricate cobalt silicide contacts to SiNWs. They used a metal vapor vacuum arc ion source to implant Co^+ ions in SiNWs presynthesized by thermal decomposition of SiO powder. Since the incident Co^+ beam was directional, only the side of the nanowire that was facing the Co^+ beam was implanted. Therefore, the contacts spanned the length of the nanowires. In this paper, we describe the fabrication of cobalt silicide nanowire contacts to silicon nanowires using the VLS technique in nanoporous alumina templates, where an interface between the cobalt silicide and Si is formed along the cross section of the wire.

Experimental

Figure 1 shows the fabrication scheme of the cobalt silicide nanocontacts to the SiNWs. We used nanoporous anodized alumina membranes with a nominal 200 nm diam as templates for nanowire growth. A thin film of approximately 150 nm Ag was sputtered on one side of the membrane to provide a conductive layer for electrodeposition within the pores. To fully cover all the pores with Ag, the membrane was subsequently placed in an electrochemical cell, and Ag was electrodeposited at 22.27 mA/cm^2 for 1 min on the conductive side of the membrane. To electrodeposit within the pores, the membrane was flipped upside down and the plating solutions were added from the open side of the membrane. Ag, Co, and Au were then sequentially electroplated within the pores. The Ag (1.125 tr. oz/qt) and Au (0.25 tr. oz/qt) plating solutions were purchased ready from Technic, Inc., while the Co bath was made by mixing 500 g/L hydrated cobalt sulfate, 17 g/L sodium chloride, and 45 g/L boric acid at 25°C. The pH of the Co bath was then adjusted to 5.[30] Ag was electroplated inside the membrane at 7.32 mA/cm^2 for 2 h to control the position of the Co and Au layers. Co was electroplated at 89.09 mA/cm^2 for 5 min. The Au was electroplated at 2.22 mA/cm^2 for various lengths of time to participate in the VLS growth of the Si nanowires. The template was next placed in a chemical vapor deposition (CVD) chamber, which was purged with hydrogen at room temperature. The temperature of the CVD furnace was then raised to 500°C and left at this temperature for about 20 min to reach thermal equilibrium. After that, a mixture of 5% silane in hydrogen was allowed to flow over the template at 500°C, and Si nanowires were grown by the VLS mechanism. At this temperature,

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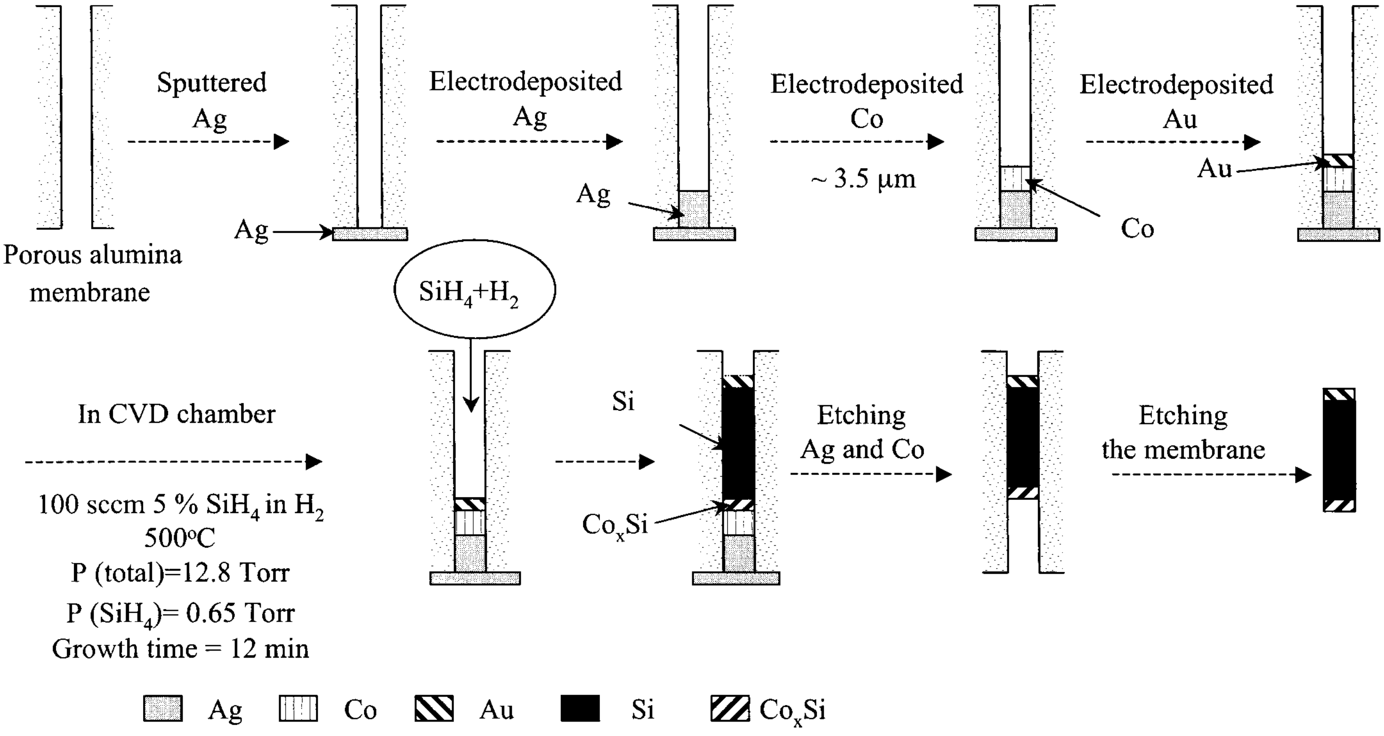

Figure 1. Fabrication scheme of the cobalt silicide contacts to the SiNWs.

the Si portion also reacted with the Co portion of the nanowire to form one or more of the cobalt silicide phases. After growth, the nanowires were released from the membranes using 8.0 M nitric acid to dissolve the Ag and the remaining metallic Co, and further treatment with 1.0 M sodium hydroxide was used to remove the alumina membrane. After several centrifugation and rinsing steps, the nanowires were then stored in deionized water.

The morphology and the chemical analysis of the different layers within the nanowires were studied using a FEI-Philips XL20 scanning electron microscope (SEM) and a Philips 420 transmission electron microscope (TEM). Both microscopes have an energy dispersive X-ray spectrometer (EDXS), which was used to identify the elements in segments of the nanowires.

Results and Discussion

Figure 2 shows a typical nanowire from our early attempts to grow multilayered nanowires, with the segments of the wires labeled according to EDXS analysis. Before Si growth, the lengths of the Ag, Co, and Au portions within the membrane were 20 μm, 3.5 μm, and 230 nm, respectively. Silane at a partial pressure of 0.65 Torr was introduced along with the carrier gas H_2 at a total pressure of 12.8 Torr at 500°C for 12 min. Gold catalyzed the decomposition of SiH_4 into silicon and hydrogen, and a ball of Au-Si liquid alloy was formed. After the liquid alloy became saturated with silicon, silicon precipitated at the interface between the liquid alloy and the remaining electrodeposited metal. These are essentially the steps for the VLS mechanism whether or not the SiNWs are grown within a membrane. However, in the present study, when the silicon comes in contact with cobalt at 500°C, another reaction takes place between the silicon and cobalt to produce one or more cobalt silicides, as has been observed in thin-film contacts to Si wafers.[31]

After cooling the CVD chamber to room temperature, the membrane was dipped in 8.0 M HNO_3 for 3 min to etch away silver and the remaining elemental cobalt. Silicon, Au, and the cobalt silicide phase are resistant to HNO_3 and are not attacked. In this study, consistent with a report on the rate of reaction in Co/Si diffusion couples by Jan *et al.*,[32] the kinetics of the silicidation reaction was relatively slow, so as not to consume all the cobalt within the short time of the growth of the SiNWs. Hence, only a short cobalt silicide segment (~0.5 μm) was obtained. We also found Au nanoparticles near the silicide segment, which appear as bright nanoparticles in Fig. 2. These Au particles along the SiNWs will likely affect the

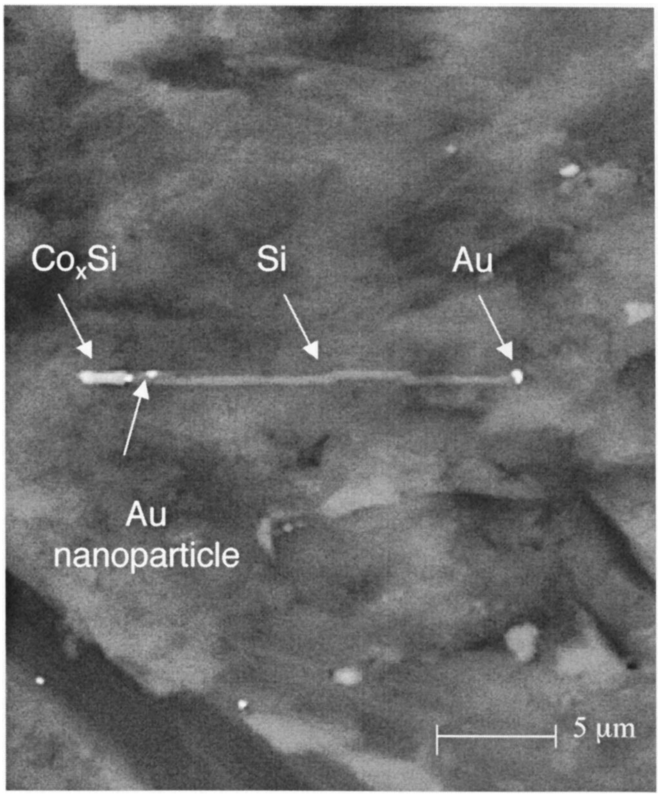

Figure 2. SEM micrograph of one of the released nanowires.

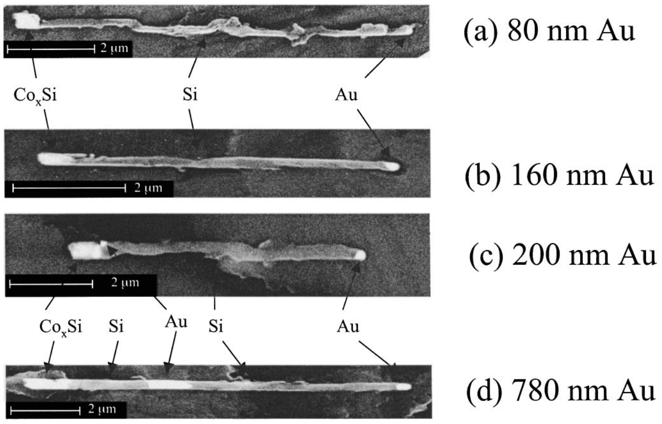

Figure 3. SEM micrographs of a single nanowire grown with different Au thicknesses of (a) 80, (b) 160, (c) 200, and (d) 780 nm.

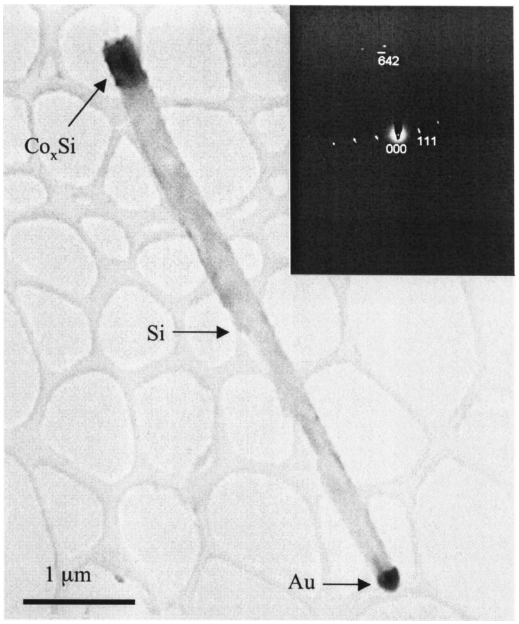

Figure 4. TEM micrograph of one of the wires that was synthesized with a Au thickness of 160 nm. The inset is a diffraction pattern near the $[\bar{1}45]$ zone axis of the Si segment, acquired transverse to the axis of the wire.

electrical performance of the wire; consequently, effort was focused on this problem.

We addressed this problem by searching for an optimal Au thickness for the nanowires to be grown without leaving any Au particles along the wires. To determine the effect of Au thickness, membranes with various Au thicknesses of 80, 160, 200, and 780 nm above the Co segment were prepared and investigated after growing the nanowires for the same period.

With the Au thickness of 80 nm, the Au particles disappeared, as shown in Fig. 3a for a nanowire with diam 152 nm. The silicon nanowire diameter was smaller than the diameters of both the cobalt plug and the alumina membrane pore, and as a result the wires did not take the exact shape of the pores during growth. They were curved and bent rather than straight. Thus, the shape of the SiNWs was not desirable. A gold thickness of 160 nm was optimal in this study. No Au particles appeared within the wires, as shown in Fig. 3b. Furthermore, the structure of the wires was good. With Au thicknesses of 200 and 780 nm, some Au was retained within the SiNWs. Not surprisingly, the amount of retained Au became greater as the thickness of the electrodeposited Au increased, as shown in Fig. 3c and d. However, the structure of the wires was good, and the silicon nanowires, the cobalt plugs, and the pore diameters are nearly the same.

Using the TEM, we found that the nanowires that were released from the alumina membranes containing the optimal Au thickness had silicon segments that were single crystals or crystalline with a small number of defects. Figure 4 shows a TEM image for one of the nanowires, and the inset is a diffraction pattern from the Si segment. From examination in the TEM of 13 nanowires, an average diam of 249 nm with a standard deviation of 32 nm was measured. The wires have a greater diameter than the nominal pore diameter, along with a spread in diameters, because the pores are not always the exact same size as the nominal value stated by the manufacturer, nor are they all the same size as each other. The SEM and TEM studies also show a little roughness along some of the wires that may be due to the use of NaOH to release the wires from the alumina membranes. The silicon segment of the nanowires is expected to be attacked by NaOH but with a much slower rate than alumina.

Several approaches were next taken to provide a formula to describe the optimal thickness (or length) of Au plug required for VLS growth. We assumed that the liquid Au-Si alloy present during VLS growth forms either a hemispherical or a spherical bead of the same diameter as the growing Si nanowire, and that the volume of the Au-Si alloy is close to that of the solid Au plug. Therefore, we calculated that we would need Au plugs that are either 1/3 D or 2/3 D thick for hemispherical or spherical beads, respectively, where D is the diameter of the nanowire. The thickness of the Au plug that worked well in our experiments, 160 nm, is very near the value of 166 nm that we predict using the formula for a spherical bead for our nanowires of average diam 249 nm. However, the prediction we make assuming a hemispherical cap (83 nm) provides a Au thickness very close to the 80 nm thickness that was insufficient in our study.

However, as we see from Fig. 5, the Au bead at the end of the Si nanowire is neither a hemisphere nor a sphere. More careful examination in the TEM of 13 nanowires was next performed. The diameter of each nanowire was measured, and the volume of the Au bead at the end of each nanowire was approximated from the TEM images. From these experiments, the starting thickness of the Au plug was estimated to vary from 0.5-0.9 D. Note that the value 2/3 D falls within this range.

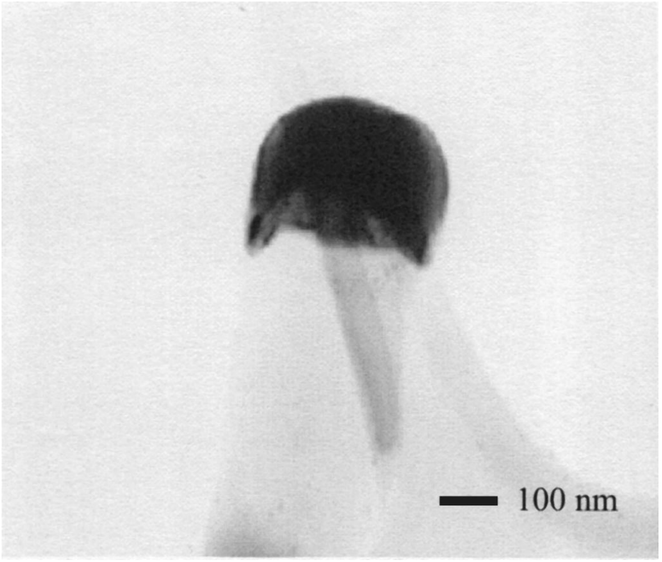

Figure 5. The Au tip at the end of a nanowire synthesized with a Au thickness of 160 nm, as revealed by TEM.

It is interesting that nothing has been reported in the literature concerning Au retention in SiNWs when they are grown on Si wafers using the VLS technique. In this case, the shape of the liquid bead is not constrained by a pore, so the bead can form a portion of a sphere of any diameter depending on the amount of Au present. Hence, no excess Au is left behind during VLS growth. Furthermore, the silicon-containing gas has easier access to the surface of the Au catalyst than it does for SiNWs growing within pores, so Au is again less likely to be retained along the length of a SiNW.

Along with the preparation of nanowires of smaller diameter, the effect of size on the electrical characteristics of the contacts and the Co/Si interfacial reaction are currently under investigation in our laboratory. Applying the same approach for different metallic contacts to the SiNWs is also one of our aims. Finally, acidic etchants for the alumina membrane are to be studied to improve the structural roughness that sometimes appears in the SiNWs.

Conclusions

We fabricated cobalt silicide contacts to single crystalline silicon nanowires. Nanoporous alumina membranes were used as templates to define the size of the wires. Ag, Co, and Au were sequentially plated electrochemically within the pores of the membrane, and the VLS growth mechanism was used to grow the silicon nanowires. The structural quality of the nanowires grown within the membranes depended strongly on the thickness of the Au catalyst used for growth. For our nanowires of average diam 249 nm and standard deviation of 32 nm, a Au thickness of 160 nm worked well. By further examining 13 of these nanowires and the shape of their Au tips in the TEM, we estimated that the starting Au thickness for high quality wires varied from 0.5-0.9 D, which is close to the value of 2/3 D corresponding to a spherical Au bead of the same diameter as the nanowire.

Acknowledgments

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List of Symbols

D diameter of nanowire

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