Growth of Si whiskers by MBE: Mechanism and peculiarities

N. Zakharov*, P. Werner, L. Sokolov, U. Gösele

Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany

Available online 7 September 2006

Abstract

We analyzed the stress-driven mechanism of MBE Si whisker growth. It is shown that the driving force for MBE whisker growth is determined by the relaxation of elastic energy stored in the overgrown layer $L_s$ due to gold intrusion. In this case the supersaturation is determined by the interplay between elastic stresses and surface energy. The latter is considerably decreased due to decoration of the Si surface by gold resulting in formation of thin liquid Si/Au eutectic layer. This suggests that in our case the Si supersaturation is not an independent growth parameter as it is in the chemical vapor deposition growth method. Instead it is determined by stress in the overgrown Si layer. This approach allows us to explain quite well the growth kinetic and the relationship between the radius and the length of the whiskers. The whisker growth in our case can be considered as a stress relaxation mechanism, where the stress relaxation occurs due to transition from the two-dimensional system to the three-dimensional one.

© 2006 Elsevier B.V. All rights reserved.

PACS: 61.46.−w; 81.07.Vb; 81.15.Hi

Keywords: Semiconductor nanostructures; Silicon nano wires; Molecular beam epitaxy

1. Introduction

The renaissance of interest in whisker growth is supported by the possibility to employ one-dimensional quantum confinement in electronic and photonic devices [1–4]. However, the first whiskers boom occurred more than four decades ago. At that time, scientists found out that the strength of crystalline materials is about three orders of magnitude lower than it should be according to the theoretical prediction [5]. The main reason is the formation of structural defects during the plastic deformation. The strength of individual whiskers approaches the theoretical limit because they can be grown practically defect-free. Although all attempts failed to develop a bulk composite material on their basis with a strength close to the theoretical predictions, a plenty of experience in whisker growth was gained at that time, and so-called vacuum liquid solid (VLS) growth mechanism was developed [6]. According to this mechanism growth of whiskers occurs on metallic droplets because of a high accommodation of the vapor-phase on the liquid surface of the Si/M eutectic, where M is catalytic metal. The necessary supersaturation of Si ad-atoms is determined by the vapor pressure in the reaction chamber and can easily be varied in wide region. The Si whiskers grow from the supersaturated liquid solution of Si in Si/M eutectic. A variety of methods such as metal organic chemical vapor deposition (MOCVD) [7–10], pulse laser deposition (PLD) [11], gas-source molecular epitaxy (GS-MBE) [12,13] and molecular beam epitaxy (MBE) [14] are nowadays used to grow Si wires on a Si(1 1 1) substrate. Each of them has its advantages and disadvantages. In this paper we would like to pay attention to the peculiarities of MBE Si whisker growth. Advantageous are the possibilities of well-controlled growing conditions (high vacuum, a clean substrate and a well-controlled environment in the growth chamber, the precise control of atomic fluxes which is extremely important for doping, temperature control, etc.). The goal of this work is to cast light on the growth mechanism and kinetic of whisker growth by MBE. To simplify the problem as much as possible we investigate the growth of elemental semiconductor Si whiskers on a Si substrate using gold droplets as a catalyst.
2. Experiment

We used \(\{111\}\) oriented 5" Si wafers cleaned by the conventional RCA (Radio Corporation of America) procedure were used as substrates. Our MBE system includes three electron-beam guns for the evaporation of Au and Si as well as of Ge \[14\]. A thin Au film with a nominal thickness of 2 nm was deposited on the substrate at a substrate temperature \(T_s = 525 \pm 1^\circ C\). During the nanowires (NW) growth the constant Si flux \(I_1\) ranged in interval 0.013–0.108 nm/s. Two growth temperatures \(T_s = 525\) and 545 \(^\circ C\) were chosen. The vacuum in the chamber during the growth was \(10^{-2}\) Pa. The samples were investigated by transmission electron microscopy (TEM) and high-resolution scanning electron microscopy (SEM). Reflection high energy electron diffraction (RHEED) was used to monitor the evolution of the surface structure during the growth process.

3. Results

The gold deposition at \(T = 525^\circ C\) resulted in the formation of Au droplets on the Si surface. The diameters of the droplets ranged from 20 to 400 nm. During the subsequent Si deposition, NWs were formed on the Au droplets (Fig. 1). Under these conditions their diameter \(d\) related to the size of the droplet and ranged from 70 to 200 nm (\(2r_c < d < 2R_c\)) (see Fig. 2a). Smaller as well as larger droplets outside of this range did not initiate whisker growth at all. The length of the grown whiskers \(L\) was proportional to the growth time \(L \sim t\) and varied in inverse proportion to the radius \(L \sim 1/R\) (Fig. 2b and c respectively).

Even though the growth rate of the whiskers \(dL/dt\) decreased with the Si flux \(I_1\), the ratio \(L/L_1\) increased as can be seen in Fig. 2d (\(L_1\) the thickness of overgrown Si layer, Fig. 6). This suggests that longer whiskers can be grown at low Si flux \(I_1\).

The base of the whiskers was always located in triangular pits formed during the growth process. This clearly indicates that some surrounding silicon material was definitely consumed by the growing whisker (see Fig. 1a,b). During the growth Si atoms diffused upward to the Au droplet and were then incorporated into the (111) Si/Au droplet interface on the top. This growth process implies the presence of an ad-atom supersaturation \(\Delta \mu/kT > 0\) due to a difference in the chemical potential between the overgrown layer and the top of the whisker. Normally grown whiskers are defect-free (see Fig. 5); however, they sometimes contain single inclined stacking fault coming from the interface between the substrate and the overgrown Si layer.

The intrusion of Au into the Si overgrown layer during whisker growth (see Fig. 3a) leads to an increase of the elastic energy and the formation of structural defects such as twins, partial dislocations and small amorphous Si/Au eutectic particles inside the overgrown layer. The presence of an Au-enriched surface layer was also demonstrated by \[15\]. The very early stage of whisker growth is shown in Fig. 3b, where the structural defects serving for elastic energy relaxation are indicated by arrows. It should be noted that the region underneath the growing whisker is defect-free. This suggests that whisker growth results from the relaxation of elastic stresses in overgrown layer.

In the cross-section TEM images at room temperature one can clearly see the presence of tiny amorphous droplets of Si/Au eutectic approximately 5 nm in diameter (see Fig. 4). We assume that at a growth temperature of 525\(^\circ C\) they turn into a thin liquid layer on the Si surface. This seems to be the case in Fig. 5, where RHEED patterns taken at temperatures 150 \(^\circ C\) (a), and 360 \(^\circ C\) (b) are shown.

4. Discussion

The growth process of whiskers by MBE is shown schematically in Fig. 6. Two fluxes of the Si ad-atoms \(I_1\) and \(I_2\) can be distinguished. The uniform flux \(I_1\) comes...
directly from the Si source and provides the component of vertical elongation equal to the thickness of the overgrown Si layer $L_s$. The whole vertical elongation of the whisker amounts to $L + L_s$. The visible whisker length $L$ is fully determined by flux $I_2$, which collects the adsorbed Si ad-atoms from a region with a radius $R$, around the whisker.

The whisker’s base is always located in pits formed during the growth process. This indicates that some surrounding silicon material is definitely consumed by the whisker (see Fig. 1). Si atoms diffuse upwards to the Au droplet and are incorporated into the (1 1 1) Si/Au droplet interface. This growth process implies the presence of an ad-atom super-saturation $\Delta \mu > 0$ due to a gradient of the chemical potential. The balance of material can be described as follows:

$$\pi R^2 \frac{dL}{dt} = \frac{D}{kT} \frac{d\mu}{dx} S \, dt,$$

with $D$ the coefficient of Si surface diffusion, $R$ the whisker radius, $\mu$ the chemical potential of the Si atoms, $S = 2\pi Ra$ the square of ad-atom’s diffusion, $a$ the lattice parameter. The result is

$$dL = \frac{2Da d\mu}{kTR dx} \, dt.$$
The effective difference between the chemical potentials of Si atoms in the overgrown layer and on the top of the whisker can be written as
\[ \Delta \mu = \Delta \sigma \omega - \frac{2 \gamma \omega}{R}, \]
where \( \Delta \sigma = (\Delta \sigma_{xx} + \Delta \sigma_{yy} + \Delta \sigma_{zz})/3 \) being the stress created in the overgrown layer \( L_s \) due to gold intrusion; \( \omega \) the atomic volume; \( \gamma \) being the surface energy of the cylindrical surface formed mainly by \{110\} and \{112\} planes which are parallel to the growth direction \{111\}. \( \Delta \sigma \) is a complex function of gold concentration in overgrown layer \( L_s \), whisker radius \( R \) and \( I_1 \). The first term is the gain in elastic energy per atom due to the strain relaxation on the top of whisker, while the second term is the loss of energy per atom due to the increase of the side surface of the whisker. This clearly shows that the supersaturation is determined by both the surface energy and the elastic energy stored in the overgrown Si layer due to Au intrusion. It is not an independent variable as the gas pressure in the case of CVD growth. The stress relaxation occurs mainly in the upper part of the whisker on the length \( \lambda \) (see Fig. 7). Thus we can write
\[ \frac{d\mu}{dx} \approx \frac{\Delta \mu}{\lambda} \]
with \( \lambda \) being the relaxation length. Finally
\[ L = \frac{2 D \Delta \sigma \omega}{kT \lambda R} \left( 1 - \frac{2 \gamma}{\Delta \sigma} \right) t. \]
Thus, the whisker growth rate \( dL/dt \) is constant. This is in good agreement with the experimental results (see Fig. 2b). The radius dependence of \( L \sim 1/R \) is also agrees quite well with the experimental data (see Fig. 2c). Of course, \( L \) also depends implicitly on the flux from the Si source \( I_1 \) through \( \Delta \sigma \), because \( \Delta \sigma = 0 \) at \( I_1 = 0 \). When \( \Delta \sigma = 2 \gamma / r_c \), the growth stops (Gibbs–Tomson effect). In our case \( r_c \approx 35 \text{ nm} \); the surface energy of side surface of the whisker \( \gamma \approx 2000 \text{ erg/cm}^2 \) [16]; it gives \( \Delta \sigma \approx 1.4 \times 10^9 \text{ erg/cm}^2 = 1.4 \times 10^{-3} E_{\text{si}} \), where \( E_{\text{si}} \) the Young modulus. Thus, the difference of the lattice parameters in the substrate and on the top of the whisker should be \( \Delta \epsilon_{zz} = \Delta \epsilon_{yy} = 1.4 \times 10^{-3} \) which...
corresponds to the supersaturation \( \Delta \sigma / kT \approx 0.02 \). Such a low supersaturation will not be sufficient to support whisker growth by classical gas epitaxy. However, the presence of the liquid Si/Au phase makes the growth possible due to a low nucleation energy in the liquid phase. Thus, the role of Au droplets in our case is the formation of the Si/Au liquid phase. The difference between \{2 2 0\} interplanar distances near the top of the whisker and in the overgrown layer measured in this investigation in HRTEM images is \( \Delta d_{zz} = \Delta d_{zz} \approx 5 \times 10^{-3} \). This should be sufficient to drive the whisker growth. A very similar mechanism of Sn whisker growth on a stressed Sn surface of Cu–Sn bimetallic film was experimentally observed by Tu [17]. In specimen maintained at room temperature, the Sn and Cu layers were both in compression and tension. The whiskers grew only on compressed Sn film. The driving force of this process was attributed to the interdiffusion and reaction that occurs in the Cu–Sn film.

The tiny amorphous particles, about 5 nm in size, are present on the Si surface at room temperature as can be seen in Fig. 4. They are most probably Si/Au eutectic particles. The RHEED in situ control of the surface structure during the heating of Si wafer deposited by 2 nm Au points to a phase transition which occurred at \( (360 \pm 20)^{\circ} \text{C} \). Above this transition temperature instead of sharp reflections from the crystalline Si, the diffuse halo appears (see Fig. 5). This is a strong indication that at a growth temperature of 525 \(^{\circ} \text{C} \) the whole specimen is covered by a thin Si/Au liquid eutectic layer. Using Eq. (5) and remembering that \( L_s = R/2 \) we can write

\[
\frac{L}{L_s} = \frac{2D_s \Delta \sigma}{kT \Delta R l} \left( 1 - \frac{2\gamma}{\Delta \sigma R} \right). \tag{6}
\]

Thus, Eq. (6) and Fig. 2d show that the elongation of whisker \( L \) is controlled by the diffusion of Si ad-atoms and stress in the overgrown layer \( L_s \).

5. Conclusions

It has been shown that the driving force for MBE whisker growth is supported by the relaxation of elastic energy stored in an overgrown layer \( L_s \) due to gold intrusion. The supersaturation is determined by the interplay between elastic stresses and surface energy (Eq. (3)). The last one could be considerably decreased due to the formation of a thin liquid Si/Au eutectic layer on the Si surface. This suggests that in our case the supersaturation is not an independent growth parameter. This, however, is not the case for the CVD growth technique where the supersaturation is determined by vapor pressure and can be easily varied as an independent parameter. This approach allows us to explain quite satisfactorily the growth kinetics and the relationship between the radius and the length of the whiskers.

The minimal radius of the whiskers is determined by an interplay between the gain in elastic and the loses in surface energies \( \tau_c = 2\gamma / \Delta \sigma \) (Gibbs–Tomson effect). The stress relaxation efficiency decreases with the radius of the whisker [18]. This results in the reduction of supersaturation for thicker whiskers with \( R > R_c \) and their growth interruption. This also explains the experimental fact that in the case of MBE thinner whiskers grow faster. The whisker growth in our case can be considered as a stress relaxation mechanism similar to the Stranski–Krastanow mechanism [19], where stress relaxation occurs by transition from two-dimensional system to three-dimensional one.

Acknowledgments

The authors would like to thank L. Schubert and A. Frommfeld for the MBE experiments, F. Syrowatka for SEM analysis, S. Hopfe for TEM specimen preparation, and M. Werner for specific TEM analysis. The work was also partially supported by European project NODE (FP6/015783) and Russian foundation of basic research (04-02-1647).

References