The influence of B_2H_6 on the growth of silicon nanowire

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Abstract

The un-doped and boron-doped silicon nanowires (SiNWs) were grown via vapor–liquid–solid (VLS) mechanism by low pressure chemical deposition (LPCVD). The diameters of un-doped and boron-doped SiNWs varied from 18.5 to 75.3 nm and 26.6 to 66.1 nm, respectively. The critical growth temperature of boron-doped SiNWs is 10°C lower than that of un-doped ones and the diameters of the boron-doped SiNWs is always larger than that of the un-doped ones under different growth temperatures. This is because that the introduction of diborane enhanced the dissociation of SiH_4 which determines the growth process of SiNW. A growth process of silicon nanowire is proposed to describe the influence of B_2H_6 .

Introduction

In recent years, silicon nanowires (SiNWs) are one of the focuses of intensive research and have been demonstrated to function as simple field effect transistor (FET), p-n junctions, bipolar transistors, biological and chemical sensors, and other devices (Westwater et al., 1997; Morales & Lieber, 1998; Zhang et al., 1998, 1999, 2002; Holmes et al., 2000; Qi et al., 2003). All these devices are fabricated with either P or N-type silicon nanowires and by incorporating diborane (B_2H_6) or phosphine (PH_3) as dopant gas, silicon nanowire can be doped either P or N-type, respectively. Since the as grown silicon nanowire is naturally P-type rather than the as grown N-type silicon wafer, it is easier to fabricate P-type SiNWs than N-type. In our works the SiNWs were grown via vapor–liquid–solid mechanism (VLS) (Frank, 1949; Webb & Forgeng, 1957; Wagner & Ellis, 1963, 1964, 1965; Wagner et al., 1964; Givargizov, 1975) by using Au nanoparticles with the well-controlled size as the catalyst.

Silane and diborane were used as silicon source and p-type dopant gas.

Experiments

Silicon wafers were used as the template in this study. A 200 nm thick buffered SiO_2 were deposited on the substrate by low pressure chemical vapor deposition (LPCVD) method. Then the silicon surface was activated by poly-L-lysine from BIOCHROM AG for better adhesion between Au nanoparticles and silicon oxide surface. The Au nanoparticles in colloid solution purchased from BB International were dripped by micro-pipette on the silicon oxide surface without spinning. The quantity is about 50 $\mu l/cm^2$. The VLS growth experiments were then carried out in an isothermal 8-inch diameter cylindrical quartz tube reactor. The system was degassed under vacuum and purged with N_2 and then heated to the growth temperature. The growth temperature is chosen initially at 420°C and raised 10°C a step to look for

the temperature at which the SiNWs started to grow. A 10% diluted SiH₄ was then introduced into the tube to initiate the SiNWs growth. The flow rate of SiH₄ was 400 sccm and the total pressure was kept at 30 Torr during the growth. As for the growth of boron-doped SiNWs the flow rate of SiH₄ and B₂H₆ was 400 and 50 sccm, respectively, and the total pressure was also kept at 30 Torr. Planar view images of SiNWs after VLS growth were performed with a 5 kV LEO 1530 scanning electron microscope (SEM).

Results and discussion

Un-doped and boron-doped SiNWs were successfully grown via VLS mechanism starting at 450°C and 440°C, respectively. The SEM pictures of un-doped SiNWs grown at 440°C and 450°C using 20-nm diameter Au nanoparticles as the catalyst are shown in Figure 1(a) and (b), respectively. The TEM picture showing the lattice image of SiNW near the Au nanoparticle of Figure 1(b) is displayed in Figure 1(c). Figure 1(d) and (e) show the boron-doped SiNWs grown at 430°C and 440°C, respectively. It was found that the critical temperature of boron-doped SiNWs is lower than that of un-doped SiNWs. The VLS mechanism is inferred that the SiH₄ gas adsorbed at the surface of Au nanoparticles. Then the dehydrogenation of SiH₄ occurred at the surface of the Au nanoparticles. The dissociated Si atoms dissolved into the Au nanoparticles to reach supersaturation and precipitated to form SiNWs at critical temperature. Hence the influence of the introduction of B₂H₆ during SiNWs growth can be explained from the view point of dehydrogenation of SiH₄. The reaction mechanism for the adsorption of SiH₄ and the subsequent elimination of hydrogen is (Hitchman & Jensen, 1993)

Here *s* refers to vacant sites and underline designates the adsorbed species. Below 500°C the growth rate is limited by reaction (a) and the introduction of B₂H₆ will enhance reaction (a). Since at lower temperature, the decomposition of B₂H₆ into BH₃ is more probable than dissociation of SiH₄ because of lower dissociation energy of B₂H₆ (Perrin et al., 1989; Yang et al., 1989; Rablen & Hartwig, 1996; Rablen 1997). Thus during the growth of boron-doped SiNWs the B₂H₆ first dissociated into BH₃ with the reaction formula: B₂H_{6(g)} → 2BH_{3(g)}. Then SiH₄ and BH₃ combine to form a SiH₄–BH₃ complex in the CVD mechanism, with the SiH₄ behaving as an electron donor and BH₃ as an electron acceptor. It was indicated that the complex dimer SiH₄–BH₃ is easily dissociate into SiH₃ and BH₄ radicals (Hu et al., 2002). Hence the reaction (a) is enhanced. Thus the critical growth temperature of boron-doped SiNWs becomes lower than that of un-doped SiNWs.

Another remarkable feature could be obtained by observing the morphology of un-doped and boron-doped SiNWs grown at the higher growth temperature. Figure 2 shows the dependence of the diameter of SiNWs grown with 20 nm Au nanoparticles as the catalyst on the deposition temperature, respectively. It is clear that the diameter of p-doped SiNWs becomes thicker than those of undoped SiNWs due to their faster lateral growth rate at the same deposition temperature. This result could also explain the fact that the critical temperature of boron-doped SiNWs is lower than that of un-doped SiNWs. The SEM pictures of 490°C and 510°C grown un-doped and 550°C and 600°C grown boron-doped SiNWs are shown in Figure 3(a) and (b), respectively. The density of un-doped SiNWs dropped rapidly at 510°C because the SiH₄ molecules were dissociated in the gas, and the Si atom arriving at the surface of the Au nanoparticles were too fast resulting in the deposition of amorphous-Si on the surface of Au nanoparticles which retarded the growth of SiNWs. This phenomenon is also observed in boron-doped case. But the temperature that the density of boron-doped SiNWs decreased significantly is much higher, i.e., ~600°C. This can be also explained by the dissociation rate of SiH₄. The B₂H₆ enhanced the dissociation of SiH₄ leads to the faster growth rate of boron-doped SiNWs. Thus the dissociation rate of SiH₄ in the gas must be further raised to retard the growth of

Figure 1. The SEM pictures of un-doped SiNWs grown at (a) 440°C and (b) 450°C. (c) The TEM picture of sample shown in (b). The SEM picture of boron-doped SiNWs grown at (d) 430°C and (e) 440°C using 20 nm Au nanoparticles as the catalyst.

boron-doped SiNWs. Although the B_2H_6 enhanced the dissociation of SiH_4 whether in the gas or on the Au nanoparticles surface, it seems that the change of SiH_4 dissociation rate on the Au nanoparticles surface is more significant than that in the gas at lower temperature ($<550^\circ\text{C}$). However the dissociation of SiH_4 in the gas becomes dominant at higher temperature, i.e. $>550^\circ\text{C}$. Hence the amorphous-Si are formed and deposited to suppress boron-doped SiNWs growth. HRTEM

images were shown as the evidence to illustrate the growth phenomenon in Figure 4(a)–(c). The Au catalyst used is 20 nm and the growth temperature of boron-doped SiNWs is 450°C , 470°C and 490°C , respectively. The inset shows the electron diffraction patterns of the SiNWs, respectively. It is clear from Figure 2 that the diameter of SiNWs doesn't change with the rise of process temperature until 480°C . And the HRTEM image and electron diffraction patterns in Figure 4(c) show

Figure 2. The diameter of un-doped and P-doped SiNWs grown with 20 nm Au nanoparticles as the catalyst versus deposition temperature.

that there exists an amorphous shell outside the single crystal SiNW. Once the growth temperature exceeds 480°C, the B_2H_6 assisted dissociation process will start not only on the Au surface but also on other place and lead to the coating of

SiNWs. The deposition or coating rate of amorphous-Si will increase the diameter of SiNWs as the process temperature increase and result in the rapid slope change in Figure 2. The growth windows which are defined to be the temperature range that the un-doped and boron-doped SiNWs kept its diameter the same as Au catalyst are determined and listed in Table 1. For the un-doped SiNWs, the growth process starts at 450°C and rapidly increases lateral growth after 490°C. For the boron-doped SiNWs, the growth process starts at 440°C and rapidly increases lateral growth after 480°C. And the stopping growth of

Table 1. The growth window of un-doped and boron-doped SiNWs using 20 nm Au nanoparticles as the catalyst

	Un-doped SiNWs	Boron-doped SiNWs
Start to grow (°C)	450	440
Start to coat (°C)	490	480
Stop growing (°C)	510	600

Figure 3. The SEM pictures of (a) un-doped SiNWs grown at 490°C and 510°C, (b) boron-doped SiNWs grown at 550°C and 600°C with 20 nm Au nanoparticles as the catalyst.

Figure 4. The TEM pictures of boron-doped SiNWs grown at (a) 450°C, (b) 470°C and (c) 490°C with 20 nm Au nanoparticles as the catalyst.

un-doped and boron-doped SiNWs are also shown in Table 1 as 510°C and 600°C, respectively.

Conclusions

In conclusion, the enhancement of dissociation of SiH_4 under the introduction of B_2H_6 is reasonably explained. This effect is due to the reaction of transient complex product $\text{SiH}_4\text{-BH}_3$ and result in the 10°C process temperature shift. The growth windows of un-doped and boron-doped SiNWs were also found. The growth window for un-doped SiNWs is start from 450°C to 490°C and for boron-doped SiNWs is start from 440°C to 480°C, respectively. The cause for rapidly increase in diameter is due to the increased dissociation rate of SiH_4 in the air, which will deposit and coat on the surface of SiNWs and further increase the diameter. For the boron-doped SiNWs, the growing process

end up at 600°C which is 90°C higher than the un-doped SiNWs which is due to the asymmetrical increment of SiH_4 dissociation rate on Au catalyst surface and in the air, respectively.

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