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Wirelike Growth of Si on an Au/Si(111) Substrate by Gas Source Molecular Beam Epitaxy

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Ultrafine Si nanowires are grown on an Au/Si(111) substrate using gas source molecular beam epitaxy. These Si wires with cross-sectional dimensions between 50 nm and 2 µm grow mainly with a growth axis parallel to the <111> direction. The growth rate of nanowires is independent of their diameters, i.e., nanowires with different diameters have the same growth rate. From the dependence of source gas concentration on the growth rate we conclude that this independence is a fundamental one even when gas pressure ranges as high as 1×10^{-4} Torr. This method provides a possible alternative means for fabricating ultrafine silicon quantum wires.

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Recently, Si-based nanostructures such as Si quasi-one-dimensional wires have attracted much attention in the semiconductor science and technology field due to their importance in novel optoelectronic and thermoelectric properties, and potential device applications. Most of experimental attempts to fabricate Si nanowires have been reported by using nanofabrication definition or selective growth techniques on patterned substrates.[1-3] The advantage of such Si nanostructures is the accurate control of wire position. An alternative fabrication method is to generate *nanowhiskers* on an Si substrate by so-called vapor-liquid-solid (VLS) growth mechanism.[4,5] In this process, a small amount of a liquid-forming material such as Au, Pt, or Ga is used to form a liquid alloy droplet, which acts as a preferred site for Si from the vapor. As the growth progresses, the droplet is separated from the substrate and rides on the top of the growing whiskers. Such whiskers have been suggested as novel nanostructures for applications in vacuum microelectronics.[6] Moreover, if the control of ultrafine wirelike growth becomes possible, it would be useful to apply these wires to the fabrication of Si quantum wires and related quantum function devices.[6,7]

Conventional VLS growth of Si nanowires is totally based on a chemical vapor deposition (CVD) technique. For those wires grown by CVD, it has been demonstrated that the growth rate is quadratically dependent on their diameters.[7,8] Such wires with different heights usually are not uniform in both fundamental studies and practical applications. Alternate epitaxial growth techniques such as gas source molecular beam epitaxy (GS-MBE) are progressively emerging as a unique tool for providing improved control of growth. Thus there is an essential need to grow ultrafine wirelike semiconductor crystals by GS-MBE since it now allows thickness control down to the monolayer level.

In this paper, we report on ultrafine Si wire growth on Au/Si(111) substrates using GS-MBE. The results observed here are illustrated using scanning electron microscopy (SEM). The Si wires with diameters ranging from as small as 50 nm to as large as 2 µm grow mainly with a growth axis parallel to the <111> direction. Different from previous reports,[7,8] our results show that the growth rate is independent of their diameters, i.e., nanowires with different diameters have the same growth rate. The dependence of the growth rate on the source gas concentration is also investigated.

The starting materials are n-type Si(111) wafers with resistivity of 3-5 Ω cm. After the standard Shiraki cleaning process,[9] a 16 nm Au film is deposited on the substrates. Prior to growth, the substrates are heated at 900°C in a GS-MBE chamber for 20 min without any source gases present in order to form Au/Si eutectic and remove any surface oxide. Growth of the Si wires is achieved at 700°C by the introduction of 4 standard cubic centimeters per minute (sccm) Si_2H_6. The base pressure in the chamber is in the range of 10^{-10} Torr, which is very low compared with conventional CVD growth.

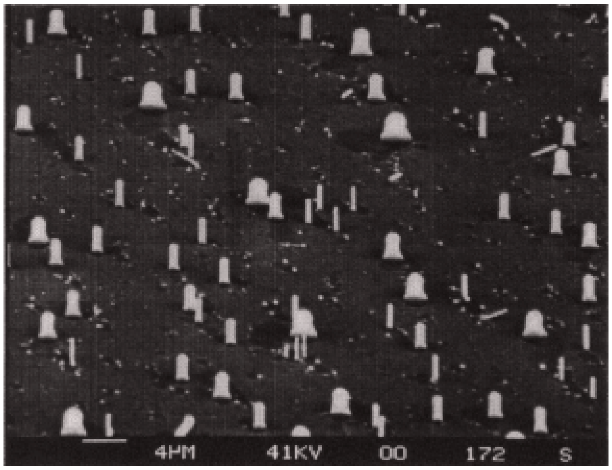

Figure 1. SEM image of Si wires grown on Au/Si(111) substrate. Most of the wires having diameters ranging from 0.1 to 2 µm grow normally to the substrate, while some of them are oriented along the <100> direction.

Figure 1 is a SEM image of a typical sample in which Si wires are grown on Si(111) substrate with a Si_2H_6 process and with Au as a liquid forming agent. The growth pressure is kept at around 10^{-7} Torr. Most wires with diameters between 0.1 and 2 µm grow normally to the substrate, i.e., parallel to the <111> direction. Note that these wires have the same height, which indicates that all the wires have the same growth rate irrespective of their different lateral dimensions. This phenomenon is discussed below. In addition, some wires with smaller diameters are inclined to the substrate. As seen from Fig. 1, the angle between the growth direction of the Si wires and the substrate surface is about 35°, which indicates that these wires are oriented along the <100> direction. It appears that these thin inclined wires have a higher growth rate than the thick normal ones.

Figure 2a shows the heights of the Si wires as a function of their diameters. Curves 1-3 correspond to the wires prepared at gas pressure of 7×10^{-7} Torr for 30, 120, and 180 min, respectively. Size data are obtained from SEM micrographs. It is obvious that for a certain growth period, all wires have nearly the same height. The longer the growth time is, the higher the wires are. The average diameter and height of Si wires are shown in Fig. 2b as a function of growth time. Note that both the average diameter and height increase linearly as the growth time increases. The growth rate can be obtained from the

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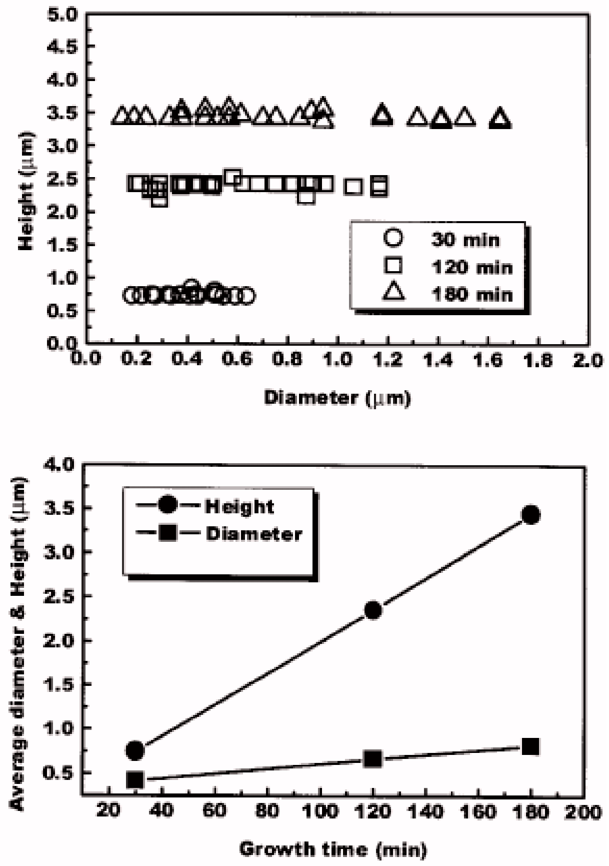

Figure 2. (a) Height of the Si wires as a function of the diameter, and (b) average diameter and height of Si wires as a function of growth time.

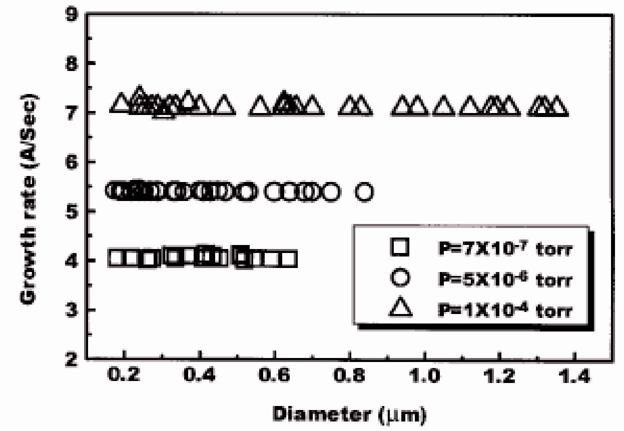

Figure 3. Growth rates of Si wires as a function of their diameter for two gas source Si_2H_6 concentrations in the chamber.

slopes of the straight lines in Fig. 2b. Obviously, the vertical growth rate of 3 Å/s is about ten times that in the lateral direction. In addition, it should be noted that with the same growth condition and without growth-promoting Au, the growth results in high-quality film, and the growth rate is as low as 0.4 Å/s,[10] which is about eight times less than that of the present wire growth. This may be due to high absorption ability of Au/Si liquid droplets, so that Si_2H_6 is abundantly absorbed on the droplets rather than on the surrounding Si surface. As a result, Si is deposited under the droplets and wires are formed.[4,5]

Figure 3 shows the dependence of Si_2H_6 concentration on the growth rate of Si wires. These wires are grown at 700°C with the Si_2H_6 process for 30 min. Three different Si_2H_6 concentrations, which correspond to different gas pressures, are shown in the inset of Fig. 3. Under these growth conditions, the growth is stopped before Au is consumed. As seen from Fig. 3, the growth rate increases as the Si_2H_6 concentration increases. Moreover, wires with different diameters still exhibit the same growth rate even though the gas pressure is as high as 1×10^{-4} Torr.

It is well known that Si whiskers grown by CVD depend on the whisker diameters for their axial growth rate, i.e., thin whiskers grow slower than thick ones.[7] For the present GS-MBE growth, however, growth rate of vertical Si wires is independent of wire diameters. Thus, understanding the growth mechanism is important for fabricating well-controllable ultrafine nanowires. According to the Gibbs-Thomason effect, the thermodynamic equation of the Si wire growth process can be expressed as[7]

$$\Delta\mu = \Delta\mu_0 - 4\Omega\alpha/d \qquad [1]$$

where $\Delta\mu$ is the effective difference between the chemical potentials of Si_2H_6 and Si in the wire, $\Delta\mu_0$ is the same difference on a Si planar surface, α is the specific free energy of the wire surface, Ω is the atomic volume of Si, and d is the diameter of the wire. The dependence of the growth rate V on the effective chemical potential difference is given as[7]

$$V = b(\Delta\mu/kT)^n \qquad [2]$$

where b is a coefficient, k is the Boltzmann constant, T is the growth temperature, and n is an integer (equal to 2 in CVD). In order to simplify the analysis, we suppose that the same flux of source gas Si_2H_6 is introduced to the growth chamber for both CVD and GS-MBE. For the CVD method, as the growth proceeds, it is evident that the gas pressure is high, and accordingly, a high Si_2H_6 concentration is available in the chamber. This, in turn, suggests that $\Delta\mu_0$ is comparable to $4\Omega\alpha/d$, showing size dependence. For GS-MBE growth, on the other hand, there is a relatively small concentration of Si_2H_6 in the growth chamber, hence $\Delta\mu_0$ is much larger than $4\ \Omega\alpha/d$, even for wires with smaller diameters. In Eq. 1, the second term can be omitted. It is why the growth rate of the Si wires is independent of their diameters. This independence can be used for an analysis of the wire growth mechanism in GS-MBE. A detailed investigation of the mechanism is in progress.

It was shown previously that an Au layer on the Si substrate was broken up into many small droplets of different diameters when annealing, and each droplet gave a Si wire. For the present GS-MBE growth, as discussed above, the growth rate of very thin wires is the same as that of thick ones. Thus, it is possible to grow very thin Si wires with very small separation among them by controlling the annealing process and growth conditions. Arrays of Si quantum wires may be fabricated by this method.

Conclusion

We have reported on the wirelike growth of Si on Au/Si(111) substrate by GS-MBE. The Si wires with width between 50 nm and 2 μm grow mainly with a growth axis parallel to the <111> direction. It is found that the growth rate of nanowires is independent of their diameters, i.e., nanowires with different diameters have the same growth rate with the gas pressure range as high as 1×10^{-4} Torr. One mechanism is provided to explain the wire growth difference by GS-MBE and CVD, indicating that the improved wire uniformity in length using GS-MBE is due mainly to the relatively lower gas pressure compared with CVD growth.

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