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AuPd CATALYTIC NANOPARTICLE SIZE EFFECT ON THE FORMATION OF AMORPHOUS SILICON NANOWIRES*

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Amorphous silicon (a-Si) nanowires have been prepared on SiO_2/Si substrates by AuPd nanoparticles / silane reaction method. Field-emission scanning electron microscopy and transmission electron microscopy were used to characterize the samples. The typical a-Si nanowires we obtained are of a uniform diameter about 20 nm and length up to several micrometers. The growth mechanism of the nanowires seems to be the vapor-liquid-solid mechanism. The catalytic particle size effect on the formation of the nanowires and the cause of forming amorphous state Si nanowires are discussed.

Keywords: chemical vapor deposition, nanowires, nanoparticles
PACC: 6855, 8115H, 6140

I. INTRODUCTION

Nano-materials are attracting much attention because of the electronic, magnetic, optical, biological, and chemical characteristics that are not obtained with conventional materials. Among these nano-materials, one-dimensional materials, such as nanotubes,[1−4] semiconductor nanowires[5−8] and metal nanowires[9] have attracted much interest because they offer fundamental scientific opportunities for investigating the influence of size and shape on optical, electronic, and mechanical properties. For silicon, it is promising to emit visible light by reducing its dimension, in which the motion of carriers is confined, causing a possible transformation of the electronic band structure from indirect band gap to direct band gap. This has stimulated intensive in terest in preparing silicon nanowires. To date, crystalline state silicon nanowires have been successfully prepared through different ways, such as excimer laser ablation,[10,11] vapor-liquid-solid (VLS) Au/Si reaction,[12,13] stress limited oxidation.[14,15] However, all of these previous studies have got crystalline silicon nanowires with a thin oxide cover layer.

In this paper, we report a method to synthesize large-scale amorphous silicon nanowires by thermal chemical vapor deposition method. The effect of the catalytic particle size on the formation of nanowires is discussed. And the cause of forming the amorphous state nanowires are also taken into account.

II. EXPERIMENTAL

We used n-type Si (100) wafers with an oxide layer about 60 nm in thickness as the substrate. Before the growth, the surfaces of the substrates were cleaned by ultrasonically stirring for 30 min the acetone solution in which the substrates were dipped. Then the substrates were deposited with AuPd alloy about 0.5 and 1 min, respectively, by using E1001 film deposition system. Next the substrates were placed in a quartz boat, which was introduced in the reaction chamber of a tube furnace that has been described elsewhere.[16] The reaction temperature was controlled at about 800°C. During the growth process of silicon nanowires, the mixture of $5cm^3$/min silane and $100cm^3$/min He was introduced into a vacuum chamber. The total pressure was kept at about 2×10^4 Pa. The typical deposition time was 2 h.

The as-grown silicon nanowires were examined by a scanning electron microscope (SEM; S-4200, Hitachi), and energy-dispersive X-ray (EDX) spectra were recorded by SiLi detector attached to the SEM. A transmission electron microscope (TEM; JEOL JEM-200CX at 200kV) was used to characterize the structures of silicon nanowires.

III. RESULTS AND DISCUSSION

Figure 1 shows the low-magnification SEM images of the silicon nanowires on the substrate, which was

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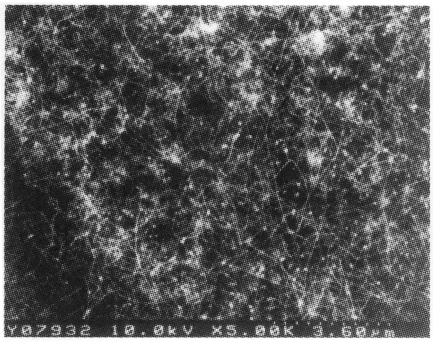


Fig.1. SEM images of a-Si nanowires grown on the substrate with 0.5 min deposition of AuPd alloy. A large amount of a-Si nanowires is formed on the surface of SiO_2/Si substrates.

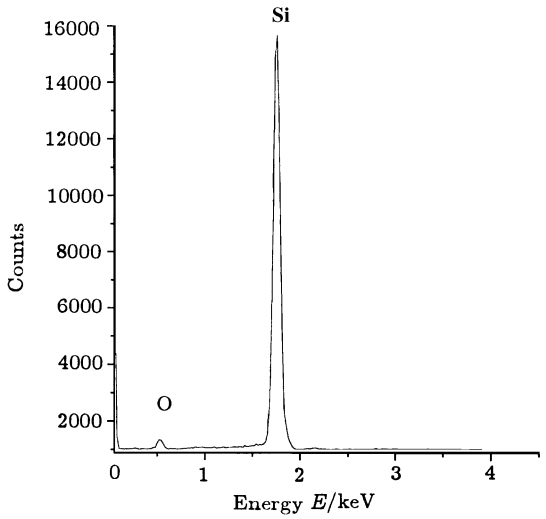


Fig.2. EDX spectra of a-Si nanowires, showing the nanowires are composed of silicon and a small amount of oxygen.

deposited with AuPd alloy for 0.5 min. From Fig.1, we can see that a large amount of random-distributed nanowires are formed, which are of a uniform diameter of about 20 nm and of lengths up to several micrometers. At the same time, we can also find nanoparticles on the end of a nanowire. The EDX spectra taken from these nanoparticles showed the presence of gold, palladium, oxygen and silicon (0.6, 0.3, 26.6 and 72.5at%, respectively). Figure 2 shows the EDX spectra of the nanowires. Compared with the nanoparticles, the nanowires are composed of silicon and a small amount of oxygen, indicating that no catalytic elements exist in the nanowires.

High-resolution TEM was employed to detect the structure of the nanowires in detail. From Fig.3, we can see that the nanowires are of a uniform diameter

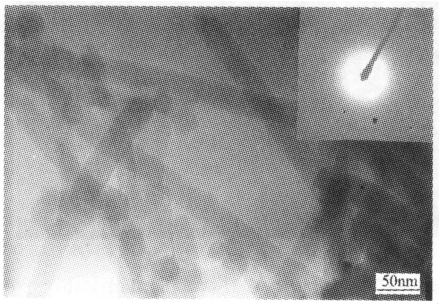


Fig.3. High-resolution TEM observations of a-Si nanowires, The inset is the selected-area electron diffraction of a-Si nanowires.

of about 20 nm and have smooth surfaces. Furthermore, TEM reveals that the nanowires are in a perfect amorphous state. The selected-area electron diffraction of silicon nanowires shown in the inset of Fig.3 confirms this point.

We think that the growth mechanism in our experiment may be the vapor-liquid-solid (VLS) one, which has been put forward by Wagner.[17] This growth mechanism requires the formation of silicide/metal liquid drops first. When we annealed our substrate coated by AuPd thin film in the growth system in vacuum, we found the silicide/AuPd nanoparticles formed on the surface of the substrate. Figures 4 and 5 show the SEM images of annealed substrates after 0.5 and 1 min deposition of AuPd alloy, respectively. From Figs.4 and 5, we can see that the distributions of the nanoparticles are uniform. The average size of the nanoparticles after 0.5 min deposition of AuPd alloy is about 30 nm, which is smaller than that of the nanoparticles (average size about 50 nm) after 1 min deposition. The silane introduced into the reaction chamber can decompose into Si and H_2 on the surface of the nanoparticles. When the concentration of Si absorbed in the nanoparticles is supersaturated, the Si atoms will diffuse from one side of the particle to the opposite side, giving rise to the formation of silicon nanowires directly on the surface of catalytic nanoparticles. From Fig.6, we can see that large-scale amorphous silicon nanowires are obtained. The diameter of the nanowires is about 20 nm. But we only get a small amount of nanowires with diameter about 40 nm by using the substrate after 1 min AuPd deposition (see Fig.7).

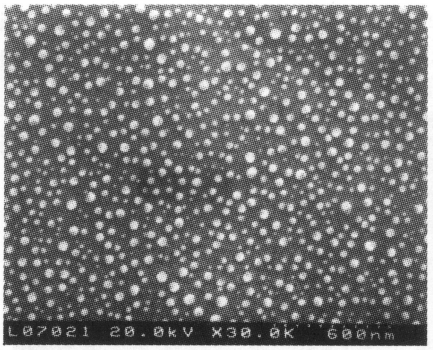


Fig.4. SEM image of the annealed substrates after 0.5 min deposition of AuPd alloy. The Si/AuPd nanocomposite particles with average sizes of 30 nm are distributed evenly on the surface of silicon wafer.

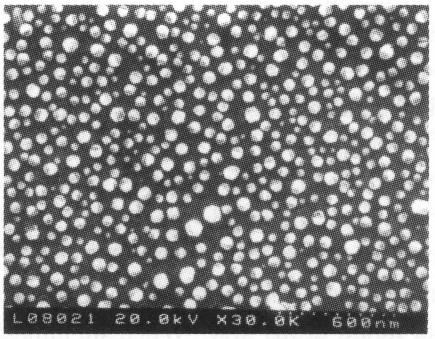


Fig.5. SEM image of the annealed substrates after 1 min deposition of AuPd alloy. The Si/AuPd nanocomposite particles with average sizes of 50 nm are distributed evenly on the surface of silicon wafer.

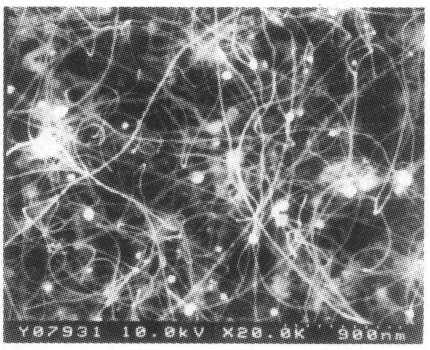


Fig.6. SEM image of the a-Si nanowires on the substrates after 0.5 min AuPd deposition; the diameter of the a-Si nanowires is about 20 nm.

Different from other work on silicon nanowires by VLS methods,[12,13] we have obtained amorphous state silicon nanowires instead of crystalline state nanowires. High silane partial pressure (about 2×10^3 Pa) and higher growth temperature (up to 800°C) were employed besides different catalytic particles in our experiments. According to Langmuir-Hinshelwood model,[18] we can get decomposition rate of silane gas given by the following equations:

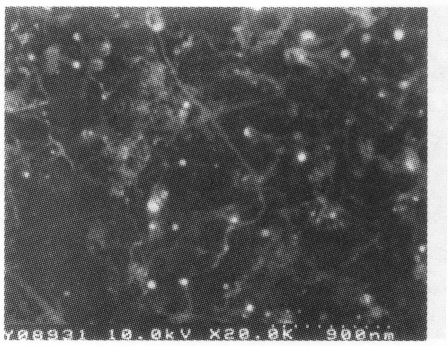


Fig.7. SEM image of the a-Si nanowires on the substrates after 1 min AuPd deposition; the diameter of the a-Si nanowires is about 40 nm.

$$\gamma = kP_{\text{silane}}, \tag{1}$$

$$k = A\exp[(\gamma - E_s)/RT]. \tag{2}$$

Here, γ is the decomposition rate of the silane gas; k is a constant of decomposition rate; E_s is the reactive excitation energy of vapor/liquid (V/L) interface; λ is the heat of chemical adsorption. From the above equations, we can see that the decomposition rate of silane will increase with the increase of silane partial pressure and growth temperature. Bootsman[19] reported that silane decomposition at the V/L interface is the rate-limiting step in the wire growth from silane. That is to say, the diffusion process of Si atoms in the liquid droplet is faster than the silane decomposition process. And once Si atoms are absorbed at the V/L interface, they will diffuse rapidly to the liquid/solid (L/S) interface to participate the nanowires growth. As a result, the increased rate of the nanowires growth, which tends to occur at high pressure and high temperature, leads to growth defects. That is why we got amorphous state silicon nanowires in the end under our experimental condition.

Under the same growth condition, such as the same growth temperature and the same working pressure, the yields of the amorphous silicon nanowires are different according to the different size of catalytic particles employed. So we can say that the decomposition process of silane is not the sole factor affecting the growth process of the nanowires. We use the following concentration distribution model for the V/L and L/S interfaces to describe the situation. Let C_{g} be the Si atom concentration in the gas atmosphere. C_{I} and C_{II} correspond to Si atom concentrations on V/L and

L/S interfaces respectively. $C_{\rm II}$ is equal to $C_{\rm e}$, which is the solubility of Si in AuPd alloy at the growth temperature (about 0.01at%[20]). In order to simplify the question, we suppose the catalytic nanoparticles in our experiment are ideal spherical droplets with a diameter R and surface tension σ. The inner pressure in the liquid droplet, which is caused by Si atom concentration distribution, will balance with the surface tension and the partial pressure of Si atoms outside. We can describe this point by the following equations:

$$k_{\rm B}T(C_{\rm I}+C_{\rm II})/2 = 2\sigma/R + C_{\rm g}k_{\rm B}T,$$

$$\begin{aligned} &k_{\rm B}T(C_{\rm I}-C_{\rm e}) = 4\sigma/R + 2k_{\rm B}T(C_{\rm g}-C_{\rm e}),\\ &\Delta C = (C_{\rm I}-C_{\rm e}), \end{aligned} \tag{3}$$

$$J_{\rm Si} \propto -D_{\rm Si}\Delta C/2R, \quad D_{\rm Si} \propto \exp(-E/k_{\rm B}T), \tag{4}$$

$J_{\rm Si}$ is the diffusion flux of Si atoms in the liquid droplet. $D_{\rm Si}$ is the diffusion coefficient of Si atoms. $k_{\rm B}$ is Boltzmann constant. From Eqs. (3) and (4), we can get the following result:

$$J_{\rm Si} \propto -D_{\rm Si}[2\sigma/k_{\rm B}TR^2 + (C_{\rm g}-C_{\rm e})/R]. \tag{5}$$

We can get that the diffusion flux $J_{\rm Si}$ is inversely proportional to R^2. As the catalytic particle size R increases, $J_{\rm Si}$ will reduce. From Eq.(5), we can find that $J_{\rm Si}$ will be zero as $R \to \infty$. That is to say, the AuPd alloy film on the silicon wafer will make the growth stop. So with increasing catalytic particle size the diffusion process will retard in the formation of the nanowires. This fact cannot be ignored when $J_{\rm Si}$ is up to the same magnitude of decomposition rate γ. The nanowire growth is actually the combinative result of the two processes. In our work, we find that when the size of the catalytic particles is up to 50 nm, the diffusion process in the liquid droplets, which affects seriously on the formation of the nanowires, cannot be ignored. That is why we got little of the nanowires with 50 nm catalytic particles and more with 20 nm catalytic particles under the same growth conditions.

IV. CONCLUSIONS

Large-scale amorphous silicon nanowires have been obtained by AuPd nanoparticles / silane reaction on SiO_2/Si substrates. The average diameter of the amorphous silicon nanowires is about 20 nm and the length of them is up to several micrometers. The growth mechanism of amorphous silicon nanowires is mostly the VLS one. High growth temperature and high pressure play a positive role in forming amorphous states. With the increase of the catalytic particle size, the diffusion process of Si atoms in the liquid droplet will be notable. The diffusion process in the liquid droplets cannot be ignored when the AuPd catalytic particles are up to 50 nm. It is possible that these amorphous silicon nanowires may offer more opportunities for both fundamental researches and technological applications.

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