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Growth of Si whiskers on Au/Si(1 1 1) substrate by gas source molecular beam epitaxy (MBE)

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Abstract

The vapor–liquid–solid growth of Si whiskers from disilane has been studied in a gas source MBE system. The wire-like Si crystals are grown on Si(1 1 1) substrates in a temperature range of 600–800°C, a disilane pressure between 1×10^{-4} and 1×10^{-7} Torr, and using Au as a growth-promoting agent. The morphology of the Si whiskers is investigated. It is found that the growth rate of the vertical wires is independent of the wire diameter (i.e. whiskers with different diameters have the same growth rate). The growth rate of the wires in the vertical direction increases with increasing substrate temperature and disilane pressure, and is about 8–10 times larger than the growth rate of the planar film on the substrate and the width of the whiskers. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, there have been considerable attempts to fabricate Si quasi one-dimensional wires due to the interest in their novel electronic, optoelectronic and thermoelectric properties as well as potential device applications [1–3]. The formation of wire-like silicon crystals by a vapor–liquid–solid (VLS) mechanism is one such process in this field [4,5]. Some of the most promising characteristics of VLS wires are that the crystals are pure, stoichiometric, and perfect to a high degree and that they do not contain any growth-promoting impurities [6]. This fact suggests applications in the fields of vacuum microelectronics [7], field emission devices [8] and scanning instruments [9]. Other potential applications of the VLS wires include the fabrication of Si quantum wires and related quantum functional devices.

The idea of the conventional growth of VLS Si whiskers, which has been based on chemical vapor deposition (CVD), was established by Wagner and Ellis [4,5], and detailed by Givargizov [10,11]. In this process, a small amount of a liquid-forming

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material such as Au, Pt, or Ga is used to form a liquid alloy droplet. The alloy droplet then absorbs Si from vapor gases such as silane (SiH_4), disilane (Si_2H_6), or silicon tetrachloride and hydrogen ($SiCl_4 + H_2$). As the growth proceeds, the supersaturated droplet is separated from the substrate and rides on the top of the growing whiskers. For such wires grown by CVD, it has been demonstrated that the growth rate is quadratically dependent on the diameter. Such wires usually are not uniform enough in length for either fundamental studies or potential applications. Recently, we have presented a novel approach to grow ultra-fine wire-like Si crystals using Si_2H_6 and with Au as a liquid-forming agent by gas source MBE (GS-MBE) [12]. It is found that the growth rate is independent of the wire diameter (i.e. nano-wires with different diameters have the same growth rate). In this paper, we report the growth of VLS wires by GS-MBE.

2. Experimental procedure

N-type Si(1 1 1) wafers with the resistivity of 3–5 Ω cm were used. First, the substrates were prepared using a standard Shiraki cleaning method [13]. A 15 nm gold layer was then deposited via e-beam evaporation at a deposition rate of 0.2 Å/s. The standard base pressure of the evaporator was 5×10^{-7} Torr. An atomic force microscope (AFM) was used to measure the thickness of the Au layer. After the Au was deposited, the substrate was immediately introduced into a GS-MBE chamber. The base pressure in the growth chamber was in the range of 10^{-10} Torr, which is much lower than conventional CVD. The substrate temperature was raised to 900°C over a period of 2 h and heated at this temperature for 20 min, without any source gases present, in order to form a Au/Si eutectic and to remove any surface oxide. The wire growth was performed by introducing pure Si_2H_6 at a pressure between 1×10^{-4} and 1×10^{-7} Torr, and at temperatures ranging from 600 to 800°C.

After growth, all of the as-grown samples were analyzed by scanning electron microscopy (SEM). The thin layer of gold on the surface of the substrate (deposited prior to MBE growth) alleviated the problem of sample charging, thus giving excellent contrast for the SEM images obtained.

3. Results and discussions

3.1. Morphology of Si whiskers

Fig. 1a is a side view SEM image of a typical as-grown sample. For this particular sample, the growth pressure was maintained at 10^{-7} Torr and

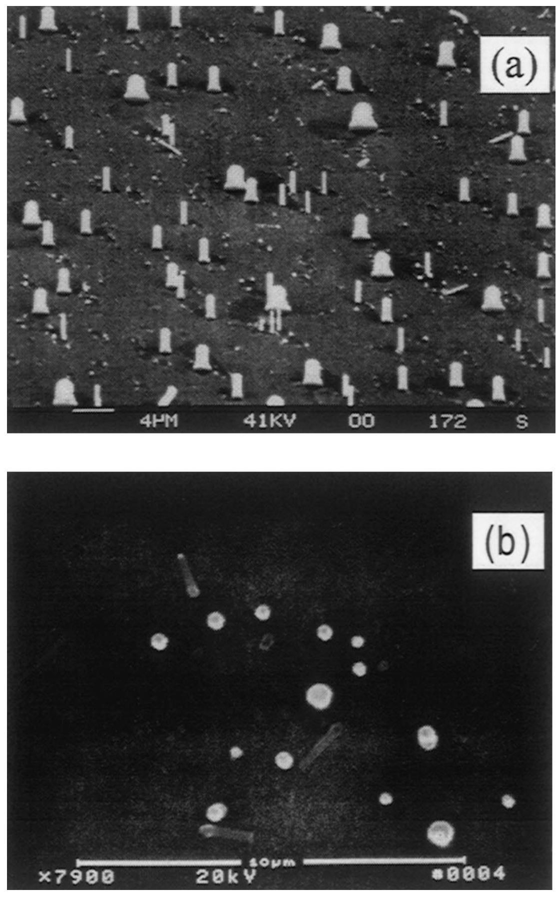

Fig. 1. (a) Side view SEM image of a typical sample in which the Si whiskers are grown on a Au/Si(1 1 1) substrate. Most of the wires have a diameter in the range of 0.1–2 μm and grow normally to the substrate, while some whiskers are oriented along the ⟨1 0 0⟩ direction, and (b) top view SEM image of the Si whiskers. The vertical wires appeared as bright dots and have a hexagonal cross section.

a growth temperature of 700°C. The majority of the wires have a diameter in the range of 0.1–2 μm and are positioned normal to the substrate surface (i.e. parallel to the ⟨1 1 1⟩ direction). It can be seen that all these wires have nearly the same height, which indicates that all the wires have the same growth rate regardless of their lateral dimensions. The cross-sectional view of the thin whiskers and the thick ones vary in that the thin whiskers (width smaller than 1 μm) do not change in width along their lengths, while whiskers with larger diameters (larger than 1 μm) usually have a larger base and develop into a constant cross section in the upper portion of the whisker. In addition, some of the thin whiskers are inclined relative to the substrate. As seen from Fig. 1a, 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 ⟨1 0 0⟩ direction. It appears that these inclined wires have a higher growth rate than the normal ones. It is believed that these inclined wires have a stepped liquid–solid interface [14]. Due to a decrease in the activation energy of nucleation, such {1 0 0} interfaces are known to the enhance growth rate compared to the {1 1 1} interface.

Fig. 1b is a top view SEM image of the whiskers grown on the Si(1 1 1) substrates. The vertical wires appear as bright dots and the inclined wires appear as lines. It is observed that the vertical wires have a hexagonal cross section with six {1 1 0} side facets. This phenomenon is closely related to the fact that Si has a diamond crystal structure and grows in the ⟨1 1 1⟩ direction.

3.2. *The growth rate dependence on temperature and Si_2H_6 pressure*

In this section, we focus on the temperature and Si_2H_6 pressure dependencies of the growth rate of the vertical wires on Si(1 1 1) substrates. The growth rate of the wires at a specific substrate temperature and Si_2H_6 pressure is shown in Fig. 2. Fig. 2a depicts the height of the vertical Si wires as a function of their diameter. The figure shows the height versus diameter of the Si wires at a constant substrate temperature of 700°C and gas pressure of 7×10^{-7} Torr for varying growth times (30, 120, and 180 min). The size data were obtained from SEM micrographs. This data suggests that for a given growth time period, the wires have nearly the same height. As the growth time is increased, so too increases the height of the wires. The average diameter and height of the Si wires are shown in Fig. 2b as a function of growth time. It can be seen that both the average diameter and height increase linearly as the growth time increases. From the slope of the lines in Fig. 2b, the growth rate can be obtained. The vertical growth rate of 3 Å/s is about 10 times larger than that in the lateral direction (about 0.3 Å/s). It is important to note that under identical growth conditions, the growth rate on the Si(1 1 1) surface without the growth-promoting Au, is as low as 0.4 Å/s [15] which is about eight times less than that of the wire growth rate (in the vertical direction). The slow growth of the whiskers in the

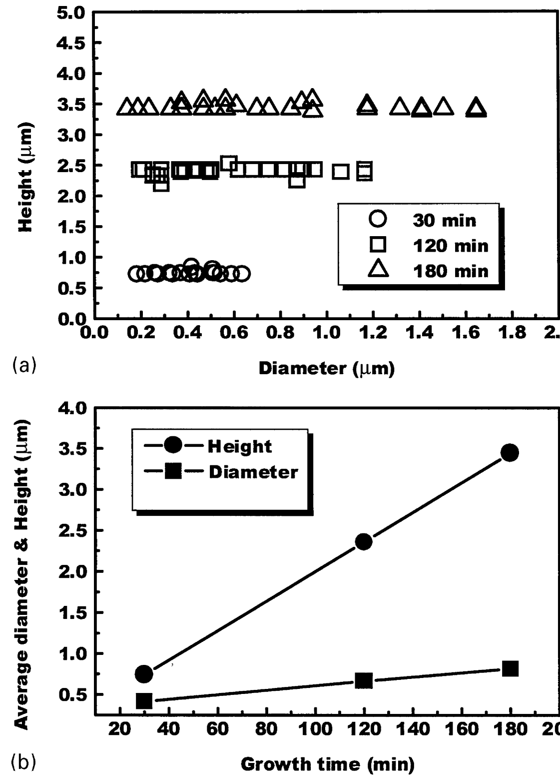

Fig. 2. (a) Height of the Si whiskers as a function of the diameter, and (b) average diameter and height of Si whiskers as a function of growth time.

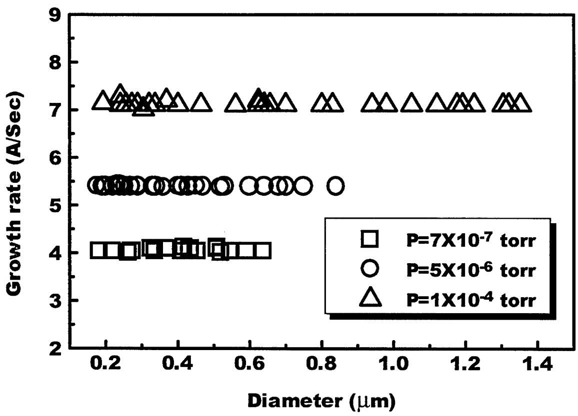

Fig. 3. Growth rate of the Si whiskers as a function of their diameters for various Si_2H_6 pressures.

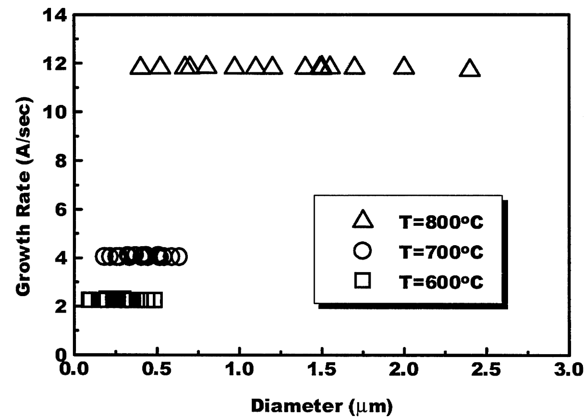

Fig. 4. Growth rate of the Si whiskers as a function of their diameters for various growth temperatures.

lateral direction is believed to be resultant from a two-dimensional growth mechanism [16], while the fast growth of the whisker length is related to the fact that the Au/Si liquid phase reduces not only barriers for chemical reaction on the vapor–liquid interface [17], but also the activation energy of nucleation at the liquid–solid interface [18].

Fig. 3 shows the growth rate dependence of the Si wires at various Si_2H_6 pressures. The wires were grown at a growth temperature of 700°C and a fixed growth time of 30 min. Under these growth conditions, the growth stops before all of the Au is consumed. As seen in Fig. 3, the growth rate increases as the Si_2H_6 pressure increases. Moreover, the wires still exhibit a diameter-independent growth rate even for gas pressures as high as 1×10^{-4} Torr.

In Fig. 4, the results for three substrate temperatures are plotted as a function of the whisker diameter. The wires were grown at the gas pressure of 7×10^{-7} Torr. The rate still appears to be constant for different diameters. The growth rate of the wires increases with increasing substrate temperature. The temperature dependence of the growth rate can be used to determine the activation energy of the VLS process, which contributes to the rate-limiting step. In order to better quantify this, a wider range of temperature-dependent growth data is needed.

3.3. *Principles of the whisker growth by GS-MBE*

According to the existing theories [10,19–21], there are three kinds of VLS growth mechanisms that contribute to the axial growth of whiskers. The first one consists of four main steps [10,19]: (a) mass-transport of the whisker growth species in the vapor phase to the vapor–liquid interface; (b) chemical reaction of the gaseous species at the vapor–liquid interface; (c) dissolution of the Si atoms into and subsequent diffusion through the liquid alloy phase, and (d) the incorporation of the growth species into a crystal lattice at the liquid–solid interface. The second theory emphasizes the liquid-alloy droplet surface as an important mass-transport path [20]. In this theory, the whisker growth species formed at the liquid alloy surface diffuses along the surface to the periphery of the liquid–solid interface, followed by liquid–solid interfacial diffusion from the periphery towards the center of the interface. The third theory suggests that the growth species impinging on the side surfaces of the whiskers diffuse along the sides to the liquid-alloy droplet resulting in the vertical growth of whiskers [21]. For the present whisker growth by GS-MBE, further empirical and theoretical analysis needs to be obtained in order to determine the dominant growth mechanism. A first-order analysis of the mechanism that yields the independent axial growth rate of whiskers on their diameters can be performed by considering the thermodynamic process of whisker growth.

Generally speaking, the thermodynamic equation of the Si whisker growth process can be expressed as [10]:

$$\Delta\mu = \Delta\mu_0 - \frac{4\Omega\alpha}{d}, \tag{1}$$

where $\Delta\mu$ is the difference between the effective chemical potentials of Si_2H_6 and Si in the whisker, $\Delta\mu_0$ is the difference between the effective chemical potentials of Si_2H_6 and Si on a Si planar surface, α is the specific free energy of the whisker surface, Ω is the atomic volume of Si, and d is the diameter of the whisker. The dependence of the growth rate γ on the effective chemical potential difference is given as [10]:

$$\gamma = b(\Delta\mu/kT)^n, \tag{2}$$

where b is a coefficient, k is the Boltzmann constant, T is the growth temperature, and n is an integer which is equal to 2 in CVD [10] and also implies a dependence of the axial growth rate on the whisker diameter. If we suppose that the same flux of source gas is introduced into the growth chambers for both CVD and GS-MBE, then in CVD, where the gas pressure is high, a high Si_2H_6 concentration is available in the chamber during growth. This, in turn, suggests that $\Delta\mu_0$ is comparable to $4\Omega\alpha/d$, resulting in axial-dependent whisker growth. 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 is much smaller and can be omitted. This explains why the growth rate of the Si wires is independent of the diameter.

4. Conclusions

We have presented GS-MBE growth of Si whiskers on Au/Si(1 1 1) substrates. The Si whiskers were grown in a temperature range of 600–800°C and a disilane gas pressure between 1×10^{-4} and 1×10^{-7} Torr. The morphology of Si whiskers formed perpendicular to the surface was investigated. It was found that the growth rate of the wires in the vertical direction increased with increasing substrate temperature and Si_2H_6 pressure, and about 8–10 times larger than the rates on a bare substrate. One mechanism for the observed independence of the growth rate on whisker diameter is studied, indicating that the improved wire uniformity in length using GS-MBE is mainly due to the relatively lower gas pressure compared with CVD growth.

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