

DOI: 10.17725/rensit.2022.14.381

On the Stability of Catalyst Drops at the Vapor-Liquid-Solid Contact during the Nanowires Growth

Valery A. Nebol'sin, Vladimir A. Yuriev, Nada Swaikat, Valeria V. Korneeva

Voronezh State Technical University, <http://www.cchgeu.ru/>

Voronezh 394006, Russian Federation

E-mail: vcmsao13@mail.ru, yuryeva@gmail.com, nada.s84@mail.ru, vkorneeva@vgasu.vrn.ru

Evgeniy N. Vasnin

Experimental Design Bureau of Motor Engineering, <http://www.okbm.ru/>

Voronezh 394055, Russian Federation

E-mail: vasnin11@gmail.com

Received September 22, 2022, peer-reviewed September 29, 2022, accepted October 6, 2022.

Abstract: This paper gives a physical justification for the wettability conditions for the limited area crystal surface by a small-volume catalyst droplet at the end of the growing nanowires (NW) characterized by a contact angle β , shown that under the stationary conditions NW's growth with a singular facet, there are the only values of the angles β and γ (the inclination angle of the crystal side surface to this facet), which correspond to the minimum increment of the free energy three-phase system $\alpha_{LV}\cos\beta + \alpha_{SL} = \alpha_{SV}\cos\gamma$ and defines the catalyst droplet's steadiness at the NW's top. With the cylindrical NWs growth, the conditions of indifferent equilibrium are realized at the drop wetting perimeter. A drop, due to the dissolution of a crystallizing substance or its separation from a liquid solution, can take an equilibrium shape with a contact angle β that does not satisfy the equilibrium contact angle condition θ in the Young equation. A concentric fracture (rib) at the NW top should increase the observed wetting angle θ and lead to contact angle hysteresis. The defined restrictions imposed on the contact angle value of a stable catalyst drop at the NW's top. The catalyst drop will take an equilibrium shape if the hysteresis angle β is in the range $\theta < \beta \leq \theta' + \gamma$ (θ' is the wetting angle of the NW side walls). For the growth of semiconductor NWs in the form of a straight cylinder, $\gamma = 90^\circ$ and therefore always $\beta > 90^\circ$. Shown that the direction of the three-phase line displacement relative to the droplet surface is determined by the growth angle φ_0 : for the nonwetting growth mode of NWs (with a cross facet) $\varphi_0 = \beta - \gamma$; for the wetting growth mode (with an end curved surface near the three-phase line) $\varphi_0 = \arccos((\alpha_{SV}^2 + \alpha_{LV}^2 - \alpha_{SL}^2) / 2\alpha_{SV}\alpha_{LV})$.

Keywords: nanowires, growth, catalyst, droplet, wetting, contact angle, semiconductor, three-phase line

UDC 548.52:539.216

Acknowledgments: The study was supported by the Russian Science Foundation grant no. 22-22-00449, <https://rscf.ru/project/22-22-00449/>.

For citation: Valery A. Nebol'sin, Vladimir A. Yuriev, Nada Swaikat, Valeria V. Korneeva, Evgeniy N. Vasnin. On the Stability of Catalyst Drops at the Vapor-Liquid-Solid Contact during the Nanowires Growth. *RENSIT: Radioelectronics. Nanosystems. Information technologies*, 2022, 14(4):381-392e. DOI: 10.17725/rensit.2022.14.381.

CONTENTS

1. INTRODUCTION (382)

2. MATERIALS AND METHODS (383)

3. RESULTS AND DISCUSSION (383)

3.1. SOLID BODY WETTING WITH A LIQUID DROPLET (384)

3.2. THE EQUILIBRIUM DROPLET AT THE NWs TOP WITH A SINGULAR CROSS FACET (385)

3.3. THE EQUILIBRIUM DROPLET AT THE NWs TOP WITH AN END CURVED SURFACE (389)

4. CONCLUSION (390)

REFERENCES (391)

1. INTRODUCTION

Semiconductor nanowires (NWs) of materials such as Si, Ge, GaAs, InSb, GaP, InAs, etc., are a perspective crystal basis for an element base creation of new generation radio-electronic devices: broadband nanoantennas of the optical range, highly sensitive nanosensors, efficient thermoelectric nanogenerators, microminiature frequency mixers and phase detectors, operating in the range up to 100 MHz at 300 K, and others [1,2]. The most widespread method NWs growing vapor-liquid-solid (VLS), in which is used a nano-sized droplets of metals in liquid-phase as a catalyst for effective collection and decomposition of precursors [3-5].

In the process of VLS growth, the NWs have a lateral crystal surface which is formed without contact with the walls of a crucible or container, such as in many other crystallization methods, which allows providing a high structural perfection of the grown crystals, rule out the appearance dislocations and the emergence of mechanical stresses. At the same time, the NW's morphology and transverse sizes are determined by the shape and volume drops of catalyst on the top of a growing crystal, also the formation conditions of the curved surface of a catalyst drop near the triple phase boundary vapor, liquid, crystal, and strongly depend on the parameters' growth process. Along with the surface energy, a key parameter, characterizing the meniscus of the liquid phase on the NW's top is the contact angle β , defined between the tangent to the surface liquid at a point on the three phases conjugation line and the end facet of NWs. The form of crystalline phase (zinc blende (ZB) or wurtzite (WZ) for nanowires AIII BV) depends on the value of the contact angle, spatial direction of growth,

crystallographic orientation (usually $\langle 111 \rangle$ for Si and Ge NWs), edge polarity (111)A or $(\bar{1}\bar{1}\bar{1})$ B GaAs NWs, etc. [6-8].

The contact angle is a controlled technological parameter, which makes the possibility to ensure stable repetition of crystals growth with a needed structure and specified electrical characteristics. However, regarding the contact angle of the catalyst drop, there is a misunderstanding and confusion in the literature of the NWs growth [9-13]. So, despite the fact that the equation $\alpha_{SL} = -\alpha_{LV} \cos\beta$, where α_{LV} and α_{SL} are specific free surface energy of interfaces liquid/vapor and crystal/liquid respectively [9], is determining the droplet equilibrium condition on the cylindrical NW's top, which wide applied and used, Recently was written a number of international works which is considering the doubts about indicated expressions and estimates of the angle β , determined by this equation [10,11,13-15]. In most of these works, the droplet contact angle at the NW's top is analyzed based on Young's equation for wetting liquid of an extended solid surface [10-12]. However, the problem is that the contact angle of the catalyst drops on top cylindrical NW is always greater than 90° and does not satisfy the contact angle condition θ in Young's equation [16]. Important works were published important work regarding a role of crystal edges [11,12,14,15,17,18] and the influence of droplet volume to the contact angle [19,20]. In works [11,12] is stated that, to describe the equilibrium wetting condition a catalyst drop of the end surface of a cylindrical crystal which limited by a three-phase line (TL), Young's equation cannot be satisfied, since it includes the specific free surface energy of crystalline phase α_{sv} , characterizing the extended surface of the solid body. Thus, the authors of [14] believe that in some cases, the equilibrium angle predicted by Young's equation can performed only at certain points

on TL. However, according to these authors, such considerations do not mean that a drop is in balance. As a result, hastily is that no conclusions about the quantities specific free surface energy interfaces based on contact angle drops of catalyst on top of the NW cannot be obtained [11,15].

Considering the fundamental angle value of the catalyst drop contact for controlled growth and physical properties of NWs, the goal of this work is the physical substantiation of wettability conditions crystalline surface limited area with a small volume liquid on the NWs top and resolution of the misunderstanding problem of equilibrium conditions for a catalyst drop with an angle contact on the end face of the crystal.

2. MATERIALS AND METHODS

Si and Si_xGe_{1-x} NWs were grown in an oven term concept (GNA, USA) by the crystallization method from the gas phase in the hydrogen chloride process using Ni and Au particles as catalysts from 200 nm. Temperature range of NW growth was 1273-1373 K. Used for growing NW H₂ was purified by modern methods and had a dew point of 215 K mixture H₂ and SiCl₄ (SiCl₄ + GeCl₄) was prepared in standard liquid sources bubbling type mole ratio components M_{SiCl4}/M_{H2} (M_{SiCl4} + GeCl₄/M_{H2}) was maintained in the range from 0.005 to 0.01. Growth substrates were polished monocrystalline silicon wafers brand KEF-20(111).ETO.0.035.TU.400±20 μm with orientation {111}. NWs Growth Rate was determined by the "time marks" method [2]. For reproducible results and exclusion of the influence of NWs on each other it is important that the crystals are isolated, those located on the substrate at a sufficient distance (~1 μm). Dependence on NW length Si and Ge on the process temperature in the range from 773 K to 1273 K crystals on the VAK-501 installation (Evatec, Switzerland) by molecular beam

epitaxy (MBE). Grown NWs were studied by transmission methods (TEM) 100-BR (Ukraine) and raster electronic microscopy JSM-6380LV (JEOL, Japan), whose resolution is less than 1-2 nm, which is sufficient to determine the NW growth rate with the required accuracy.

Information about the growth parameters of Si NWs, Ge, GaAs, etc. were also analyzed according to literary sources.

3. RESULTS AND DISCUSSION

Observations of the growth of Si, Ge and Si_xGe_{1-x} NWs, having a circular cross section show that drops of M(metal)-Si, M-Ge and M-Si Ge_{1-x} do not descend on the side surface of the NWs, and wets the vertex flat face {111}. Drop M-catalyst on the NWs top is a truncated spherical segment of an almost perfect spherical shapes (Fig. 1a,b). In this case, the contact angle value on the face {111} Si, Ge, and Si_xGe_{1-x} NWs always exceeds 90°. The NW crystallization front, as a rule, represented by a crystallographic face family {111}. With good wettability crystal surface catalyst (in systems AuAl-Si, AuGa-Si, Au-Ge, Au-Si, etc.) front crystallization is curved. On Fig. 2 shown TEM images vertices of Si NWs obtained in [22]. Under conditions of stationary growth of NWs semiconductors, a certain interface area ratio drops of SSL and SLV catalyst, consequently, constant ratio of the crystal radius and droplet radius r/R (Fig. 1a,b). Specified the ratios are obviously geometrically related to the contact angle

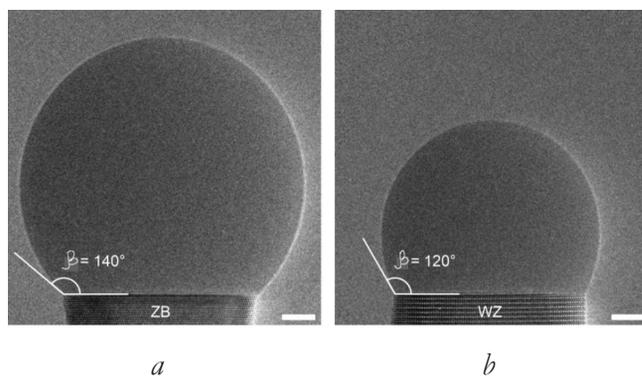


Fig. 1. TEM images of GaAs NW vertices with structure ZB (a) and WZ (b) and a singular end face [21]. Scale bars 5 nm.

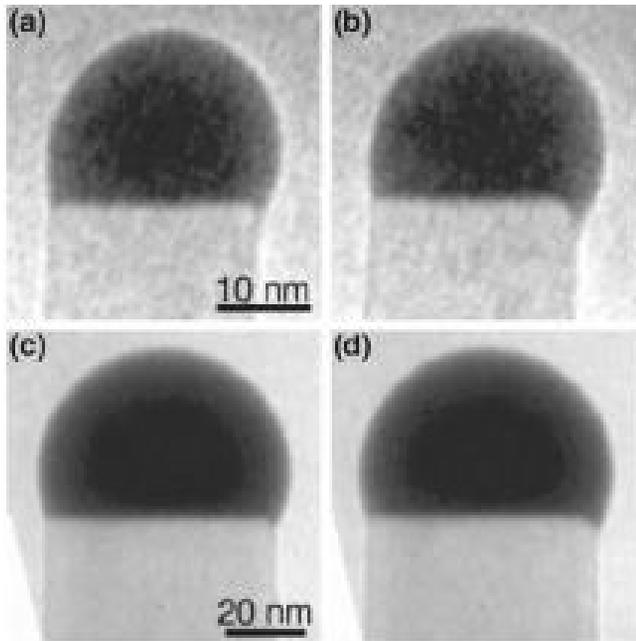


Fig. 2. TEM images of Si NW vertices with particles AuAl-Si (a, b), AuGa-Si (c, d) and curved near TL by the crystallization front [22].

of the catalyst drop β on the NW's top. In a real system, it is difficult to eliminate random variations of crystallization conditions. Therefore, random breaks and fragmentation of catalyst drops, leading to NW branching (Fig. 3a), bends crystals (Fig. 3b), movement of catalyst droplets on the side walls of the crystal (Fig. 3c).

3.1. SOLID BODY WETTING WITH A LIQUID DROPLET

It is known [23] that for all possible variations catalyst drop shape during growth NWs under conditions of constant temperature, mass and volume of phases free energy of the system

liquid-vapor-solid F must remain constant value (minimum for stable equilibrium), i.e. $\delta F = 0$. In hydrostatic approximation equilibrium the shape of the surface of the liquid drop at the top NW is described by the capillary equation Laplace [24]

$$\alpha_L \left(\frac{1}{R_1(A)} + \frac{1}{R_2(A)} \right) + \rho g w = const, \quad (1)$$

where $R_1(A)$ and $R_2(A)$ – principal radii of curvature liquid/vapor interface element ds in point A on it, ρ is the density of the liquid phase, g is the free fall acceleration, w is the height of the surface element above selected level. Radius $R_1(A) > 0$ and $R_2(A) > 0$ if positive direction normal n to the curve on the drop surface goes inside the liquid, and $R_1(A) < 0$ and $R_2(A) < 0$ if – from liquid. The w axis is directed vertically up. The value of const depends on the choice of start reference coordinate w and is equal to the pressure, under which contains a drop of catalyst in plane $w = 0$. When the origin coordinates w coincides with a flat surface liquids on a flat crystallization front, then $const = 0$.

The distribution of the liquid is a peculiar mechanism of its creeping onto hard surface. Considering it, it's easy to understand that if the drop is on the surface solid body, then a complete change in the free energy of the system is expressed as [25]

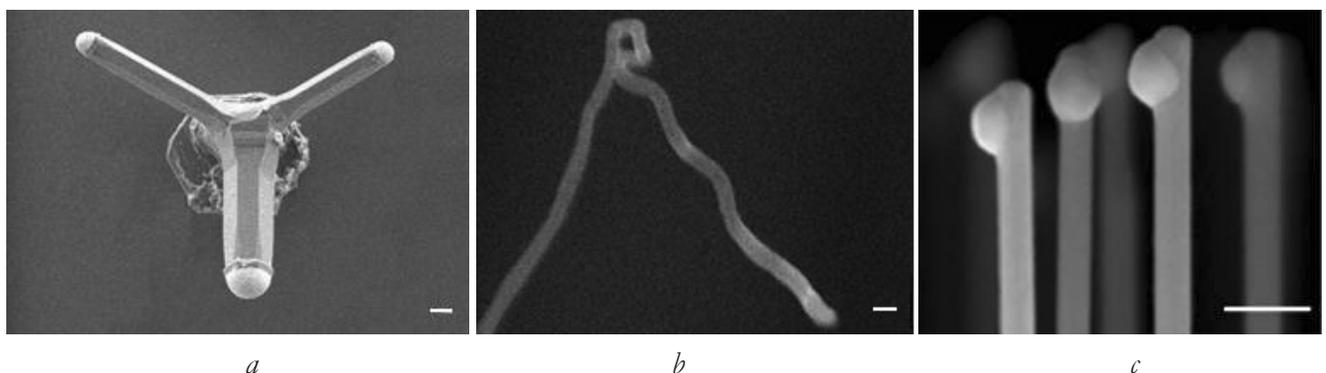


Fig. 3. Uncontrolled PEA growth: (a) NWC Si_xGe_{1-x} with droplet rupture and crystal branching, (b) Si NWs with bends, (c) InAs NWs with droplet migration to the side walls [11]. Scale bars 100 nm.

via nucleation and growth in the tangential direction of steps of monoatomic height b . Let the steps be generated or absorbed TL in such a way that the emergent of the side surface of the NW at point A is inclined to the horizontal, i.e. to the singular face $\{111\}$, at an angle γ (Fig. 4a). Then, when varying the drop height single crystal layer b crystal lengthens by $l_s = b/\sin\gamma$, $\{111\}$ face of the front crystallization is grow down by $l_{SL} = l_s \cos\gamma$, and the surface of the drop is reduced by $l_L = l_s \cos(\beta - \gamma)$.

Change in free energy F_s , associated with a change in the areas of three adjacent surfaces when the TL is displaced from point A to point B will be [26]

$$F_s = 2\pi r (\alpha_s l_s - \alpha_{SL} l_{SL} - \alpha_L l_L), \quad (5)$$

or per unit length TL

$$F_s = \frac{h}{\sin\gamma} [\alpha_s - \alpha_{SL} \cos\gamma - \alpha_L \cos(\beta - \gamma)]. \quad (6)$$

In expression (5), through $2\pi r l$ (l with indices S, L, SL) marked by the area increment phase boundaries crystal/vapor S , liquid/vapor L and solid/liquid SL , respectively. Sign "-" before the second and third terms in (6) means when TL is displaced from the point A to point B corresponding surface decreases.

Further, to simplify in expression (6) denote $\alpha = F_s/b$. Then the change in specific free surface energy $\Delta\alpha$ three-phase system when absorbing a step (calculated per unit of length TL and per one the absorbed step with height b) can be written as

$$\Delta\alpha = \alpha - \alpha_{SL}. \quad (7)$$

It consists of a term $-\alpha_{SL}$ (disappearance steps) and the term α associated with the change areas of all three adjacent surfaces [26]. If $\Delta\alpha < 0$, then single-crystal steps can be absorbed (generated) by the line separation of three phases, forming a side surface NWs at an angle γ . This is possible if $\varphi_0 < \theta$, where φ_0 – corner inclination of the segmental surface of the drop to the displacement direction of the

line of three phases. Then the drop will move at an angle, sliding down along the step of the formed crystalline layer, reducing the area of its wetting. Drop wetting perimeter will decrease. With such a displacement of the drop changes the location of all three adjacent surfaces near TL, as a result of which is the increase in the angle of inclination of the segmental surface of the catalyst drop at point A on the wetting perimeter to the NW growth axis φ , and, respectively, φ_0 to equilibrium θ values.

To fix the condition $\Delta\alpha < 0$, the angle contraction (expansion) NW γ must correspond to minimum free energy of three-phase system after the absorption of the monolayer by the height b , i.e. meet the minimum value α . The minimum value $\alpha = \alpha_{\min}$ is reached, when for all possible variations of the form liquid surface (while maintaining its volume) free energy F_s remains constant value (minimum for stable equilibrium), i.e. at $dF_s/d\gamma = 0$.

Differentiating (6) to the angle γ and equating zero derivative, we obtain the condition where the minimum $F_s(\gamma)$ is reached

$$\alpha_{LV} \cos\beta + \alpha_{SL} = \alpha_{SV} \cos\gamma. \quad (8)$$

Expression (8) is mechanical balance of forces corresponding to free surface energies of three phases in point A on the wetting perimeter. Equation (8) obtained under the assumption that it is not taken into account free surface anisotropy energies of lateral i -faces of NWs $\left(\sum_i \frac{\partial\alpha_s^i}{\partial\gamma} = 0\right)$, the contribution of the linear tension is neglected, and the volume of the catalyst droplet V_L in the process NW growth remains constant ($dV_L = 0$), that it must be done the requirement for absolute rigidity of a solid body and its insolubility in liquid. Condition constant volume of liquid catalyst drop and insolubility in it crystallized material can be admitted if we consider stationary process of NW growth at $T = \text{const}$ in the absence of chemical carryover and physical evaporation

of the material of the liquid phase, as well as not take into account the loss of metal due to dissolution in solid state and surface diffusion.

From expression (8) it follows that in each time point of NW growth with a transverse singular face, there are only the values of the angles γ and β , i.e. actually implemented such an angle of contraction (expansion) of the crystal γ and such a drop contact angle β that correspond to the minimum increment free energy of a three-phase system after absorption monolayer height b

$$\gamma = \arccos\left(\frac{\alpha_{LV} \cos \beta + \alpha_{SL}}{\alpha_{SV}}\right). \tag{9}$$

Thus, for constant values specific free energy of boundaries phase separation α_{SV} , α_{LV} and α_{SL} and when performing above requirements contact angle γ is nonlinearly related to the angle β (Table 1). Offset direction TL relative to the surface of the drop at point A on the dividing line of three phases adjacent to transverse singular face $\{111\}$ of the front crystallization, will be determined by the angle $\varphi_0 = \beta - \gamma$, which we will call the growth angle (crystallization) NW, which, in turn, can be found from the expression

$$\varphi_0 = \beta - \arccos\left(\frac{\alpha_{LV} \cos \beta + \alpha_{SL}}{\alpha_{SV}}\right). \tag{10}$$

It must be said that the growth angle φ_0 (10) should not be confused with contact angle θ . Corner wetting characterizes partial equilibrium relative to the movement of a liquid through a solid body and, in contrast to φ_0 , not directly associated with the process of crystal growth. As the angle β increases in the interval $0 \leq \beta \leq 1800$, the angle γ also increases.

Table 1

Calculated values of the angle γ depending on the angle β for the Au–Si system for $\alpha_{SV}\{111\} = 1.23 \text{ J/m}^2$ and $\alpha_{LV} = 0.91 \text{ J/m}^2$

β , degree	90	100	110	120	130	140	150	160	170	180
θ , degree	-	-	0	32	45	54	61	66	68	69

For $\gamma = 0$ in according to (8) and (9), we obtain the condition equilibrium of a drop lying on a horizontal extended surface (Fig. 4c)

$$\alpha_{LV} \cos \beta + \alpha_{SL} = \alpha_{SV}, \tag{11}$$

those, known Young equation for mechanical equilibrium of a drop on a flat surface (at $\beta = \theta$). Displacement of TL from the equilibrium position here can only be carried out at an angle θ horizontally along an extended solid surfaces.

At $\gamma = 90^\circ$, from (8) follows the growth condition cylindrical NWs of constant diameter (see expression (2) for $g = 0$ and $V_L = \text{const}$) [6]

$$\alpha_{SL} = -\alpha_{LV} \cos \beta = \alpha_{LV} \sin \varphi. \tag{12}$$

Expression (12) reflects the equilibrium form drops of catalyst on top of a growing NWs in a state of indifferent equilibrium on the wetting perimeter. Through the dissolution crystallizable substance or its excretion from a liquid solution of a drop of M -catalyst on at the top of the NWs, the wetting perimeter of the drop is not fixed, and the latter can take balanced form.

From (12) it follows that under conditions of indifferent equilibrium on the wetting perimeter on a round contour at the point of contact with the NW end face A the drop must form a fixed equilibrium angle $\beta = \text{const}$ (or $\varphi = \text{const}$) with the surface of the crystal. Therefore, than the larger the droplet radius R , the larger should be the radius r of the NW:

$$\frac{r}{R} = \sqrt{1 - \left(\frac{\alpha_{SL}}{\alpha_L}\right)^2} = \sqrt{1 - \sin^2 \varphi} = \sqrt{1 - \cos^2 \beta}. \tag{13}$$

Thus, the equilibrium form drops on top of the NWs is the result of aspirations of her free superficial energy to a minimum and directly related with its liquid-phase state of aggregation. Here the shape of the drop reaches a stable equilibrium, which ensures self-stabilization of dimensions and cross-sectional shapes of NWs in the process growth.

According to equation (13), the condition minimum free surface energy of an equilibrium drop at the top NWs is proportionality specific free surface energy segments of liquid/vapor interfaces and liquid/solid their distances up to drop center. The more free energy section of the interphase boundary, the farther it located from the center of the drop and the smaller it has a surface.

If a three-phase system due to kinetic limits cannot be reached or maintained the only values of the equilibrium angles γ and β defined by expression (9), then for ensure the indifferent balance of the drop at the top of the NW, the contact angle β must meet the following conditions

$$\begin{cases} \alpha_{LV} \cos \beta \leq \alpha_{LV} \cos \theta \\ \alpha_{LV} \cos(\beta - \delta) \geq \alpha_{LV} \cos \theta' \end{cases} \quad (14)$$

Passing from cosines, directly, to corners, we have

$$\theta \leq \beta \leq \theta' + \gamma \quad \text{при } \gamma > 0 \quad (15)$$

or

$$\theta - \gamma \leq \beta - \gamma \leq \theta' \quad \text{при } \gamma < 90^\circ. \quad (16)$$

Similarly, for $\gamma = 90^\circ$ and $\beta - 90^\circ = \varphi$ we have

$$\theta - 90^\circ \leq \varphi \leq \theta' \quad (17)$$

or

$$\theta \leq \varphi + 90^\circ. \quad (18)$$

The first non-strict inequality in (14) determines the boundary condition under which the drop cannot slide along the transverse singular face, increasing the perimeter wetting and decreasing the contact angle. The second inequality (14) specifies the condition at which the drop cannot fall on lateral surface of the NW. In this way, for the equilibrium position of the drop at $\theta < 90^\circ$ and $\gamma > 0$ contact angle β must be in the interval from θ to $\theta' + \gamma$. Therefore, on singular extended substrate, when $\gamma = 0$, the equilibrium angle β is fixed: $\beta = \theta$ or $\beta = \theta'$, depending on the orientation.

Within the limits specified in inequalities (14) - (18) the range of angle change β drop can maintain an indifferent balance wetting perimeter. This combination phases in practice gives a continuous range contact angle values. Theoretically, in according to contact angle hysteresis maximum contact angle $\beta = \beta_A$ ($\beta_A = \theta' + \gamma$) is called the leakage angle, and the minimum wetting angle $\beta = \beta_R$ - receding angle. For example, for the data in Table 1 $\theta = 35^\circ$ and $\beta_A = 125^\circ$. Next, we explain the occurrence droplet wetting hysteresis at the top NWs.

Let a drop of liquid catalyst spreads spontaneously crystal surface, which is the vertex face of the NW $\{111\}$, in the x direction (Fig. 5). Free surface energy of a three-phase system F_s in this process should decrease: $dF_s/dx < 0$. In this case, will continuously decrease and droplet contact angle $\beta = f(x) \cdot (d\beta/dx < 0)$. For smooth face $\{111\}$ this condition is satisfied all the way. Let now on a smooth surface face has a concentric fracture (edge) in the form of a circle. Tilt angle the outer edge of the fracture to the horizon can be arbitrary, but in the case of growth of NWs of constant diameter it is 90° . At the presence

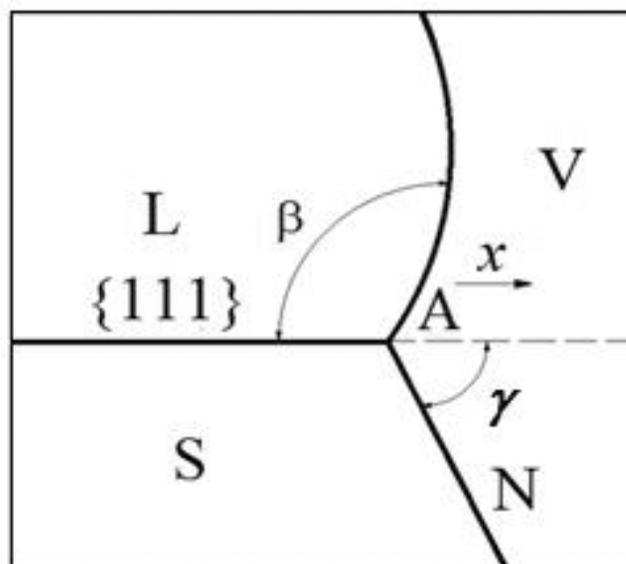


Fig. 5. Stopping the contour of a spreading drop at concentric break AN (edge) on the end face $\{111\}$ NWs.

of a fracture on the periphery of the end faces {111} for droplet spreading situation is complicated, since when fluid flows behind fracture increases its surface area stronger than when moving the TL along a smooth surface along the x direction (dotted line in Fig. 5). The power of the surface tension acts in relation to new direction of spreading AN under angle $(\beta - \gamma)$. Fracture resistance can be overcome by a drop only on condition that the angle formed by the surface liquid and the outer surface of the fracture (NW side surface) $(\beta - \gamma)$, more contact angle θ between the drop surface liquid and smooth solid surface. Using equation (12), one can find overflow condition: $\beta > (\theta' + \gamma)$. For $\beta < (\theta' + \gamma)$ the break at the top of the NW is an insurmountable barrier to cross TL can only under external influences (e.g. vibrations) or rather strong energy fluctuations near TL. From here, the contact angle of leakage on side surface of NWs: $\beta_A = \theta' + \gamma$.

Under conditions where $\beta > (\theta' + \gamma)$, the drop falls on the side walls of the NW. Sank at this wetting perimeter provides the possibility of growth expanding to top of the crystal. As a result of growth expanding crystal contact angle side surface will decrease and, in the limit, reaches the receding angle on the side face $\beta_R = \theta - \gamma$. As a result, TL is inevitable should rise to the edge (break) of the crystal. For $\gamma = 90^\circ$, this edge is line of intersection of the transverse singular NW faces with a set of faces crystallographic belt having axes, parallel to the NW axis.

However, if the contact angle θ' of the drop catalyst saturated with crystallizable substance exceeds 90° , then at $\gamma = 90^\circ$ the drop is unable to land on side surface of NWs, because in this case $\beta = \beta_A > 180^\circ$. This means the absence contact of the catalyst drop with the crystal.

Thus, a concentric fracture on top of the NW should increase the observed contact angle

(during leakage), which is noted in experience. Available at the top of the NWs hysteresis of the contact angle appears or wettability hysteresis.

It must be said that the occurrence during the growth of NWs significant temperature gradients, significant fluctuations in the flows of crystallized substances, concentration disturbances can remove the drop at the top of the NW from the state indifferent equilibrium (14) and lead to irreversible consequences (fragmentation drops and branching NNK, creeping drops on the lateral surface of the crystal, bends and changes in spatial direction of growth, sharp jumps in diameter and others (Fig. 3)).

3.3. THE EQUILIBRIUM DROPLET AT THE NWs TOP WITH AN END CURVED SURFACE

Equilibrium on the wetting perimeter drops of catalyst can be obtained by growing NWs with a curved near TL end surface (Fig. 2). If for NW with a curved end surface write down the components of the projections of force vectors, corresponding free surface energies of the interfaces α_{SV} , α_{LV} and α_{SL} in point A on the TL to the continuation direction the existing side surface of the NWC, and also in a direction perpendicular to it, in form of a system of equations and express the angle φ_0 in explicitly, we get the expression

$$\varphi_0 = \arccos \left(\frac{\alpha_{SV}^2 + \alpha_{LV}^2 - \alpha_{SL}^2}{2\alpha_{SV}\alpha_{LV}} \right). \tag{19}$$

Expression (19) characterizes the growth angle (crystallization) NW φ_0 in full balance of forces on the wetting perimeter (Fig. 6). This state of steady equilibrium can only be realized when good wettability of the crystalline surface with a drop of catalyst ($\theta < 90^\circ$). For the values of the Au-Si system $\alpha_{SV}\{110\} = 1.50 \text{ J/m}^2$, $\alpha_{LV} = 0.91 \text{ J/m}^2$ and $\alpha_{SL} = 0.75 \text{ J/m}^2$ [4,9] from expression (19) we obtain the value growth (crystallization) angle of NWs $\varphi_0 = 23.5^\circ$.

- and electronic properties of InSb nanocrosses. *Nat. Nanotechnology*, 2013, 8(11):859-864.
- Kammhuber J, Cassidy MC, Pei F, Nowak MP, Vuik A, Gül Ö, Car D, Plissard SR, Bakkers EP, Wimmer M, Kouwenhove LP. Conductance trough a helical state in an Indium antimonide nanowire. *Nat. Nanotechnology*, 2017, 8(1):478-484.
 - Wagner RS, Ellis WC. Vapor-liquid-solid mechanism of single crystal growth. *Appl. Phys. Lett.*, 1964, 4(5):89-95.
 - Givargizov EI. Fundamental aspects of VLS growth. *J. Cryst. Growth*, 1975, 31:20-30.
 - Güniat L, Caroff P, Fontcuberta i Morral A. Vapor Phase Growth of Semiconductor Nanowires: Key Developments and Open Questions. *Chem. Rev.*, 2019, 119(15):8958-8971.
 - Yuan X, Caroff P, Wong-Leung J, Fu L, Tan H H, Jagadish C. Tunable Polarity in a III-V Nanowire by Droplet Wetting and Surface Energy Engineering. *Adv. Mater.*, 2015, 27(40):6096-6199.
 - Tornberg M, Dick KA, Lehmann S. Thermodynamic Stability of Gold Assisted InAs Nanowire growth. *J. Phys. Chem. C*, 2017, 121:21678-21684.
 - Jacobsson D, Panciera F, Tersoff J, Reuter MC, Lehmann S, Hofmann S, Dick KA, Ross FM. Interface dynamics and crystal phase switching in GaAs nanowires. *Nature*, 2016, 531:317-339.
 - Nebol'sin VA, Shchetinin AA. Role of Surface Energy in the Vapor-Liquid-Solid Growth of Silicon. *Inorg. Mater.*, 2003, 39(9):1050-1055.
 - Dubrovskii VG. Development of Growth Theory for VLS NWs: Contact Angle, Facets, Crystal Phase. *Cryst. Growth Des.*, 2017, 17(5):2544-2548.
 - Ghisalberti L, Potts H, Friedl M, Zamani M, Güniat L, Tütüncüoğlu G, Carter WC, Fontcuberta i Morral A. Questioning liquid droplet stability on nanowire tips: from theory to experiment. *Nanotechnology*, 2019, 30:285604-285613.
 - Nebol'sin V, Levchenko EV, Swaikeat N, Yuryev V. About a fundamental uncertainty of the contact angle of the catalyst drop on the top of the nanowire. *J. Appl. Phys.*, 2021, 129:164302-164314.
 - McIntyre PC., Fontcuberta i Morral A. Semiconductor nanowires: to grow or not to grow? *Mater. Today Nano*, 2020, 9:100058-100065.
 - Krogstrup P, Curiotto S, Johnson E, Aagesen M, Nygård J, Chatain D. Impact of the Liquid Phase Shape on the Structure of III-V Nanowires. *Phys. Rev. Lett.*, 2011, 106:125505.
 - Fang G, Amirfazli A. Understanding the Edge Effect in Wetting: A Thermodynamic Approach. *Langmuir*, 2012, 28:9421-9430.
 - Young T. An Essay on the Cohesion of Fluids. *Philos. Trans. Roy. Soc. London*, 1805, 95:65-87.
 - O'Dowd BJ, O'Dowd1 BJ, Wojtowicz T, Rouvimov S, Liu X, Pimpinella R, Kolkovsky V, Wojciechowski T, Zgirski M, Dobrowolska M, Shvets IV, Furdyna J. Effect of catalyst diameter on vapour-liquid-solid growth of GaAs nanowires. *J. Appl. Phys.*, 2014, 116 063509.
 - Schmidt V, Wittemann JV, Senz S, Gösele U. Silicon Nanowires: A Review on Aspects of their Growth and their Electrical Properties. *Adv. Mater.*, 2009, 21(25-26):2681-2702.
 - Jacobsson D, Panciera F, Tersoff J, Reuter MC, Lehmann S, Hofmann S, Dick KA, Ross FM. Interface dynamics and crystal phase switching in GaAs nanowires. *Nature*, 2016, 531:317-339.

20. Kolíbal M, Vystavěl T, Varga P, Šikola T. Real-Time Observation of Collector Droplet Oscillations during Growth of Straight Nanowires. *Nano Lett.*, 2014, 14:1756.
21. Panciera F, Baraissov Z, Patriarche G, Dubrovskii VG, Glas F, Travers L, Mirsaidov U, Harmand J-C. Phase selection in self-catalysed GaAs nanowires. *Nano Lett.*, 2020, 20(3):1669-1675.
22. Wen C-Y, Tersoff J, Hillerich K, Reuter MC, Park JH. Periodically Changing Morphology of the Growth Interface in Si, Ge, and GaP Nanowires. *Phys. Rev. Lett.*, 2011, 107:025503-025507.
23. Nebol'sin VA, Suyatin DB, Dunaev AI, Shmakova SS, Zavalishin MA, Ivannikova EV. Contribution of the Free Energy of the Three Phase Line of Contact to the Thermodynamic Equilibrium Conditions of a Metal Solvent Droplet in Si and Ge Whisker Growth. *Inorg. Mater.*, 2015, 51(3):191-196.
24. Landau LD, Lifshitz EM. Mekhanika sploshnykh sred [Continuum mechanics]. Moscow, Gostekhteorizdat Publ., 1953, 737 p.
25. Gibbs DV. *Thermodynamic works*. Moscow-Leningrad, GITL Publ., 1950, 492 p.
26. Nebol'sin VA, Dunaev AI, Tatarenkov AF, Shmakova SS. Scenarios of Stable VLS Nanowire Growth. *J. Cryst. Growth*, 2016, 450:207-214.