Modeling the crystal phase switching in self-catalyzed GaAs nanowires

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Abstract— A model is proposed to depict the crystal phase switching in the self-catalyzed GaAs nanowires considering different shapes of the nanowire growth facet.

Keywords— III-V nanowires; vapor-liquid-solid growth

Semiconductor III-V nanowires (NWs) are promising nanomaterials for the fabrication of novel optoelectronic devices [1]. It is of high importance to control the morphology, crystal structure and composition of NWs to produce devices with desirable characteristics. In this report, we present a theoretical study of self-catalyzed GaAs nanowire growth via molecular beam epitaxy and focus on the investigation of the zinc-blende (ZB) – wurtzite (WZ) switching. The ZB–WZ switching in the vapor-liquid-solid (VLS) III-V nanocrystals (whiskers and NWs) is often observed during the growth in the [111] direction. In this case, even a single stacking fault, for instance, in the ZB stacking sequence leads to the formation of a WZ segment. The presence of polytypes is usually unwanted because they may have different physical properties. This problem of polytypism has been studied for decades. Nevertheless, the control of the NW crystal phase is still challenging due to the stochastic nature of the nucleation-limited growth mechanism of NWs in the [111] direction. Recent results of in-situ TEM (transmission electron microscopy) studies of self-catalyzed GaAs NW growth [2] have allowed to gain more insight into the microscopic mechanism of the polytypism phenomenon. Particularly, it was found that the WZ phase formation occurs when the average contact angle of the catalyst droplet belongs to the specific range of values, 100°–125°. At the boundaries of this range, the NW crystal phase becomes very sensitive to small variation of the contact angle. In most previous theoretical studies, the NW top facet was considered in the form of a circle and, therefore, the contact angle was assumed to be a constant along the NW top facet edge. These assumptions allowed to perform simple analysis of the problem. Herein, we consider the NW growth facet in the form of a hexagon with truncated corners (the size of which is determined by the central angle α) [3]. We use a numerical approach to find the equilibrium shape of the droplet (Fig. 1a) and the dependence of the contact angle on the coordinate at the triple phase line, $\beta(\xi)$. This allows us to describe correctly the crystallography of GaAs crystals and observe new effects associated with the variation of the NW growth facet shape.

In this study, we use the classical nucleation theory to calculate the nucleation rate of the GaAs islands on the catalyst-NW interface. The equilibrium shape of the droplet is found using Surface Evolver software [4]. Also, the thermochemical data and the reference data on the surface energies obtained by the density function theory are used to calculate the nucleation rates of *c* and *h* islands (*c* island corresponds to the ZB stacking sequence, i.e. the cubic phase; and *h* island corresponds to the WZ stacking sequence, i.e. the hexagonal phase). A typical result of the calculation of the $\beta(\xi)$ dependence is shown in Fig. 1b. It is seen that the deviation of the local contact angle from the value of the average contact angle can be as much as 50°. This leads to the following results. We find that the island nucleation at the triple phase line occurs preferentially at the corners of the growth facet due to the presence of the wide range of contact angles [3]. Also, we find that the decrease of α causes the shift of the nucleation probability curve to the right [3]. The result of the calculation of the nucleation probability of wurtzite phase in self-catalyzed GaAs NW for the growth conditions of the experiment [2] is shown in Fig. 1c. It is seen that the theoretical predictions are in agreement with the experimental data [2].

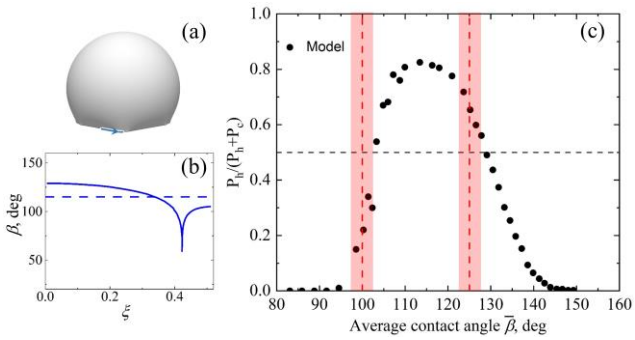

Fig. 1. (a) The equilibrium shape of the droplet sitting on the hexagonal facet. (b) The variation of the contact angle with the coordinate at the triple phase line. For comparison, the value of the average contact angle of 115° is also shown (the dashed line). The range of values of ξ corresponds to the highlighted region at the triple phase line in (a). (c) The relative nucleation probability of *h* islands versus the average contact angle. The experimental data [2] shown by the red lines. The error estimated using the data of the Supporting Information [2] is shown by the highlighted regions.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support of St. Petersburg State University under the research grant No. 94033852.

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