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Arrays of Quasi-One-Dimensional GaAs Nanocrystals Grown on the Oxidized Surface of the Si/GaAs(001) Heterostructure: Effect of the Si Epitaxial Layer on the Array Structure

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Structures with arrays of planar and tilted quasi-one-dimensional GaAs nanocrystals have been grown on GaAs(001) substrates. An epitaxial silicon layer oxidized in air was used as a passivation coating. The amount of silicon deposited varied from structure to structure and was equivalent to 1, 2, 4, and 6 atomic layers. It has been found that in the case of a passivation layer based on silicon with a thickness of 1 atomic layer, an array of planar nanocrystals is formed, and in other cases, inclined quasi-one-dimensional nanocrystals. Nanocrystals are surrounded by crystallites, the shape, size, orientation, and distribution density of which change with the amount of silicon. The lowest density of crystallites was achieved with a silicon layer 6 atomic layers thick.

Keywords: molecular-beam epitaxial, GaAs, Si, quasi-one-dimensional nanocrystals, vapour−liquid−crystal.

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The size and shape of $A^{III}B^{V}$ nanowires (NWs), which are crystals with high length-to-diameter ratios, translate into unique physical properties. Both individual NWs and their arrays are regarded as promising materials for advanced semiconductor devices and objects for fundamental physical research [1].

$A^{III}B^{V}$ NWs may be grown in the vapor−liquid−solid (VLS) system using the molecular beam epitaxy (MBE) technology [2]. The VLS mechanism is realized if a liquid catalyst droplet is present at the NW growth front [3–6]. It is known that atoms of gold, which often serves as such a catalyst, form nonradiative recombination centers in $A^{III}B^{V}$ materials [7]. Self-catalyzed growth of crystals (with a group III element found in an $A^{III}B^{V}$ compound acting as a catalyst) solves this problem [8].

The substrate surface prepared for self-catalyzed growth of $A^{III}B^{V}$ NWs needs to be passivated. This passivation layer (mask) resists the MBE process and provides an opportunity to set specific sites for initiation of VLS growth. Silicon oxide often acts as a mask. Masks on Si substrates are produced by oxidizing the silicon surface in air [9] or in certain specific environments [10]. In the case of $A^{III}B^{V}$ substrates, masks are formed by plasma-chemical deposition [8] or annealing of organosilicon films on a substrate [11]. A method for surface passivation by oxidation in air of an epitaxial Si film grown by MBE on GaAs (100) and (111)*B* surfaces was proposed in [12,13]. An epitaxial Si film was oxidized at 300°C in [12] and at room temperature in [13]. The authors of [8,9] have demonstrated that the thickness of a silicon oxide film is the parameter governing the quality of a NW array grown on Si substrates. In view of this, masks based on epitaxial Si grown by MBE on $A^{III}B^{V}$ substrates are of special interest, since they provide an opportunity to control the amount of deposited silicon with an accuracy down to a single atomic layer.

NWs may be positioned in the substrate plane [4] or at a certain angle to it [3]; the specifics of positioning have a significant effect on their physical properties and applicability. The issues of fabrication of vertical NWs have been discussed thoroughly [3]. Planar nanorods (PNRs) were regarded as second-rate objects [4]. However, PNRs were found to be promising in terms of application in the standard planar technology for fabrication of semiconductor devices of various purpose [14].

The methods and conditions of fabrication of perfect arrays of planar and non-planar NWs of $A^{III}B^{V}$ compounds by self-catalytic VLS growth are still being studied theoretically and experimentally. The present study is focused on examining the influence of thickness of a mask based on an oxidized epitaxial silicon layer on the structure of a GaAs NW array grown with the use of fluxes of Ga atoms and As_4 molecules on GaAs substrates that deviate by no more than 0.1° from face (001).

Four structures (St1, St2, St3, St4) with NW arrays, which differed only in the amount of silicon deposited by MBE to form a mask, were grown. The thickness of epitaxial silicon films (d_e) expressed in atomic layers (AL) was 1, 2, 4, and 6 AL in St1, St2, St3, and St4, respectively. Samples were grown using a „Shtat“MBE setup for $A^{III}B^{V}$ compounds. A buffer GaAs layer 0.32 μm in thickness was grown first, and an epitaxial silicon layer was then formed

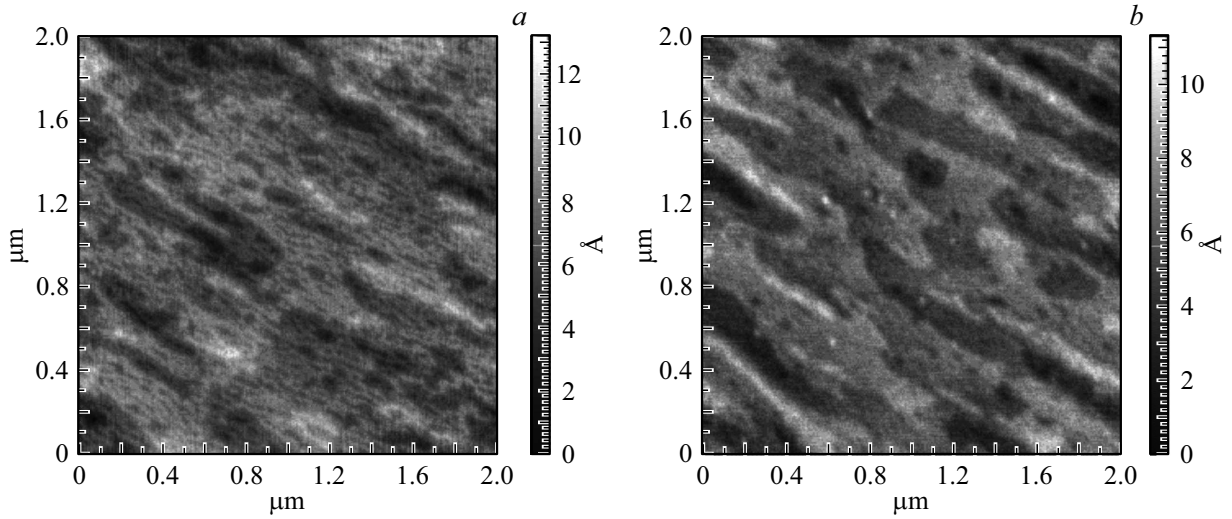

Figure 1. AFM images of the GaAs(001) surface covered with a mask based on an oxidized epitaxial silicon film with thickness $d_e = 1$ (*a*) and 6 AL (*b*).

on top of it at a temperature of 510°C. At the next stage, silicon was oxidized in a lock chamber in air atmosphere at room temperature. NWs were grown on the masked surface with the use of fluxes of Ga atoms and As_4 molecules at a temperature of 620°C. The flux density of Ga atoms was $1.6 \cdot 10^{14}\,\mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$, and the ratio of equivalent pressures in molecular fluxes As_4/Ga was ~ 20. The NW growth time was 15 min. The surface state was monitored by reflected high-energy electron diffraction at all stages (except for the oxidation process). The process and procedure specifics were detailed in [13]. Grown structures were examined with a Hitachi SU8220 scanning electron microscope (SEM).

Thin Si films grow epitaxially on a GaAs(001) surface (see, e.g., [15]). They remain smooth up to a thickness on the order of 6 AL and do not exert any significant influence on the initial surface relief. Figure 1 shows the GaAs(001) substrate surface imaged with an atomic force microscope (AFM) after deposition and oxidation of a Si layer with $d_e = 1$ (*a*) and 6 AL (*b*). The lateral non-uniformity of the oxidized epitaxial silicon layer in Fig. 1, *a* becomes significantly less pronounced when the film thickness increases to 6 AL (Fig. 1, *b*).

Figures 2, *a*–*c* present SEM images of the St1 surface with $d_e = 1$ AL. The structure contains an array of PNRs aligned with direction $[\bar{1}10]$. The array density is $\sim 7.8 \cdot 10^7\,\mathrm{cm}^{-2}$ for nanocrystals with a characteristic length of ~ 700 nm, a base width of ~ 200 nm, and a height of ~ 150 nm. The directions of PNR growth (indicated with white arrows in Fig. 2, *a*) match directions $[\bar{1}10]$ and $[1\bar{1}0]$. The faceting and orientation of grown PNRs agree well with literature data (e.g., [16]). The crystallographic directions of samples St1–St4 were determined by referencing their cleaved faces to the superstructure cell (2×4) on GaAs(001) observed *in situ* in the growth setup by reflected high-energy electron diffraction. PNRs are surrounded by smaller GaAs nanocrystals (nanocrystallites) of an irregular shape with no clear faceting (Fig. 2, *b*). These nanocrystallites have a height of $\leqslant 12$ nm and lateral dimensions ranging from ~ 12 to ~ 50 nm. Their density is $\sim 1.2 \cdot 10^{11}\,\mathrm{cm}^{-2}$. The surface also has isolated agglomerates of nanocrystals that are similar in faceting and orientation to PNRs, but are significantly smaller in size (outlined with white dashed curves in Fig. 2, *a*).

SEM images of the St2 surface with $d_e = 2$ AL are presented in the left column in Fig. 3. Long (with a characteristic length of 900–1200 nm at a thickness of ~ 40 nm) inclined NWs aligned with directions $\langle 111\rangle A$ are dominant. The density of these inclined NWs is $\sim 2.9 \cdot 10^8\,\mathrm{cm}^{-2}$. Shorter inclined NWs with a density of $\sim 3.3 \cdot 10^8\,\mathrm{cm}^{-2}$ oriented along $\langle 111\rangle B$ are also present. In addition to long and short inclined NWs, one sees an array of crystallites of irregular shapes and sizes stretching in direction $[\bar{1}10]$ with a density of $\sim 4.2 \cdot 10^8\,\mathrm{cm}^{-2}$. Their longitudinal and transverse dimensions fall within the ranges of 170–690 and 60–170 nm, respectively.

The presence of inclined NWs with orientation $\langle 111\rangle A$ was not expected. It is known from literature [16] that the direction of VLS growth of GaAs NWs is set by faces $\{111\}B$; thus, inclined NWs on GaAs(001) grow in directions $\langle 111\rangle B$. The probable reasons behind the emergence of inclined NWs oriented along $\langle 111\rangle A$ are discussed below.

SEM images of the St3 surface with $d_e = 4$ AL are presented in the center column in Fig. 3. The length of inclined NWs with orientation $\langle 111\rangle A$, which form the primary NW array, falls within the range from 1000 to 1470 nm, while their thickness is ~ 60 nm. The density of these NWs is $\sim 1.7 \cdot 10^8\,\mathrm{cm}^{-2}$. The population of inclined NWs with orientation $\langle 111\rangle B$ is small compared to the primary array. Their density does not exceed $\sim 1.6 \cdot 10^7\,\mathrm{cm}^{-2}$. In addition to inclined NWs, the surface has an array of elongated nanocrystallites lying in the substrate plane. They have

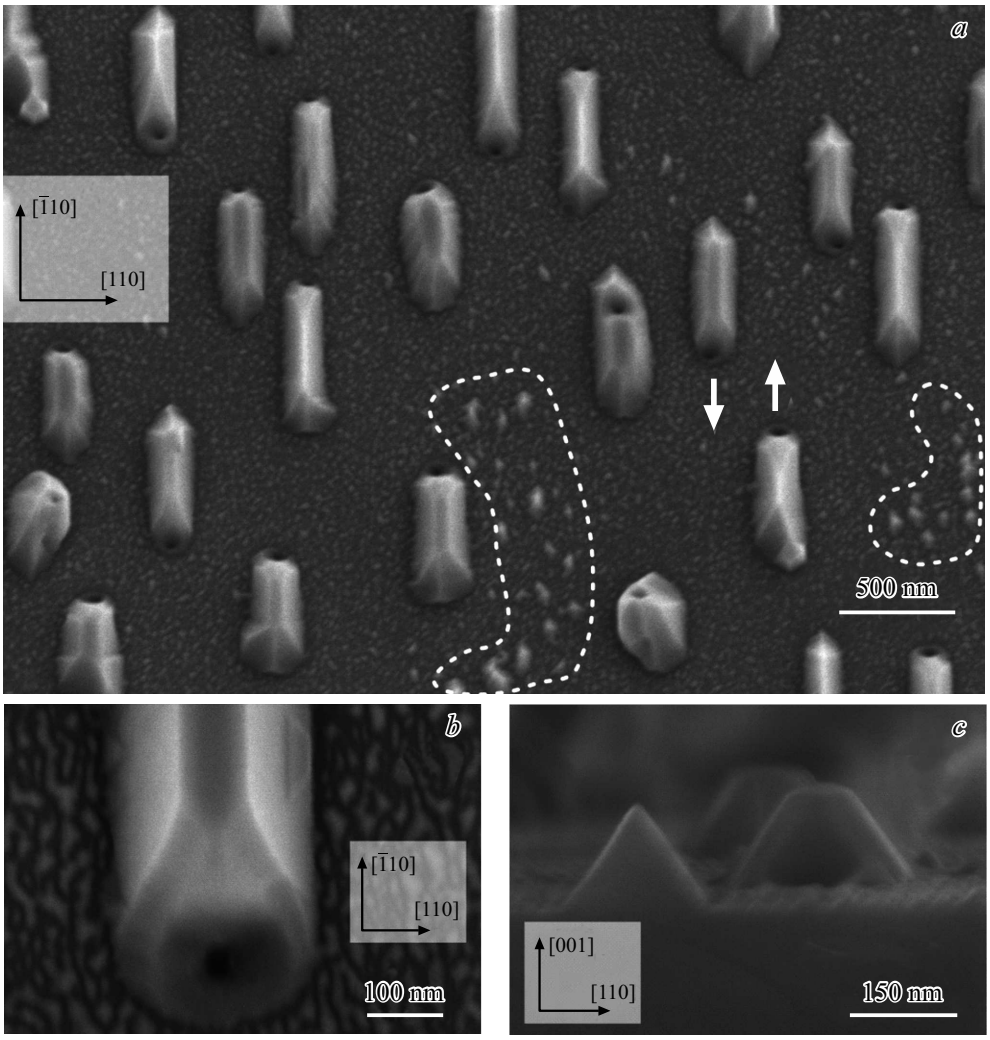

Figure 2. SEM images of the surface of structure St1. *a* and *b* — top view, *c* — sectional view.

irregular lateral dimensions (longitudinal: 240–580 nm; transverse: 80–190 nm), shape, and orientation. Their estimated density is close to $\sim 1.5 \cdot 10^8$ cm^{-2}.

The St4 surface with $d_e = 6$ AL is populated primarily by inclined NWs with orientation $\langle 111 \rangle A$ (right column in Fig. 3). The length varies from 200 to 530 nm at a thickness of ~ 40 nm. The density of these NWs is $\sim 2.7 \cdot 10^8$ cm^{-2}. Nanocrystallites with lateral dimensions no greater than 330×140 nm and a density of $\sim 4 \cdot 10^7$ cm^{-2} are also observed.

It was established in the present study that the structure of forming NW arrays depends to a considerable extent on the thickness of an epitaxial silicon film. Specifically, PNRs oriented along [$\bar{1}$10] and [1$\bar{1}$0] nucleate and grow on GaAs(001) substrates with a mask based on an epitaxial silicon film with a thickness of ~ 1 AL. Inclined NWs oriented both in $\langle 111 \rangle A$ and in $\langle 111 \rangle B$ directions form in all the other cases. The surface density of inclined NWs with orientation $\langle 111 \rangle A$ varies only slightly from sample St2 to sample St4, while the density of inclined NWs with orientation $\langle 111 \rangle B$ decreases by more than two orders of magnitude. Arrays of crystallites with their morphology, size, and surface density being dependent on the epitaxial Si layer thickness form alongside inclined NWs. The density of crystallites decreases by an order of magnitude as d_e increases from 2 to 4 and further to 6 AL.

The dependence of the observed structural features of NW arrays (specifically, the presence of inclined NWs with orientation $\langle 111 \rangle A$) and their environment on the initial thickness of the epitaxial silicon layer may be induced by the following factors. First, oxidation of epitaxial silicon films is limited to the uppermost (1–3) atomic layers [13]. A layer of Si atoms, which are bound directly to As or Ga atoms of a GaAs substrate, between silicon oxide and GaAs is presumably retained in the process. This assumption is based on the results reported in [17,18]. Second, liquid gallium has the capacity to dissolve both silicon oxides and epitaxial silicon layers. Third, the sequential order of layers of Ga and As atoms in the upper epitaxial GaAs layer in a GaAs/Si/GaAs(001) heterosystem changes relative

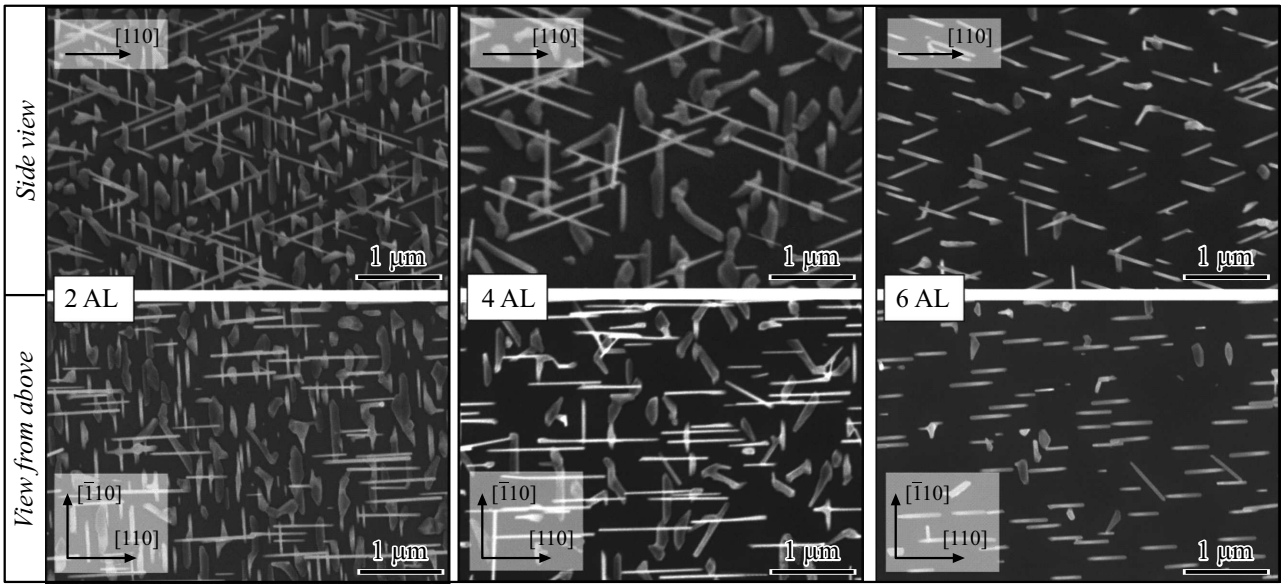

Figure 3. SEM images of the surface of structures with a mask based on a silicon layer with a thickness of 2 AL (left column), 4 AL (center column), and 6 AL (right column). Upper images — side view at an angle of $\sim 30^\circ$ to plane (001); lower images — top view.

to the sequential order of atoms in a GaAs(001) substrate depending on the number of silicon layers (N) [19].

In the present case, an epitaxial layer of Si atoms formed on a Ga-stabilized GaAs(001) surface [13]; therefore, silicon atoms from the substrate side are bound to gallium atoms. GaAs nucleation on the Si film surface proceeds below a Ga droplet under the conditions of strong depletion in arsenic, which gives rise to a .../As/Ga/Si/... heterojunction. At odd N values, a sequence of layers .../As/Ga/Si_{As}/... /Si_{Ga}/Si_{As}/Ga/As/... forms; at even N, the sequence is .../As/Ga/Si_{Ga}/.../Si_{Ga}/Si_{As}/Ga/As/.... Here, symbols Si_{As} and Si_{Ga} denote layers of silicon atoms positioned in place of layers of arsenic and gallium atom layers, respectively. Since the direction of self-catalyzed VLS growth of GaAs NWs is set by faces $\{111\}B$, it is fair to assume that the direction of NW growth in the reference frame of a substrate with a mask based on oxidized epitaxial Si/GaAs(001) layers should be specified by the parity of the number of Si layers remaining on the GaAs surface after dissolution of silicon oxide. Inclined NWs with orientation $\langle 111\rangle B$ nucleate if zero (or an odd number) of Si layers remain below a droplet, while orientation $\langle 111\rangle A$ corresponds to an even number of Si layers.

In the case of St1, gallium droplets moved along the heterostructure surface, presumably dissolving completely an extremely thin masking layer below them. This violated the conditions of formation of inclined NWs and triggered the growth of PNRs. The lateral non-uniformity of the mask (Fig. 1, *a*) probably facilitated its dissolution. It is likely that this non-uniformity was also conducive to the formation of an array of small nanocrystallites (Fig. 2, *b*), which are not observed for other samples. An increase in the amount of deposited silicon (to 2 AL and above) induces a qualitative change in the effect of interaction of gallium droplets with the mask and the crystal surface free from oxide. In the case of masks based on epitaxial silicon films thicker than 2 AL, the properties of the SiO_x/Si/GaAs system become similar to those of SiO_2/Si.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] E. Barrigón, M. Heurlin, Z. Bi, B. Monemar, L. Samuelson, Chem. Rev., **119** (15), 9170 (2019). DOI: 10.1021/acs.chemrev.9b00075
[2] H.-J. Choi, in *Handbook of crystal growth: thin films and epitaxy*, 2nd ed. (Elsevier, Amsterdam, 2014), p. 399–439.
[3] K.A. Dick, Prog. Cryst. Growth Charact. Mater., **54** (3-4), 138 (2008). DOI: 10.1016/j.pcrysgrow.2008.09.001
[4] S. Breuer, M. Hilse, A. Trampert, L. Geelhaar, H. Riechert, Phys. Rev. B, **82** (7), 075406 (2010). DOI: 10.1103/PHYSREVB.82.075406
[5] V.G. Dubrovskii, N.V. Sibirev, G.E. Cirlin, J.C. Harmand, V.M. Ustinov, Phys. Rev. E, **73** (2), 021603 (2006). DOI: 10.1103/PHYSREVE.73.021603

[6] J.C. Harmand, G. Patriarche, N. Péré-Laperne, M-N. Mérat-Combes, L. Travers, F. Glas, Appl. Phys. Lett., **87** (20), 203101 (2005). DOI: 10.1063/1.2128487
[7] S. Breuer, C. Pfuller, T. Flissikowski, O. Brandt, H.T. Grahn, L. Geelhaar, H. Riechert, Nano Lett., **11** (3), 1276 (2011). DOI: 10.1021/nl104316t
[8] A. Fontcuberta i Morral, C. Colombo, G. Abstreiter, J. Arbiol, J.R. Morante, Appl. Phys. Lett., **92** (6), 063112 (2008). DOI: 10.1063/1.2837191
[9] F. Matteini, G. Tütüncüoğlu, H. Potts, F. Jabeen, A. Fontcuberta i Morral, Cryst. Growth Des., **15** (7), 3105 (2015). DOI: 10.1021/acs.cgd.5b00374
[10] F. Matteini, G. Tütüncüoğlu, D. Rüffer, E. Alarcón-Lladó, A. Fontcuberta i Morral, J. Cryst. Growth., **404**, 246 (2014). DOI: 10.1016/j.jcrysgro.2014.07.034
[11] T. Rieger, S. Heiderich, S. Lenk, M.I. Lepsa, D. Grützmacher, J. Cryst. Growth., **353** (1), 39 (2012). DOI: 10.1016/j.jcrysgro.2012.05.006
[12] S. Ambrosini, M. Fanetti, V. Grillo, A. Franciosi, S. Rubini, AIP Adv., **1** (4), 042142 (2011). DOI: 10.1063/1.3664133
[13] E.A. Emelyanov, A.G. Nastovjak, M.O. Petrushkov, M.Yu. Esin, T.A. Gavrilova, M.A. Putyato, N.L. Schwartz, V.A. Shvets, A.V. Vasev, B.R. Semyagin, V.V. Preobrazhenskii, Tech. Phys. Lett., **46** (2), 161 (2020). DOI: 10.1134/S1063785020020194.
[14] P. Aseev, A. Fursina, F. Boekhout, F. Krizek, J.E. Sestoft, F. Borsoi, S. Heedt, G. Wang, L. Binci, S. Martí-Sánchez, T. Swoboda, R. Koops, E. Uccelli, J. Arbiol, P. Krogstrup, L.P. Kouwenhoven, P. Caroff, Nano Lett., **19** (1), 218 (2019). DOI: 10.1021/acs.nanolett.8b03733
[15] M. López, Y. Takano, K. Pak, H. Yonezu, Jpn. J. Appl. Phys., **31** (6R), 1745 (1992). DOI: 10.1143/JJAP.31.1745
[16] R.S. Dowdy, D.A. Walko, X. Li, Nanotechnology, **24** (3), 035304 (2013). DOI: 10.1088/0957-4484/24/3/035304
[17] I. Jiménez, F.J. Palomares, J. Avila, M.T. Cuberes, F. Soria, J.L. Sacedón, K. Horn, J. Vac. Sci. Technol. A., **11** (4), 1028 (1993). DOI: 10.1116/1.578808
[18] J. Ivanco, T. Kubota, H. Kobayashi, J. Appl. Phys., **97** (7), 073712 (2005). DOI: 10.1063/1.1873037
[19] S. Koh, T. Kondo, T. Ishiwada, C. Iwamoto, H. Ichinose, H. Yaguchi, T. Usami, Y. Shiraki, R. Ito, Jpn. J. Appl. Phys., **37** (12B), L1493 (1998). DOI: 10.1143/JJAP.37.L1493