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Vapor-liquid-solid growth of Ge nanowhiskers enhanced by high-temperature glancing angle deposition

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We have demonstrated that the vapor-liquid-solid (VLS) growth of Ge nanowhiskers is significantly enhanced by high-temperature glancing angle deposition (HT-GLAD). At the substrate temperature of 420 °C, the Ge nanowhiskers grow on the sample deposited at the deposition angle of $\alpha = 85^\circ$, whereas no long nanowhisker grows on the samples deposited at $\alpha \leq 73^\circ$. The kinetic growth model that takes into account the directional incidence of the vapor flux agrees with the experimental results and suggests that the atoms deposited on the side surface of the nanowhiskers play an essential role in the HT-GLAD assisted VLS growth. Supplying the atoms on the side surface of the nanowhiskers is expected to accelerate the growth of the nanowhiskers in any vapor phase growth methods, such as molecular beam epitaxy and chemical vapor deposition. © 2011 American Institute of Physics. [doi:10.1063/1.3664777]

Nanowires or nanowhiskers of various materials are attracting considerable attention in recent times because of their useful properties for applications in nanoelectronics, nanophotonics, and sensors. Although nanowire devices have been fabricated by top-down processes until now, bottom-up processes are expected to enable cost-effective and well-controlled fabrication of such devices. It is well known that semiconductor nanowhiskers of materials such as Si and Ge are grown by the vapor-liquid-solid (VLS) growth technique using Au particles as catalysts. The source materials are usually transported onto the substrate with Au catalyst in low vacuum or at atmospheric pressure using carrier gases or reactive gases. This results in the efficient growth of many long nanowhiskers. On the other hand, electron beam (EB) evaporation or molecular beam epitaxy (MBE) process in ultrahigh vacuum results in the growth of only short nanowhiskers out of the thick underlayer. Thus, it is implied that the growth efficiency of the processes carried out in low vacuum is much higher than that of the processes carried out in high vacuum.

On the other hand, we have found that nanowhiskers of various metals are grown when the metals are deposited on a substrate heated to a temperature higher than 1/3 of the melting point of the metals at a deposition angle typically higher than 80°. This deposition process is termed as high-temperature glancing angle deposition (HT-GLAD). Deposition at a glancing angle is crucial for the growth of metal nanowhiskers. Although the growth mechanisms of the nanowhiskers have not yet been completely understood, the vapor supply on the side surface of the nanowhiskers is considered to play an important role. From this point of view, HT-GLAD is an ultimate condition to supply atoms on the side surface of nanowhiskers.

Therefore, we conducted HT-GLAD assisted VLS growth method for growing Ge nanowhiskers and attempted to determine the influence of the vapor supply on the side surface of nanowhiskers and enhance the efficiency of the VLS growth. The knowledge obtained from this investigation will be useful for the enhancement of the growth efficiency and the development of processes to integrate nanowhiskers into microelectronic devices.

All deposition processes were performed in an EB evaporation apparatus specially designed for HT-GLAD. Prior to HT-GLAD of Ge, Au was deposited on the Si substrate up to the average thicknesses of 0, 1, 5, and 10 nm. After deposition, the sample was heated to 420 °C by irradiation from a halogen lamp to induce the formation of Au particles on the substrate. Ge was deposited on the substrate with the Au catalyst at a substrate temperature of 420 °C. The average thickness of the deposited Ge was 23 nm. Deposition angle $\alpha$, which is defined as the angle between the substrate normal and the incident direction of the deposition flux, was set between 58° and 85°. During the deposition of Ge, the deposition rate was maintained constant at 0.03–0.05 nm/s, and the pressure was less than 8 × 10⁻⁴ Pa. The samples were characterized using a transmission electron microscope (TEM) and a scanning electron microscope (SEM).

Figure 1(a) shows an SEM image of a cross section of a Ge film deposited directly (i.e., without Au catalyst) on the Si substrate at $\alpha = 85^\circ$. No growth of Ge nanowhiskers was observed at the substrate temperature of 420 °C. This is in contrast to the self-catalyzed growth of metal nanowhiskers as reported in our previous paper. Thus, we conclude that a catalyst is required for the growth of Ge nanowhiskers even when the HT-GLAD method is employed.

Figure 1(b) shows the SEM image of the cross section of the sample deposited on a 5-nm-thick Au catalyst layer at $\alpha = 85^\circ$. Many nanowhiskers can be clearly observed in this image. Growth of nanowhiskers was observed on all the samples deposited on the Au catalyst substrate at $\alpha = 85^\circ$, although the number and length of Ge nanowhiskers found on the samples deposited on 1-nm- and 10-nm-thick Au catalyst are 1/20 and 1/2, respectively, of those on 5-nm-thick Au catalyst. The TEM observations revealed that these nanowhiskers have a unique structure.
nanowhiskers have the particle of the Au catalyst. This suggests that the Ge nanowhiskers in Fig. 1(b) were grown by the VLS growth mechanism, although further analysis is required to determine the detailed structure of the Ge nanowhiskers.

The number and length of the Ge nanowhiskers strongly depend on the deposition angle, as shown in Figs. 1(b)–1(d). The samples deposited at \( \alpha = 85^\circ \) contain many nanowhiskers with lengths of up to 1500 nm. In contrast, fewer and shorter (with length up to 300 nm) Ge nanowhiskers were observed in the case of samples deposited at \( \alpha = 73^\circ \), and no Ge nanowhisker could be observed in the case of samples deposited at \( \alpha = 58^\circ \). HT-GLAD enabled the growth of Ge nanowhiskers even under the conditions that prohibited growth by the ordinary vacuum evaporation method involving deposition of Ge normal to the surface. Moreover, as the amount of the deposited Ge is extremely small (the average thickness of the deposited Ge is only 23 nm), we can conclude that HT-GLAD significantly enhances nanowhisker growth.

To understand the impact of HT-GLAD on the VLS growth, we analyzed the growth of the nanowhiskers based on the model developed by Dubrovskii \(^8\) et al. We slightly modified their VLS model to take into account the directional incidence of the vapor flux in the case of HT-GLAD. Figure 2 presents the growth model. We assume that a nanowhisker with a length \( L \) and a constant radius \( R \) grows in the direction normal to the substrate surface. At the top of the nanowhisker, there is a hemispherical sink of adatoms, which corresponds to the Au catalyst. The well-collimated Ge vapor is incident at an angle \( \alpha \) with a uniform intensity \( J = V/\Omega \) (\( V \) is the rate of deposition, and \( \Omega \) is the atomic volume in the solid state). The lifetimes of adatoms on the substrate surface and side surface are \( \tau_s \) and \( \tau_f \), respectively. Under the steady-state condition of growth, the concentration of adatoms on the substrate surface, \( n_s \), and on the side surface of the nanowhiskers, \( n_f \), obeys the following diffusion equations:

\[
D_s \Delta n_s + \frac{J \cos \alpha}{\pi} - \frac{n_s}{\tau_s} = 0, \tag{1}
\]

\[
D_f \frac{d^2 n_f}{dz^2} + \frac{J \sin \alpha}{\pi} - \frac{n_f}{\tau_f} = 0, \tag{2}
\]

where \( D_s \) and \( D_f \) are the diffusion coefficients of adatoms on the substrate surface and the side surface of the nanowhiskers, respectively, and the diffusion length on the side surface of the nanowhiskers is \( k_f = \sqrt{D_f \tau_f} \gg R \). Solving these equations under the appropriate boundary conditions, for example,

\[
\lim_{r \to \infty} \frac{dn_s}{dr} = 0, \tag{3}
\]

\[
D_s \frac{dn_s}{dr} \bigg|_{r=R} = D_f \frac{dn_f}{dz} \bigg|_{z=0}, \tag{4}
\]

we obtain the diffusion flux

\[
j_{\text{diff}}(z) = -D_f \cdot 2\pi R \frac{dn_f}{dz}. \tag{5}
\]

The length of the nanowhiskers is calculated by the following rate equation:

\[
\frac{\pi R^2 dL}{\Omega \frac{d}{dt}} = \frac{V \delta - V_s}{\Omega} \pi R^2 - \frac{4\pi R^2 \omega}{2 \Omega \tau_f} + j_{\text{diff}}(L), \tag{6}
\]
where $\pi R^2 \delta = \pi R^2 (1 + \cos \alpha)/2$ is the projected area of the hemispherical catalyst in the incident direction of the vapor flux, $V_s = V \cos \alpha$ is the growth rate of the underlayer, and $\omega$ is the spacing between atomic layers. The first term on the right hand side of Eq. (6) is the contribution to the growth of the nanowhiskers from the direct incidence of the vapor on the top of whiskers and from the growth of the underlayer. The second term is the effect of re-evaporation of the adatoms from the top of the nanowhiskers. These two terms are insignificant when HT-GLAD is used. We calculate the length of the nanowhiskers numerically at time $t = 23 \, \text{nm}/V \cos \alpha$.

Figure 3(a) indicates the relation between the deposition angle and the length of the nanowhiskers for various values of the diffusion length on the substrate surface $\lambda_s = \sqrt{D_s \tau_s}$, where we assume $R = 25 \, \text{nm}$ and $\lambda_f = 10 \, \mu \text{m}$. Generally, longer nanowhiskers grow at higher deposition angles. The long diffusion length of $\lambda_s$ (100 nm), which is required for the conventional VLS growth of semiconductors, enables the growth of long nanowhiskers even at low deposition angles. However, if the vapor is deposited at a glancing angle, whiskers can grow even with very short diffusion lengths. This is consistent with the experimental observation that Ge nanowhiskers can grow only at a high deposition angle. In fact, some dust particles, which were present on the substrate surface prior to the deposition of Ge, cast a clear shadow on the surface. Therefore, $\lambda_s$ of the Ge adatoms deposited on the substrate at 420°C is probably as short as a few tens of nanometers.

On the other hand, $\lambda_f$ does influence the length of the nanowhiskers grown at high deposition angles, as shown in Fig. 3(b), where $R = 25 \, \text{nm}$ and $\lambda_f = 10 \, \text{nm}$. To reproduce nanowhiskers longer than 1 $\mu \text{m}$ at $\alpha = 85^\circ$, a long diffusion length of $\lambda_f \geq 1 \, \mu \text{m}$ is required. Thus, we can conclude that the adsorbates supplied on the side surface of the nanowhiskers play an essential role in the growth of the Ge nanowhiskers. In other words, supplying the adsorbates on the side surface of the nanowhiskers is expected to accelerate the growth of the nanowhiskers in any vapor phase growth technique such as MBE and CVD.

In summary, we demonstrated the HT-GLAD of Ge on Au island films. We observed the growth of Ge nanowhiskers when the deposition was performed at a substrate temperature of 420°C and at a deposition angle of 85°. The kinetic growth model that takes into account the directional incidence of the vapor flux agrees with the experimental results. The VLS growth of Ge nanowhiskers is enhanced significantly by HT-GLAD owing to the effective supply of the vapor flux on the side surface of the growing nanowhiskers.

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