Growth and Optical Properties of Self-Organized Au₂Si Nanospheres Pea-Podded in a Silicon Oxide Nanowire**

By J. S. Wu, S. Dhara, C. T. Wu, K. H. Chen, Y. F. Chen, and L. C. Chen*

There is a great impetus in the research on semiconductor-based nanostructures due to their unusual optoelectronic properties that result from quantum size effects.^[1] The recent success of silicon-based nanostructures^[2–6] with interesting optical^[7,8] and electronic^[9] properties has renewed interest in this relevant field of study. Exotic structures of silicon-based nanowires with self-organized silicon nanospheres have also been reported^[10] furthering the “bottom-up” paradigm for device fabrication. The formation of silicon-based nanowhiskers, following the vapor–liquid–solid (VLS) growth mechanism and using a metal catalyst has been described in all these reports.^[2–10] Metals play a major role in the catalytic action, and a detailed study of the metal–silicon interaction is a subject of considerable interest^[11] with regard to both fundamental studies and technological applications. However, except for the formation of CoSi₂/Si and NiSi₂/Si nanocomposites, and possible implications in the electrical contact formation for silicon nanowhiskers,^[4] very little attention has been given to the possible manifestations of the metal–silicon interaction during the growth of nanowires. Gold is the most widely used catalyst in the VLS growth of silicon-based nanowhiskers, as the Au–Si system is a simple eutectic with the eutectic point at 363 °C at about 19 at.-% silicon.^[12] Over the last three decades, the Au–Si system has been the most well-studied system, with research concentrating on its possible applications in microelectronic devices. Different metastable phases within the composition ranges of Au₂Si to Au₇Si, with different structural and electronic properties, have been reported.^[12] Despite the early setback of metallization with gold in silicon, as the device property is degraded by a high diffusion rate of gold in silicon, it still has an advantage in bipolar and radio frequency power transistors, as well as for chip capacitors used for internal matching.^[13]

We report here the growth and optical properties of a unique structure comprised of silicon-based nanowires with self-assembled gold silicide nanospheres embedded in it. High-resolution transmission electron microscopy (HRTEM), along with analytical electron microscopic (AEM) analyses and selected-area electron diffraction (SAED) studies have been used to characterize the nanowire and the pea-podded nanoclusters. Morphological studies aiding the description of the growth mechanism have been performed using field emission scanning electron microscopy (FESEM). The optical photoluminescence (PL) properties of the noble silicon-based nanowire were studied using the 532 nm line of a Nd:YAG laser in the backscattering configuration of a micro-PL setup.

A morphological study showed (Fig. 1a) a noble type of one-dimensional nanocomposite with nanocrystals of mostly spherical (5–30 nm), and a few cylindrical, shapes embedded in the nanowires. These nanocomposites were obtained by thermal annealing of gold/amorphous-silicon (Au/a-Si) bilayers at 1030 °C in a nitrogen ambient atmosphere. Most of the wires are straight and have a smooth morphology. It is worth mentioning that no nanowires were formed during the low-temperature (500 °C) treatment of Au/a-Si bilayers.

A microstructural study using HRTEM (Fig. 1b) indicated that the nanowire possesses an amorphous structure. The SAED pattern in the inset (Fig. 1b) also shows amorphous rings that support this fact. The chemical compositions of the nanowires were determined by AEM. A selected-area AEM analysis on the matrix of the wire revealed silicon and oxygen to be the main constituents of the amorphous nanowires, as indicated in Figure 1b. Since there was no oxygen source during the growth process, the oxygen content in the nanowire may have originated partly from the residual oxygen gas in the furnace, and most likely from the ambient after the sample was taken out of the tube furnace. Due to its high surface area to volume ratio, the silicon nanowire could spontaneously oxidize immediately upon exposure to ambient air. However, exposure of an a-Si layer to the atmosphere before coating with a gold overlayer, and the high-temperature processing in the quartz tube, may also contribute as an important source of oxygen, which plays a role in the oxidation of the nanowires. We will designate this new type of amorphous nanowire as SiONW. The oxidation of silicon nanowhiskers has also been reported at high temperature (1250 °C) and low pressure (10^{−5} torr) in a quartz tube furnace during the formation of Si nanospheres embedded SiONW.^[10] VLS growth of nanowires with silicon in the core and oxide as a cladding layer has been reported both by thermal evaporation^[8] and laser ablation^[6] techniques at high temperature (1200 °C) and relatively low pressure (100–500 torr) in a quartz tube furnace. The nanoparticles in the present study were found separately distributed along the long axis of the nanowire. The average diameter of the nanocrystals increased with increasing diameter of the host nanowires. As shown in Figure 1c, the HRTEM image of the nanocrystals exhibit clear lattice fringes. The *d* spacings of 0.245 and 0.346 nm can be attributed to the [800] and [440] planes of gold silicide with the phase

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Fig. 1. a) Morphological (FESEM) image of nano-pea-podded silicon oxide nanowires. b) Microstructural (HRTEM) image and AEM analysis of whisker and pea-podded nanospheres. The inset shows the amorphous pattern corresponding to nanowires. c) Lattice HRTEM image of gold silicide nanospheres pea-podded in a silicon oxide nanowire.

Au_2Si ,^[14] this composition is also close to the AEM data, as indicated in Figure 1b.

To control the growth of the composite Au_2Si embedded in SiONW ($\text{Au}_2\text{Si}@\text{SiONW}$), the thickness of both the Au and the a-Si layers was adjusted. Figure 2 shows that as the a-Si layer thickness increases, the number density of the one-di-

Fig. 2. Variation of the number density and length of Au_2Si nano-pea-podded silicon oxide nanowires with variation in thickness of a-Si/Au bilayers.

mensional composite remained almost constant, with a fixed gold layer thickness; as the gold layer thickness increased, the number density of the one-dimensional composite decreased. Conditions were kept similar for these studies, with a nitrogen gas flow rate of 50 sccm at 1030 °C for 10 min. The average diameter of the nanowires was found (by analyzing high magnification images not shown in the figures) to increase with increasing gold layer thickness, and remained the same for the samples grown with the same gold layer thickness. However, the length of the nanowire was observed to increase with increasing a-Si layer thickness (Fig. 2). This can be explained by the following facts. For a fixed gold layer thickness, the nucleation density of catalyst is the same, with the formation of Au–Si islands (detailed later) at the high processing temperature (1030 °C) of the a-Si/Au system. On the other hand, with increasing gold layer thickness, the nucleation density of the Au–Si island is expected to decrease with increasing grain size. The increasing diameter of the nanowire with increasing gold layer thickness (Fig. 2)

can be correlated to the increasing grain size of the Au–Si islands. The nucleation density of the Au–Si islands decreased as a direct consequence of the increase in grain size. Thus, the simultaneous decrease in the number density of the nanowires with increasing gold thickness (Fig. 2) can be related to the decreasing nucleation density of the Au–Si islands. The increasing length of the nanowire may be correlated to the abundance of a silicon vapor source taking part in the VLS process with the increase in the a-Si layer thickness. However, irrespective of the layer thickness of gold and a-Si, the number density of SiONWs increased with increas-

ing growth time, but with rare gold silicide nanoparticles embedded inside (Fig. 3a). Au_2Si nanostructures embedded inside SiONWs play the role of a catalyst, forming branched nanowires and thereby increasing the number density of nanowires, as shown in the magnified image (Fig. 3b).

Now, we discuss the possible growth mechanism of the composite $\text{Au}_2\text{Si}@\text{SiONWs}$. The formation of silicon-based nanowires following the VLS mechanism using various kinds of liquid-forming catalysts, such as gold, is a well-known phenomenon and has been described in earlier reports.^[2,3,5,7–10] In the present study, the role of the catalyst is not played by gold alone. At an elevated growth temperature (1030 °C), an Au/a-Si bilayer is expected to form an alloy (silicide) owing to the large inter-diffusion of gold in silicon and the rather low eutectic temperature (363 °C) in the Au–Si system. Molten gold silicide (liquid) is formed as a droplet, as the surface energy of the silicide is lower than both elemental gold and silicon. Instability, such as an abrupt neck formation originating from thermodynamic fluctuation in different crystalline facets of the silicide, can initiate the growth of nanowires where both gold and silicon as an alloy is likely to take part. This alloy composition, at an elevated temperature, will be supersaturated with silicon as it is abundant in the system. Nanometer-scale a-Si can be vaporized above 1000 °C, owing to the effect of lowering the melting point of the nanoparticles.^[15] This constitutes the vapor–liquid interface providing the “supply” of the constituent phases. During the cooling process, silicon can precipitate, predominantly co-axially, leaving a Au–Si alloy in the core of the wire. Magnified FESEM

Fig. 3. a) High-density growth of silicon oxide nanowire with rare Au_2Si nano-pea-pods. b) High-magnification image of branched nanowires with the utilization of embedded Au_2Si as catalytic nucleation sites leading to a high-density growth of nanowires. c) High magnification image of single nanowire with Au–Si nanospheres in the core. The inset shows growth at an early stage with the formation of islands and extruded nanowires with a Au–Si core.

images of a nanowire with a Au–Si core are shown in Figure 3c, along with an image of the early growth in the inset. An island-like structure was observed in the background, with the growth of composite nanowires initiated at a few of these islands (inset Fig. 3c). A thin layer of silicon, with a lighter contrast, was shown to grow co-axially with the Au–Si alloy. A schematic diagram is also shown (Fig. 4a) to describe the process. By increasing the growth time, Au–Si nanowires in the core self-assemble, mostly into Au_2Si nanospheres (Fig. 3c),

Fig. 4. Schematic diagrams of a) the early stage of formation of Au_2Si nanopodded silicon oxide nanowires, and b) the final stage of growth and the mechanism of formation of the nanospheres in the core of the nanowire.

along with the growth of the wire. Pure gold was found (shown schematically in the final stage of growth, Fig. 4b) on the tip of the SiNWs, indicating that the VLS process was involved in the growth. The driving force for the self-assembly of the Au_2Si nanospheres might occur from periodic instability in the growth process. The formation of silicon microwhiskers with a periodically oscillating structure^[16] and, more recently, self-assembled silicon nanospheres in SiONW^[10] have been described. The origin of the periodic structure in silicon is related to the supersaturation of silicon at elevated temperatures (1020 °C and above) in the liquid Au–Si droplet,^[17] the roughening transition at the liquid–solid (LS) interface,^[18] and the area of the liquid–solid interface. The contact angle of the droplet on the top of a whisker changes periodically, also resulting in the periodic structure. A similar mechanism is conceived for the formation of the Au_2Si @SiONW reported in the present study. In the liquid–solid interface of the total VLS process, “consumption” of the constituents supersaturates the molten Au–Si alloy, and there will be an increase in the molten curvature (the beginning of the growth of nanospheres) (schematically shown, A to B, in Fig. 4b). Further extension of the nanosphere will reduce the supersaturation and thereby the curvature (B to C in Fig. 4b), finally, completing the formation of the nanosphere by dislodging from both the necks (A and C) with the limited “supply” of material. The growth of the nanocomposite with self-assembled Au_2Si nanospheres pea-podded in silicon-based nanowires (Figs. 1 and 3c) is also shown (Fig. 4b) schematically. Lastly, the high surface area-to-volume ratio of the silicon

nanowires initiates oxidation, in the atmosphere, to form SiONWs.

The PL spectrum of the Au_2Si @SiONW (Fig. 5) shows a sharp peak around 683 nm (FWHM < 1 nm), and a broad peak around 700 nm. We have compared our results with the PL spectrum (also shown in Fig. 5) of SiONW with rare Au_2Si nanospheres (grown for a longer duration). The PL spectrum for the SiONW sample with rare Au_2Si (Fig. 5) shows only a broad peak around 700 nm, indicating a major contribution

Fig. 5. Photoluminescence study of a silicon oxide nanowire pea-podded with Au_2Si nanospheres and a silicon oxide nanowire with rare Au_2Si .

originating from the SiONW corresponding to the observation of the peak. The common broad PL peak at 700 nm observed in both SiONW and Au_2Si @SiONW may be associated with surface non-bridging oxygen (NBO), attributed to the component of SiONWs, as reported earlier for mesoporous silica samples.^[19] The observation of a sharp peak around 683 nm present in Au_2Si @SiONW, but not in SiONW with rare Au_2Si nanospheres, is quite intriguing. A broad PL peak observed in gold nanoislands (≤ 10 nm) on a roughened SiO_2 surface has been assigned to the radiative decay of collective plasmon states.^[20] A comparatively sharp PL peak for gold, silver, and copper nanoislands (10–100 nm) on a roughened surface, originating from the direct radiative recombination of electrons below the Fermi level with holes in the *d* band, has been proposed,^[21] and this mechanism was also used to explain the PL observed in sufficiently large gold colloids (~ 5 nm) that showed a large dependence on surface states in the presence of different solvents.^[22] A similar recombination mechanism may also be sought for the relatively sharp 683 nm PL peak for the Au_2Si @SiONW sample in the present study. Gold silicide, with a resistivity lower than the poly-Si,^[23] and with a Fermi level slightly above gold, may also play a similar role in the electronic radiative recombination process related to interband transitions, as nanospheres of gold silicide (5–30 nm) are also embedded in amorphous SiONW with a large amount of defect states. The absence of a peak around 683 nm in the PL spectrum of the SiONW sample with rare Au_2Si suggests a definite role for the Au_2Si nanospheres in the emission process (Fig. 5).

In conclusion, the formation of a noble nanocomposite consisting of a self-organized chain of gold silicide nanocrystals pea-podded in a silicon oxide nanowire (Au_2Si @SiONW) has

been demonstrated. The diameter and the number density of nanowires were controlled by altering the gold layer thickness. The length of nanowires was controlled by adjusting the a-Si layer thickness. The number density of nanowires with rare Au₂Si nanopea-pods could be controlled by adjusting the growth time, using Au₂Si as catalytic nucleation sites. The presence of a broad PL peak around 700 nm for Au₂Si@-SiONW and, exclusively, in SiONWs with rare Au₂Si has been argued to originate from the non-bridging oxygen present solely in SiONWs. A new, sharp peak around 683 nm in the PL spectrum, observed, exclusively, in the Au₂Si@SiONW samples, has been assigned to a radiative recombination process related to interband transitions in gold silicide nanosphere pea-podded in the amorphous SiONW containing large defect states.

Experimental

For the growth of silicon-based nanowires, an a-Si thin film was first deposited on a crystalline silicon [c-Si(100)] substrate with an ion-beam sputtering deposition (IBSD) system. A detailed description of the system has been published elsewhere [24]. The a-Si film thickness was in the range of 70–140 nm; determined by FESEM (JEOL 6700) studies. The gold thin film, as the catalytic layer, was next deposited by dc sputtering (Hitachi E101) with a 20 mA sputtering current and deposition periods ranging from 15 to 300 s. The deposition rate was estimated as 4 nm min⁻¹, as determined by thickness measurements of those films, deposited for different durations, by FESEM. Finally, we put the Au/a-Si/c-Si sample into a quartz tube furnace for thermal annealing at 1030 °C in a nitrogen gas (99.9999 %) ambient for ~10–30 min. The gas flow rate was maintained at 50 sccm and the pressure of the chamber was maintained at 1 atm.

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Bicontinuous Cubic Block Copolymer Photonic Crystals**

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Photonic crystals are being aggressively pursued for their potential to revolutionize optical communication systems and optical computation.^[1] The necessary fabrication of large area, well ordered photonic crystals in three dimensions for these applications has proved to be a difficult technological hurdle. Layer-by-layer fabrication,^[2] holography,^[3] and single step deposition^[4] have been used to fabricate high-quality photonic crystals. Researchers have also turned to self-assembly as an approach for creating the large-area ordered arrays in three dimensions that constitute a photonic material.^[5–7] We employ a self-assembling block copolymer system to form the double gyroid (DG) morphology at an appropriate length scale to interact with visible light. The optical properties of the poly(styrene-*b*-isoprene) diblock photonic material are compared with expected reflectivity. The block copolymer is subjected to a UV treatment to remove the isoprene component as a method of modifying the optical properties. This process can serve as the basis for fabricating a three dimensional photonic crystal with a complete photonic bandgap at visible wavelengths from a block copolymer template.

Block copolymers (BCPs) offer an alternative means to produce self-assembled photonic crystals. BCPs are known to form ordered microstructures due to the microphase separation of their constituent polymer blocks. In poly(styrene-*b*-isoprene), also known as an SI diblock, for example, the positive enthalpy of mixing between the styrene block and the isoprene block leads to segregation of the respective blocks into microdomains with a sharp interface (~4 nm width) between the component materials. The relative composition of the copolymer determines the periodic morphology, and the molecular weight determines the repeat spacing of the microdomain structure. The potential of BCPs for producing large-area well-ordered photonic crystals has already been demonstrated for symmetric polymers forming simple one dimensionally periodic systems.^[8]

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