Formation of Nanostructures on the Surface of $CdBr_2$ and PbI_2 Crystals

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Abstract—**By using atomic force microscopy, the surface morphology of $CdBr_2$ and PbI_2 crystals was investigated close to the thermodynamic equilibrium. Results of the performed studies indicate that three types of nanostructures are formed on the $CdBr_2$ surface: triangle-shaped nanopores, nanoislands and nanowires. Principal morphological features, such as radius, height and average distance to nearest neighbor are analyzed. Time evolution of the nanostructures formation on $CdBr_2$ surface shows that nanopores and nanoislands are formed during first 72 hours of aging in air. During next 72 hours nanowires are formed. No signatures confirming the formation of nanostructures on the PbI_2 crystal surface were detected**.

Index Terms—**nanostructures, nanoclusters, nanopores, nanowires.**

I. Introduction

CdI_2 crystals are promising scintillators with relaxation time of $\tau < 1$ ns for detectors of ionizing radiation and potential candidates for optical recording due to photochromic properties. AFM studies of CdI_2 indicated that aging of crystals in air leads to the formation of cadmium oxide and cadmium hydroxide. [1-3].

In order to investigate the influence of cation and anion subsystems on the formation of surface nanostructures in CdI_2, time dynamics of surface nanostructures evolution in $CdBr_2$ and PbI_2 was studied. $CdBr_2$ and CdI_2 crystals have same Cd^{2+} cation and different anions, whereas PbI_2 and CdI_2 crystals have same I^- anion and different cations.

II. AFM Studies

AFM images showing the surface morphology of $CdBr_2$ surface after aging in air during 24 hours indicates the formation of nanostructures – triangle-shaped nanopores (A, C Fig.1, *a*) and clusters (B Fig.1, *a*).

Depth of A and C nanopores is становить 150 та 128 nm (Fig. 1, *a*, *c*), respectively. On the surfaces of crystals, these nanopores form equilateral triangles, with 1.2 and 1.3 mkm dimensions, respectively. Triangle shape of pores is due to rhombohedral crystalline structure of $CdBr_2$.

Aging of $CdBr_2$ over 72 hours is accompanied by the formation of island-like nanostructures (Fig. 2). Lateral dimensions and heights are within 200 nm ÷ 2 mkm and 10 ÷ 120 nm, respectively (table 1).

Distances between nanoiclusions are typically much larger that their sizes and fall within 1 ÷ 1.5 mkm (table 1), that may confirm the absence of interaction between them at this stage of the formation. Besides, distance distribution is Gaussian-shaped that speaks in favour of stochastic nature of the formation.

During aging of $CdBr_2$ in air for 148 hours, the number of triangular pores (fig. 3.15, *a*) and nanowires (fig. 3.15, *c*) on its surface substantially increases. Depth and lateral dimensions of nanopores are within 50 ÷ 170 nm and 1 ÷ 1.8 mkm, respectively (fig. 3, *b*, *d*).

The formation of nanowires on $CdBr_2$ surface occurs due to nanocluster aggregation (fig. 3, *a*). For example, from the nanowire profile (fig. 2, *b*) one can see that nanostructure of this type consist at least of for smaller nanostructures with lateral dimensions around 100 nm and heights of 8.6 and 10 nm.

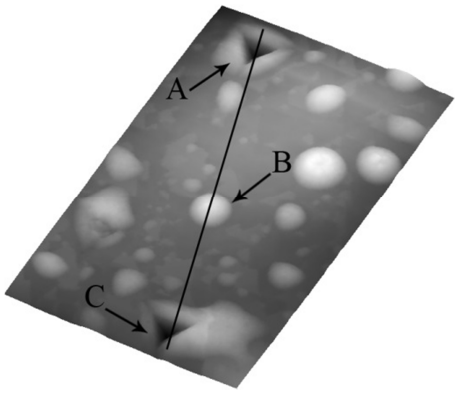
It is established, that the number of nanopores formed on $CdBr_2$ surface increases with time of aging in air. Therefore, it is most likely that they are formed due to dissolving of $CdBr_2$ during the condensation of moisture on the surface.

The surface of freshly cleaved PbI_2 crystals shows steps with atomically flat zones in between. (fig. 4 *a*). Based on the analysis of the autocorrelation function profile, one can estimate the roughness which equals to 1 nm (fig. 4 *b*). Such value of roughness is due to steps that are formed in the process of cleaving. Additional maxima in the autocorrelation function profile (A, A', B and B') indicate the formation of quasiperiodic structures with the period of 1.3 mkm.

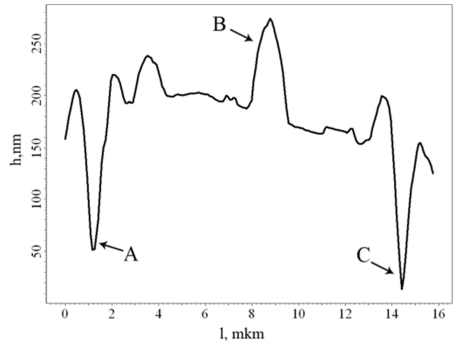
Aging of PbI_2 in air atmosphere does not stimulate the growth of nanostructures on the surface.

Conclusions

Thus, aging of $CdBr_2$ in air promotes the formation of triangular nanopores, island-like nanoclusters and nanowires. Studies of the time evolution of the formation of nanostructures on $CdBr_2$ surface during aging in air for 1 week indicated that at the same thermodynamic conditions nanostructures grow faster than in CdI_2 crystals. It is connected with higher chemical activity of Br^- anion as compared to I^-. Obtained AFM data show that the formation of nanostructures is more intensive in CdI_2 as compared to PbI_2 and even more intensve for $CdBr_2$. From the comparison of the time evolution of the formation of nanostructures on CdI_2, $CdBr_2$ and PbI_2 surfaces one can conclude that Cd^{2+} cation and I^- anion participate in the process.



a)



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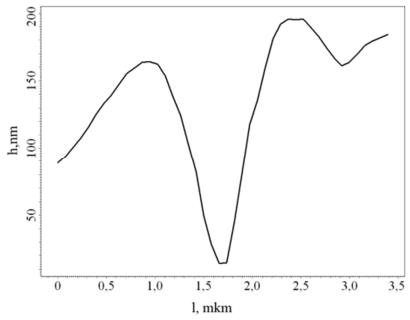
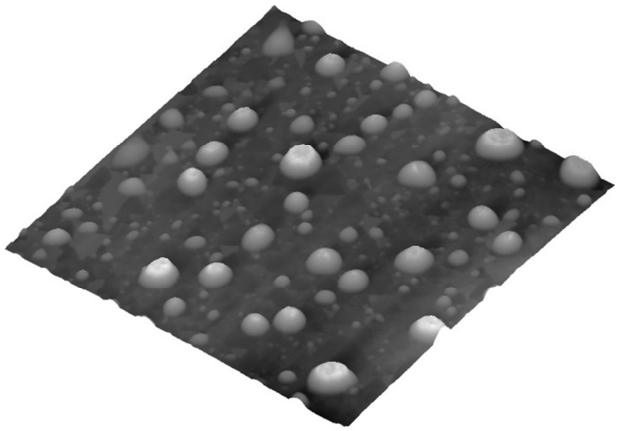
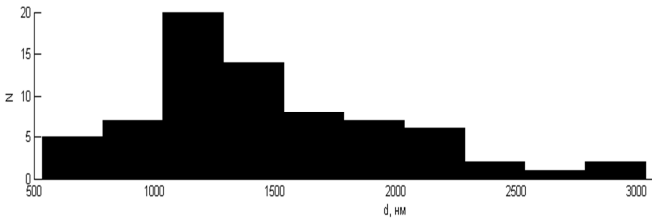


d)

Fig. 1. ACM images of nanostructures formed on the surface of $CdBr_2$ crystals during their aging in air for 24 hours. (*a*, *b*) and respective profiles (*c*, *d*): A, C – nanopores, B – cluster; sizes: *a* – 15x9 mkm; *c* – 2.8x2.4 mkm; height range: *a* –180 nm; c – 208 nm)



a)

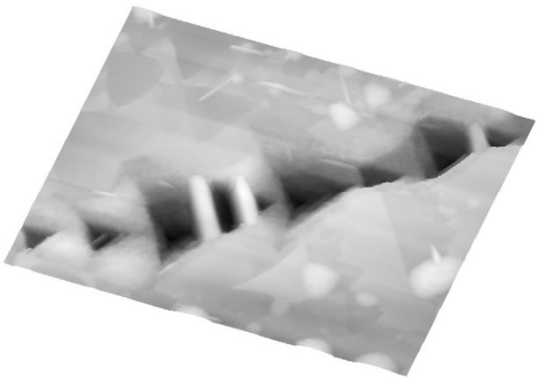


b)

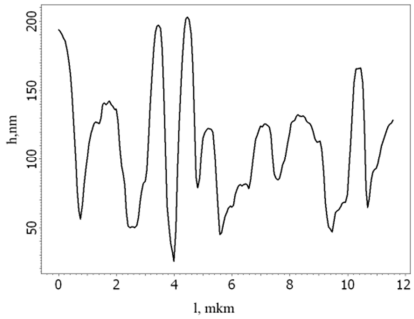
Fig. 2. Nanostructures formed on the surface of $CdBr_2$ crystals during their aging in air or 72 hours (*a*); розподіли the distribution of distances between nanostructures (area size: 17x20 mkm; height range: 170 nm)

TABLE 1. NUMERICAL ANALYSIS OF CLUSTERS, FORMED ON THE SURFACE OF $CdBr_2$ CRYSTALS DURING THEIR AGING IN AIR FOR 72 HOURS.

№	Cluster parameter	Value
1	number	72
2	min radius, nm	108
3	max radius, mkm	1.2
4	average radius, nm	431
5	min height, nm	8
6	max height, nm	123
7	average height, nm	38
8	average distance between nanostructures, mkm	1.5



a)



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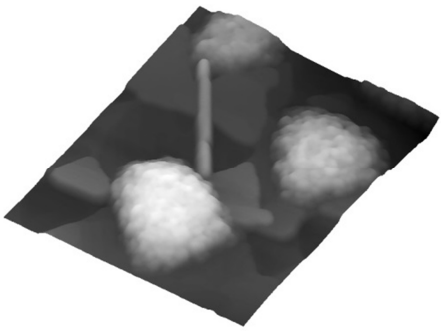

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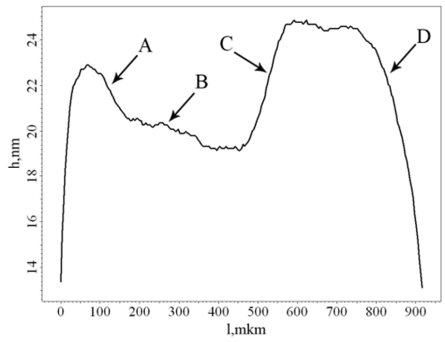
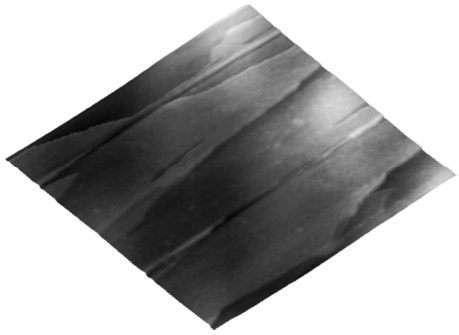


d)

Fig. 3. AFM images of nanostructures formed on $CdBr_2$ crystal surface during aging in air for 168 hours: *a*, *b*) nanopores and their profile; *c*, *d*) nanowire and its profile; (areas sizes: *a* – 8.5x10 mkm, *c* – 2.1x1.7 mkm; height range: *a* – 209 nm, *c* –57 nm).



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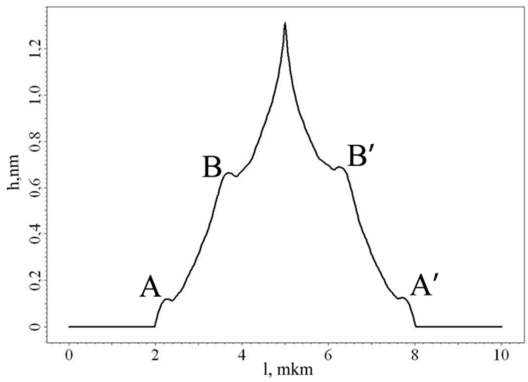

b)

Fig. 4. AFM image of the PbI_2 surface morphology during aging in air for 168 hours. (*a*); autocorrelation function profile (area size:3x3 mkm; height range: 7 nm) (*b*)

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