Journal of Crystal Growth 391 (2014) 13–17

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Study of silicon crystal surface formation based on molecular dynamics simulation results

G. Barinovs *, A. Sabanskis, A. Muiznieks †

University of Latvia, Faculty of Physics and Mathematics, Zellu St 8, LV-1002 Riga, Latvia

ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form
17 December 2013
Accepted 5 January 2014
Communicated by Y. Furukawa
Available online 11 January 2014

Keywords:
A1. Computer simulation
A1. Surface structure
A2. Growth from melt
B2. Semiconducting silicon

ABSTRACT

The equilibrium shape of ⟨110⟩-oriented single crystal silicon nanowire, 8 nm in cross-section, was found from molecular dynamics simulations using LAMMPS molecular dynamics package. The calculated shape agrees well to the shape predicted from experimental observations of nanocavities in silicon crystals. By parametrization of the shape and scaling to a known value of {111} surface energy, Wulff form for solid-vapor interface was obtained. The Wulff form for solid–liquid interface was constructed using the same model of the shape as for the solid–vapor interface. The parameters describing solid–liquid interface shape were found using values of surface energies in low-index directions known from published molecular dynamics simulations. Using an experimental value of the liquid–vapor interface energy for silicon and graphical solution of Herring's equation, we constructed angular diagram showing relative equilibrium orientation of solid–liquid, liquid–vapor and solid–vapor interfaces at the triple phase line. The diagram gives quantitative predictions about growth angles for different growth directions and formation of facets on the solid–liquid and solid–vapor interfaces. The diagram can be used to describe growth ridges appearing on the crystal surface grown from a melt. Qualitative comparison to the ridges of a Float zone silicon crystal cone is given.

1. Introduction

Growing a cylindrical rod of monocrystalline silicon by Float zone or Czochralski process, the crystal is formed from a melt. Without contact with container walls the shape of the crystal is controlled by capillary forces and by heat and mass transport in the solid–liquid–vapor system. A variety of distinguishing features may appear on an otherwise smooth external surface (solid–vapor interface) of the cylindrical crystal, see Fig. 1. Depending on their appearance they have been called as ridges [1], protrusions [2], growth lines [3], bulges [4], projections [5], etc., but they all can be described by the same growth mechanism. The theoretical description of these structures had been developed by Voronkov around the year 1980 [5–9]. It relies on the analysis of the interface free energies and on a model of curvature driven atomic diffusion along the crystal external surface.

The crystal surface is formed at the trijunction of solid–liquid, liquid–vapor and solid–vapor interfaces. The free energies of the interfaces will determine their equilibrium orientation. The dependence of the orientation of external and internal (solid–liquid interface) crystal surfaces on the free melt surface (liquid–vapor interface) angle is conveniently shown in an angular diagram. For silicon the free energies of the interfaces are not well known and the construction of the angular diagrams so far has been very simplified and schematic [9,10]. Such an approach does not use the full predictive power of the Voronkov model where the same description could be universally applied for different crystallographic orientations of growing crystals (e.g. ⟨100⟩, ⟨111⟩), for growth of different sized crystals (e.g. macroscopic or microscopic crystals), for different methods of crystal growth (e.g. Float zone or Czochralski) and, possibly, prove or disprove the validity of Voronkov's approach or show its limits of applicability.

In this paper we will show that the angular diagram for silicon could be obtained by combining the information about the interface energies from molecular dynamics studies and experimental studies. An advantage of this approach in comparison to ad hoc construction of the diagram is that it is universal for the different types of silicon crystal growth. Another advantage is that the description could be systematically improved by more accurate numerical studies.

2. Calculation of growth angle from Voronkov's model

Voronkov's approach to the theoretical derivation of crystal growth angle relies on the knowledge of all interface energies, which allows one to solve Herring's equation [11] for the

* Corresponding author. Tel.: +371 67033769.
E-mail address: girts.barinovs@lu.lv (G. Barinovs).
† Deceased

0022-0248/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2014.01.004

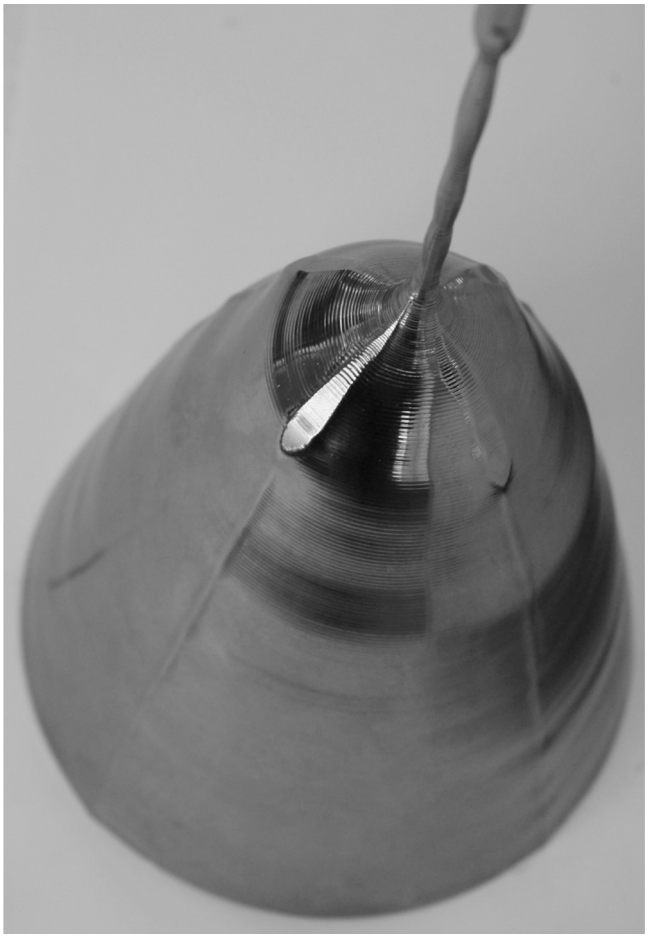

Fig. 1. Cone of a [100] Float zone crystal grown at Leibnitz Institute for Crystal Growth, Berlin. For dislocation free [100] crystals four ridges on the crystal surface are observable. Bright reflections in the middle of the photo are from a cascade of mirror like facets on the crystal surface.

equilibrium orientation of interfaces at the triple phase line (TPL):

$$\sum_i (\gamma_i \vec{e}_i + \gamma_i' \vec{e}_i^{\,+}) = 0, \tag{1}$$

where $\vec{e}_i$ are unit vectors parallel to interface i at the TPL, but $\vec{e}_i^{\,+}$ are unit vectors perpendicular to $\vec{e}_i$, Fig. 2(a). The sum is over all three interfaces and γ_i' is the derivative with respect to the corresponding angular coordinate for the interface i, Fig. 2(b).

Herring's equation can be solved graphically. First, the equilibrium shapes of the three interfaces are found by Wulff's construction, where the interface energies are drawn in a polar γ plot. The inner envelope, Γ_i, of planes perpendicular to radius-vectors is geometrically similar to the equilibrium shape of the interface [12]. Next, the obtained inner envelopes for three interfaces, Γ_{sv}, Γ_{sl} and Γ_{lv}, are used to find graphically the equilibrium orientation of the solid–vapor interface, the solid–liquid interface and the liquid–vapor interface at the TPL [6]. The graphical construction will be demonstrated in the example of silicon in the next sections. The result can be represented as a plot, angular diagram [6], that shows the equilibrium orientation of external and internal crystal surfaces as functions of the free melt surface angle. From the diagram one can find the dependence of the growth angle, $\varepsilon = \varphi_{lv} - \varphi_{sv}$, on the crystallographic orientation, as well as the orientations of the free melt surface leading to the growth of {111} facets on the crystal internal or external surface.

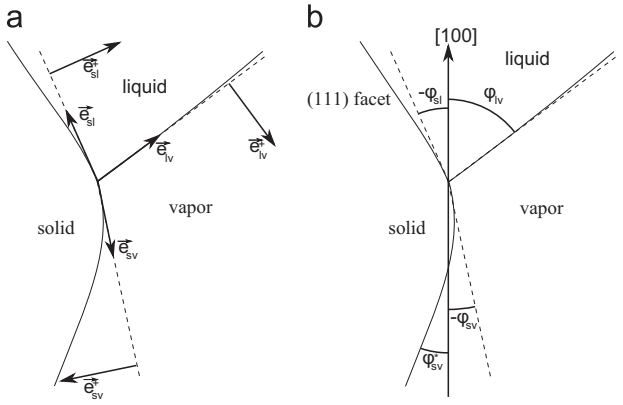

Fig. 2. (a) The orientation of unit vectors at the triple point. "sv" stands for solid–vapor interface, "lv" for liquid–vapor, "sl" for solid–liquid. (b) The angles are measured at TPL in liquid–vapor–solid direction between [100] axis and the tangent to the interface. Since, viewing from the triple point, the solid–vapor interface and the liquid–vapor interface are situated in approximately opposite directions, angular diagrams are simpler if the angles for liquid–vapor interfaces are measured from the opposite end of the [100] axis than the angle for the solid–vapor interface.

The second element of Voronkov's approach is the model of the curvature driven atomic diffusion at nanoscale. It predicts for an undercooled melt that, due to the atomic diffusion of melt atoms along the external surface, the observed orientation of the external surface, φ_{sv}^* in Fig. 2(b), can differ considerably from the equilibrium orientation at the TPL, φ_{sv}, found from the free energies. The diffusion is directed along crystal external surface away from the TPL. The undercooling is explained by lower temperatures of the melt needed for the growth of an internal {111} facet, growing by 2D nucleation, in comparison to the rest of the crystallization front growing by rough growth. Whenever the {111} internal facet appears close to the TPL, the macroscopical growth angle will be different from the growth angle in immediate vicinity of the triple point. This results in a macroscopically visible structure on the external crystal surface in Fig. 1. The difference between the macroscopically observed growth angle, ε^*, and the growth angle, ε, determined by equilibrium orientation of interfaces can be predicted as [5]

$$\varepsilon^* - \varepsilon = -C v_p^{-1/3} \Delta T, \tag{2}$$

where v_p is the crystal pulling speed, $\Delta T = T_m - T$ is the undercooling of melt below the crystal melting point T_m, and C is a coefficient that depends on material constants and temperature of the melt, T.

3. Calculation of equilibrium shape by molecular dynamics simulations

The values of the interface energies and their derivatives in Herring's equation, Eq. (1), are physical parameters that have proven to be difficult to obtain from experiments. This is especially true for the solid–liquid interface, which is hidden for external observers. On the contrary numerical modeling, for example by molecular dynamics, allows easily to visualize processes at the internal surface and to change the temperature of the system simply. Still, the derivation of the angular dependence of interface energies by molecular dynamics approach is a challenging and time-consuming task.

The experimental study of the equilibrium shape of silicon nanoparticles at 1373 K temperature has been presented in Ref. [13] and for the shape of nanocavities at 973 K in Ref. [14]. From the observed shapes the studies conclude very different