

Peculiarities of the PbTe nano-islet formation on BaF_2 substrate at "hot wall" epitaxy method investigated by atomic force microscopy

T.I.Sheremeta, I.V.Prokopenko, P.M.Lytvyn, O.S.Lytvyn, V.M.Vodop'yanov, A.P.Bakhtinov*, E.I.Slyn'ko**

V.Lashkaryov Institute for Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine
*Chernivtsi Division, I.Frantsevich Institute for Materials Science Problems, National Academy of Sciences of Ukraine, Chernivtsi, Ukraine

Peculiarities of PbTe nano-islet films formation on BaF_2 (111) fresh cleavages by hot wall epitaxy deposition have been investigated using atomic force microscopy. It has been shown that various growth mechanisms could be realized by selection of proper temperature regimes in the growth chamber: growth of three-dimensional nano-islets (Volmer-Weber mechanism) and simultaneous growth of 2D layers (by Frank-van der Merwe) with 3D islets. The nano-islet shape and size can be controlled by temperature regimes and total amount of deposited material.

С помощью атомно-силовой микроскопии исследованы особенности формирования наноостровковых пленок PbTe на свежих сколах BaF_2 (111) при осаждении методом горячей стенки. Показано, что, варьируя температурные режимы в ростовой камере, можно реализовать различные механизмы роста: рост трехмерных наноостровков (механизм Вольмера-Вебера) и одновременный рост 2D слоев (по механизму Франка — Ван-дер-Мерве) с 3D островками. При этом изменение температурных режимов роста и количества осажденного материала позволяет контролировать форму и размеры наноостровков.

The A^4B^6 semiconductors are of great interest as materials for infrared optoelectronics and thermoelectrics [1] due to their important physical properties, such as high permittivity, presence of ferroelectric phase transitions, small band gap, change of conducting and valence band depending on composition variations. The main direction of modern semiconductor device technology is miniaturization using unique properties of semiconductor systems at transition to the nanometer level. Since the physical properties of systems containing low-dimension elements depend on the shape, size and structure of the latter, it is of interest to reveal regularities in formation of A^4B^6 nano-islets and apply these regularities to designing of device structures with preset parameters and characteristics. The factors influencing the properties of low-dimensional semiconductor system could be subdivided into two groups: on the one hand, influence on growth processes material and substrate structure features and, on another one, effects of growth conditions and regimes. These problems are actively investigated not so long ago [2–4]. The main methods for A^4B^6 based low-dimensional systems production are molecular beam epitaxy (MBE) and "hot wall" epitaxy traditional for those compounds. At present, the problem consists in chances to obtain systems with ordered low-dimensional elements of preset composition and sizes with minimal deviations from the mean value. The purpose of this work was to reveal regularities in PbTe nano-islet formation on BaF_2 single crystals at deposition by "hot wall" epitaxy, which allows growing under conditions close to thermodynamic equilibrium.

PbTe was deposited on the fresh cleavages of BaF_2 (111) single crystals. The features of "hot wall" epitaxy method modification for nano-islet growing are described in [5, 6]. The substrate temperature T_{sub} was varied from 570 to 623 K, the wall one, T_w from 723 to 763 K, the evaporation temperature of T_{ev} was 677 K, stoichiometrical PbTe bein used as the vapor source. The regimes were selected specially to satisfy conditions of congruent sublimation of tin tellurides. PbTe molecules constituted the main vapor component of pair and the vapor flow mode was molecular. The substrate temperatures were below of critical one (673 K), when tellurium re-evaporation takes place. The value of incident molecular stream was ~ $10^{12}\div10^{13}$ molecules per cm^2 per second, which satisfy condition of the ratio $\mathbf{I}/\mathbf{V} \ll 1$ between the incident molecule speed **I** and the surface migration speed of adsorbed molecules, **V**. The film thickness was varied by the deposition time from 30 s (2–3 monolayers) to 5 min (up to 30 monolayers). The composition of obtained nanostructures was estimated qualitatively by the X-ray energy dispersion microanalysis system of scanning electron microscope Zeiss Ultra 55. The topomertic investigations of obtained films were performed in an atomic force microscope (AFM) NanoScope IIIa (Digital Instruments, USA) using serial silicon tips NSG-11 (NT-MDT, Russia) in the tapping mode. The tip apex radius before and after scanning was controlled by the test gratings TGT-1 (NT-MDT, Russia) and was less of 10 nm.

In the case when the AFM tip is commensurable with surface elements, its geometry can limit considerably the image resolution in horizontal plane and distort information on real shape and size of surface structures. The height values, however, are measured correctly, if distance between the structures exceeds the tip diameter. That is why the analysis of AFM data was made after their partial deconvolution [4, 9]. So, in our case, the diameter of nano-islets (NI), D, was calculated using approximate formula [4]:

$$D = d\sqrt{(1 - 8Rh/d^2)},$$

where R is the real tip apex radius; d, h are diameter and height of NI obtained from AFM-image. It must be noted that the AFM image resolution is defined also by information capacity of registrating system and is different for images of various scan sizes and height ranges ΔZ. In our case, the image includes 512×512 points in xy plane and its height is measured at a step of $\Delta Z/65536$.

The AFM investigations have shown that variation of substrate temperature at the constant wall and source temperatures influences insignificantly the density and size of mainc PbTe NI array (Fig. 1a, b, c). However, the substrate temperature has a determinative effect on the formation mechanism thereof. At low substrate temperature (~ 570 K), the growth of NI looks like three-dimensional nucleation according to the Volmer-Weber mechanism, where practically all deposited material passes into NI (Fig. 1a). The temperature increasing up to about 619 K favors the appearance of 2D plateaus (fragments of continuous film) which can cover a considerable area of substrate. In this case, NI appear both on clear substrate and on plateaus (Fig. 1b). Here, probably, the combination of Volmer-Weber growth mechanisms and pseudomorph growth of 2D plateaus followed by NI nucleation according to Stransky-Krastanov mechanism should be considered. The further relatively small increase of T_{sub} up to about 623 K defines the appearance of anomalous large NI with a pronounced crystallographic faceting (triangular pyramid) (Fig. 1c). Taking into account distribution of small NI around of anomaly large one, the anomalously large NI formation should be explained by Oswald ripening processes and intense nucleation of new NI in this region.

The wall temperature elevation (T_w = 763 K) at the average substrate temperature of about 616 K results in a substantial increase of density and sizes of NI and absence of 2D plateaus fragments (Fig. 1d). In other words, the NI growth mechanism turns again to Volmer-Weber one.

It is seen from the above that the mechanical strain relaxation processes at the condensate/substrate interface are not decisive in realization of either one or other growth mechanism of a nanostructured film

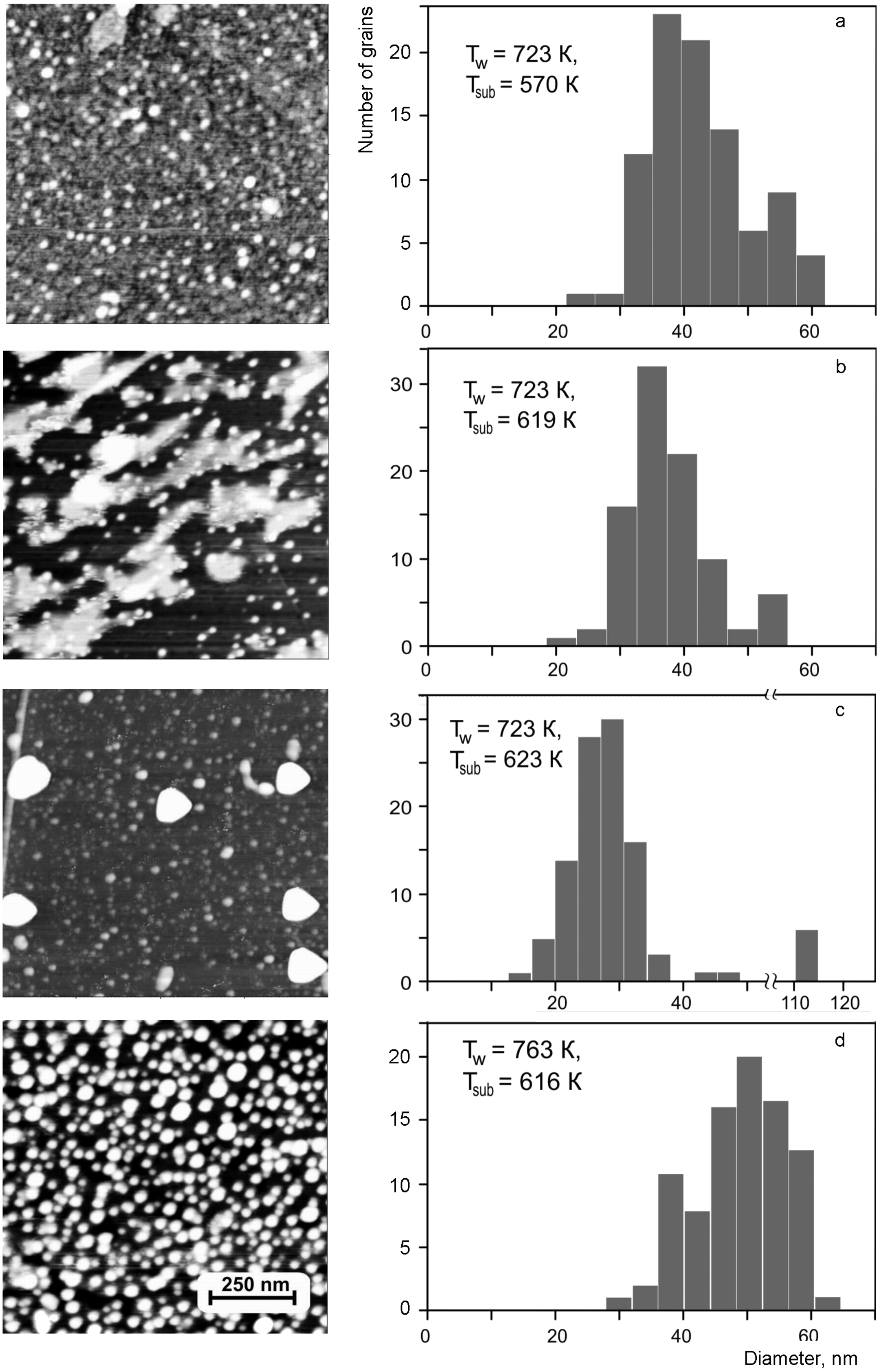

Fig. 1. AFM image of $PbTe/BaF_2$ NI grown by "hot wall" epitaxy method at different temperatures of substrate and wall. Deposition time 3 min. Z-range 20 nm. The corresponding histograms of NI diameter distribution are shown on the right-hand side.

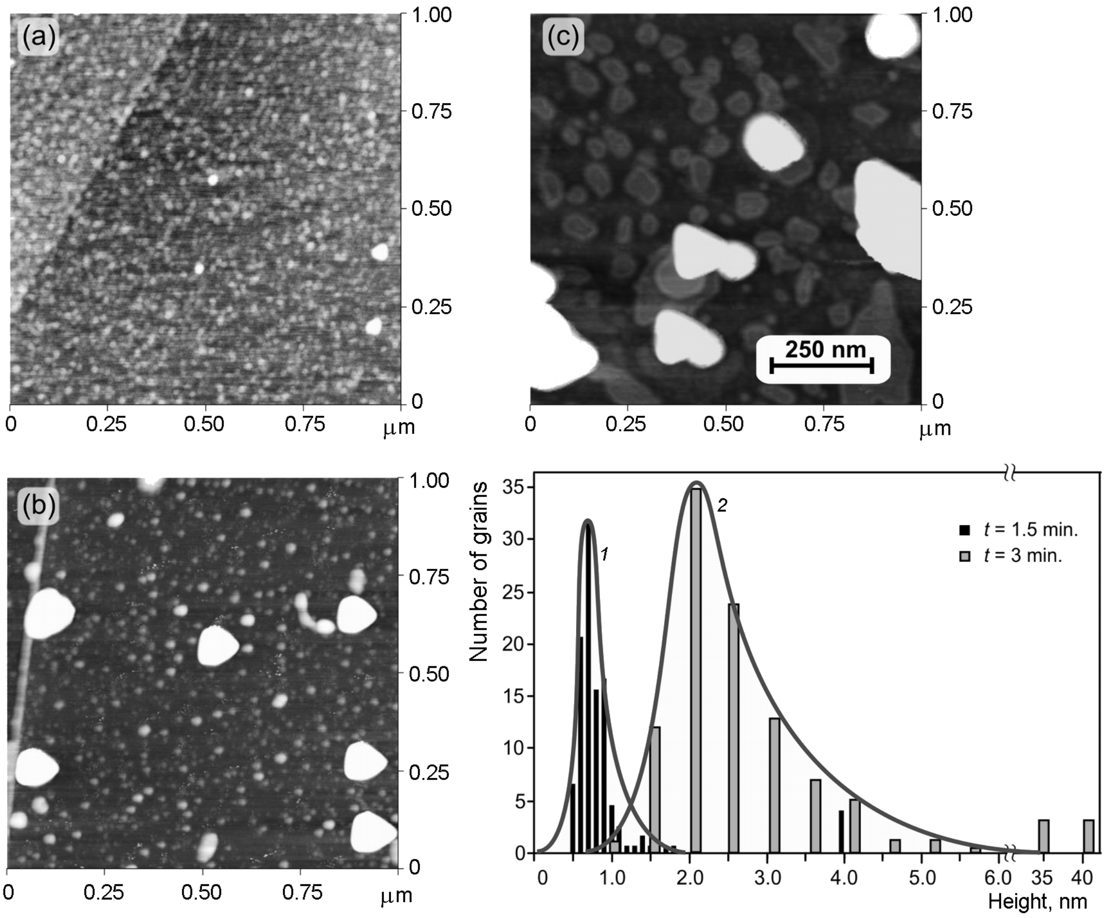

Fig. 2. Formation of $PbTe/BaF_2$ NI at different deposition stages: *a*, 1.5 min.; *b*, 3 min.; *c*, 5 min. T_{sub} = 623 K, T_w = 723 K. Histogram of NI heights distribution for cases *a* (*1*) and *b* (*2*) is shown.

with desired geometrical parameters of NI. The system $PbTe/(111)BaF_2$ at almost equal thermal expansion coefficients and film-substrate lattice mismatch of 4 % is very sensitive to changes in ratios of free energies of substrate, growth surface and energy of adatoms caused by changes of thermodynamic conditions in the quasi-closed volume of growing chamber. It is possible to realize different NI configurations in the same film-substrate system by an insignificant change of temperature conditions at deposition.

The processes of nucleation, surface diffusion and migration of nucleation centers on the growth surface can be traced stage-by-stage using different deposition time (Fig. 2). At the deposition onset, there is a lot (over 350 μm^{-2}) of small NI of 20–40 nm diameters and heights up to 2 nm (Fig. 2a and curve *1* of histogram). A further deposition of materials, the surface diffusion and small NI migration results in a significant decrease of NI density (about 200 μm^{-2}) and irregular increasing of their sizes (Fig. 2b and curve *2* of histogram). As mentioned above, large pyramidal NI appear at this stage. And finally, at t = 5 min, there are pseudomorphic 2D growth of epitaxial film and extremely large pyramidal NI with base orientation {112} on surface of substrate (Fig. 2c).

The statistical analysis of the normal orientation to each surface point has allowed to find out the trends in change of the pyramidal NI faceting. For this purpose, the 2D histograms of the normal tilt distribution were made (Fig. 3). The normal orientation was measured with respect to so-called elementary area, which contains three neighboring points of surface in AFM image. The polar angle θ of histogram corresponds to the normal slope angle to xy plane, while the azimuth angle φ, to the slope to xz plane. The amount of points in segments of histogram is denoted by grey color nuances. For convenience of analysis, fragment of the PbTe lattice stereographic

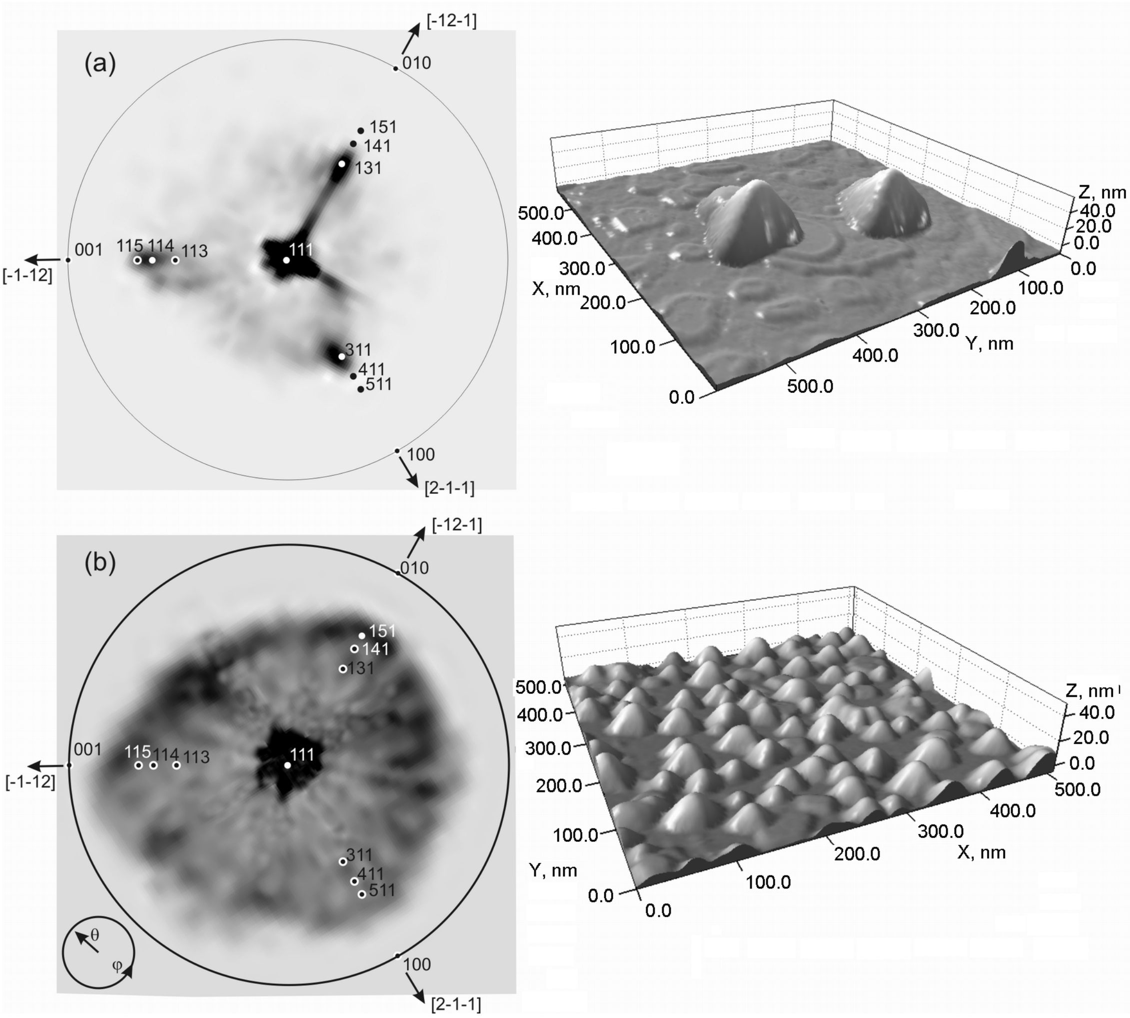

Fig. 3. 2D-histogram for analysis of NI facets (distribution of normal inclination angles in all points of AFM imaged surface). *a* — T_w = 723 K, 5 min.; *b* — T_w = 763 K. Deposition duration 3 min. AFM image of corresponding surfaces fragments are shown on the right-hand side.

projection are superimposed on obtained histograms using the same scale.

The histogram of normal orientation for the surface presented in Fig. 2c is shown in Fig. 3a. Maximum in the point (0,0) corresponds to direction [111] which is normal to the plane of substrate surface. Three maxima at θ near 29.5° located at angles $\varphi = 120°$ testify the presence of evident faceting in pyramidal islets. Comparing that histogram with the crystallographic projection, it is seen that two facets of the pyramid correspond to crystallographic planes {311}. The third facet has a larger angle of normal slope and is close to the plane (114) (tilt 35.3°). On the circle of the histogram, position of facets with minimal Miller's indices {100} (tilt 54.7°) are marked which should be most energy favorable. However, perhaps due to low growth temperature, it is just these facets that are energy preferable for growing.

Increasing of T_w by 40 K (to 763 K) and increasing of T_{sub} by several degrees results in increasing of pyramidal islets facets angles tending to formation of {100} facets (Fig. 3b). The substantial broadening of histogram is caused by small amount of deposited material (3 min against 5 min in the previous case) and, accordingly, by small sizes and high density of pyramidal NI yet not formed.

Thus, the investigations of nanostructured PbTe films formation by "hot wall" epitaxy method has shown, that this method is of good promise for preparation of model samples of semiconductor systems containing nano-islets with preset parameters. The proper choice of deposition parameters allows to realize and combine various NI growth mechanisms, to control the Oswald ripening processes and to change not only sizes but also faceting of NI. The presented phenomenological description of nanostructured PbTe film growth dependences on thermodynamic conditions can be used to compile checklists to produce nanostructured systems based on this compound and in theoretical simulation of growth processes in the nearly equilibrium conditions.

References

1. A.Rogalski, R.Ciupa, *Optoelectron.Rev.*, **5**, 21 (1997).
2. M.Pinczolitz, G.Springholz, G.Bauer, *J.Cryst. Growth*, **201/202**, 1126 (1999).
3. A.Raab, G.Springholz, *Appl.Phys.Lett.*, **77**, 2991 (2000).
4. S.O.Ferreira, B.R.A.Neves, R.Magalhaes-Paniago et al., *J.Cryst. Growth*, **231**, 121 (2001).
5. G.V.Lashkarev, M.V.Radchenko, E.I.Slynko et al., *Semiconductor Phys., Quant. Electron. & Optoelectron.*, **3**, 295 (2000).
6. V.M.Vodop'yanov, A.P.Bakhtinov, E.I.Slyn'ko et al., *Techn.Phys.Lett.*, **31**, 716 (2005).
7. D.D.Freik, M.A.Galuschak, L.I.Mezhilovskaya, Physics and Technology of Semiconductor Films, Vyscha Shkola, Lviv (1988) [in Ukrainian].
8. L.S.Palatnik, M.Ya.Fuks, V.M.Kosevich, Substructure Formation Mechanism in Condensed Films, Nauka, Moscow (1972) [in Russian].
9. O.S.Lytvyn, P.M.Lytvyn, I.V.Prokopenko, in: Abstr. of II Ukrainian Sci. Confr. on Semiconductor Physics, Chernivtsi-Vyzhnytsya, Ukraine (2004), v.1, p.174 [in Ukrainian].

Особливості формування наноострівців PbTe на підкладинках BaF_2 методом "гарячої стінки", що досліджені за допомогою атомно-силової мікроскопії

Т.І.Шеремета, І.В.Прокопенко, П.М.Литвин, О.С.Литвин, В.М.Водоп'янов, А.П.Бахтінов, Є.І.Слинько

За допомогою атомно-силової мікроскопії досліджено особливості формування наноострівцевих плівок PbTe на свіжих сколах BaF_2 (111) при осадженні методом гарячої стінки. Показано, що варіюючи температурні режими у ростовій камері, можна реалізовувати різні механізми росту: ріст тривимірних наноострівців (механізм Вольмера-Вебера), та одночасний ріст 2D шарів (за механізмом Франка-Ван дер Мерве) з 3D острівцями. При цьому зміна температурних режимів росту та кількості осадженого матеріалу дозволяє контролювати форму та розміри наноострівців.