

Surface morphology of as grown and annealed bulk GaN crystals

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Abstract

GaN single crystals have been grown from Ga solution. The crystals grow in the form of platelets with their basal plane perpendicular to the c-axis. The two opposite crystal surfaces are not equivalent since one is N- and the other Ga-terminated. Atomic force microscopy has been applied to study surface morphology on both surfaces. It was found that one side is atomically flat. The other side consists of pyramid-like structures about 25 nm in size.

The influence of annealing in an NH_3+H_2 atmosphere in the temperature range from 600°C to 900°C was investigated. Depending on crystal face the results were drastically different. It was found that on the rough side, annealing yields an atomically flat surface with terraces of monolayer height. The size of the terraces depends on the temperature of the annealing. On the originally flat side the surface becomes rougher after annealing. The transformation of surface morphology begins at temperatures below 700°C. Preliminary results of annealing in a hydrogen atmosphere are also reported. These findings are crucial for the understanding and development of GaN homoepitaxy.

1. Introduction

One of the main problems in fabricating high quality GaN layers is the lack of lattice matched substrates. Commonly used sapphire has 14% lattice mismatch. Bulk GaN crystals, grown by the high pressure method [1], have become available recently. Since those crystals are intended for use as substrates, it is important to know their morphology and stability at high temperature. In this paper we present the morphology of as-grown bulk GaN crystals. We also show how pre-growth annealing changes surface structure of GaN substrates. Our results seem to fit well into an overall picture of GaN homoepitaxial growth.

2. Experiment

GaN bulk crystals reported here were grown from a gallium solution by the high pressure method [1]. Crystals obtained by this method grow in the form of platelets 4-6 mm in diameter and having a 0.1 mm thickness. The basal planes are perpendicular to crystallographic c-axis and therefore the surfaces are polar. One is Ga terminated and the other is terminated with N. At this moment we are not able to determine the polarity of the crystals. Fortunately, the macroscopic picture of these two sides is different. One side, denoted here A, is macroscopically flat with occasional hexagonal surface defects. The other side (B) has macrosteps (about 50nm height), sometimes decorated with triangular surface defects. All annealing experiments were performed in a standard horizontal atmospheric pressure MOCVD system. Prior to processing, the two surfaces were identified and the sample was broken into two or three pieces. One piece was always used as a reference. Typically in an annealing cycle we

processed two samples: one with the A surface up and the other with B surface up. Just before annealing, the samples were etched in aqua regia, then rinsed in DI water and dried. The annealing process consisted of flushing the system with hydrogen (20 min at 250°C followed by 5 min at 450°C), then NH₃ was switched on and the temperature was raised to the target value. Upon completing the annealing process, the heater was turned off. NH₃ flow was continued until the sample temperature dropped below approximately 400°C. All annealing processes described lasted 10 min and were performed in a gas flow of 2.5 slm (standard litres per minute) NH₃ and 1 slm H₂. Investigated temperatures were in range 600-900°C. For surface imaging we have used a standard atomic force microscope (AFM) made by Digital Instruments (model Nanoscope E) working with silicon nitride tips.

We have also performed a series of experiments, using the above described recipe, but in atmosphere of pure H₂ (without ammonia). Samples after this procedure were covered with a Ga layer. Such an annealing process is equivalent to etching in liquid Ga and as such will not be reported here.

3. Results

The microstructure of the A face of a bulk as-grown GaN crystal is presented in [Figure 1a](#) (see also [Figure 3a](#)). The surface is predominantly flat, with occasional steps and hillocks. A cross-section of the surface from [Figure 1a](#) is presented on [Figure 1b](#) showing steps with a height of about 1 nm.

The morphology of the B surface, presented in [Figure 2](#), is dominated by pyramid-like structures which are 15-25 nm in diameter and 5-25 nm height. The angle between the side walls of the pyramids and the surface is around 60°. The exact shape of the pyramid's top was impossible to measure because of microabrasion.

Based on these observations we may say that as grown bulk GaN surface A is microscopically flat and surface B is microscopically rough.

The influence of annealing on the morphology of the A surface is presented in [Figure 3](#). [Figure 3a](#) features the morphology of an as-grown sample. [Figures 3b,c,d](#) show, respectively, samples annealed at 700, 800 and 900°C. Please note the different vertical scale in [Figure 3a](#). Annealing changes the face A morphology from flat to rough. The annealed surface is covered with hill-like structures with diameters of 30-100nm and heights around 3-10 nm. Even more surprising is that the highest hills are created at the lowest annealing temperature of 700°C (a sample annealed at 600°C did not show any change of surface morphology). The average hill height decreased from about 7 nm for a sample annealed at 700°C to about 2.5 nm for a sample annealed at 900°C.

The evolution of the B surface after annealing is presented in [Figure 4](#). [Figure 4a](#) shows the unannealed reference sample and [4b,c,d](#) present samples annealed at 700, 800 and 900°C accordingly. The vertical scale in [Figure 4a](#) is once again different from the others'. There is a pronounced change in the surface morphology after annealing. The pyramidal structure is replaced by a flat terrace-like structure. Height differences between terraces are about 0.25 nm; half of lattice constant in the c-direction. This means that each terrace consists of one monolayer of Ga and N. The diameter of the terraces changes from approximately 0.3 μm for the sample annealed at 700°C, to about 3μm for the sample annealed at 900°C.

4. Discussion

As the bulk GaN crystals are grown from Ga solution, the environment is Ga-rich and relatively few N atoms are available. Samples grown in these conditions have an atomically flat A face and a rough B face. After annealing in a N-rich atmosphere with no Ga available, the situation is reversed. The A face is rough and the B face becomes flat (notice the striking similarity between [Figures 2a](#) and [3b](#)). This could mean that the growth mechanism of GaN is determined mainly by the III/V ratio and that there many similarities exist between liquid and gas phase processes.

We can also look at the annealing process from another point of view. At high temperature, GaN can decompose releasing a Ga and N atom. The Ga diffuses on the surface until it reacts with an NH₃ molecule, rebonding to the GaN crystal - much like the standard MOCVD process. In this context, the roughening of the A face suggests that we are dealing with a nuclei on top of nuclei growth mechanism. The fact that the surface mobility of adsorbed species increases with temperature could explain why A face samples annealed at high temperature are less rough than annealed at 700°C.

The situation observed for B face annealing is different. Ga atoms, originating from the decomposition of GaN, are rebond with the crystal at steps, thus creating terraces. The terraces are larger after annealing at higher temperature

because of two factors. First, the Ga surface mobility is higher at higher temperatures. Second, it is very likely that the decomposition process is faster at smaller terraces leaving only the large ones remaining.

This explanation is supported by the observation of the growth of GaN homoepitaxial layers grown on bulk GaN substrates [2]. The morphology of layers grown on the A face is dominated by hexagonal pyramids suggesting a 3-dimensional or defect-related growth. The surfaces of films deposited on the B face are smooth, suggesting growth by a step flow mechanism.

5. Summary

We have investigated the surface morphology of as-grown and annealed GaN bulk crystals. It was determined that one polarity of as-grown crystals is atomically flat and the other side is rough. After annealing, the surface morphologies change. The originally flat surface becomes rough, while the initially rough side becomes atomically flat.

The behavior of the initially rough surface opens new perspectives. Spontaneous self-flattening, if well engineered, can be used for such tasks as removal of polishing damage or the preparation of epi-ready substrates. It also gives a hint about how epitaxial processes should be conducted. For example, the presented results suggest that during homoepitaxial growth we should avoid annealing of face A of bulk GaN. These findings are important for further optimization of homoepitaxial GaN growth.

References

[1]S. Porowski and I. Grzegory, in: Properties of Group III Nitrides, ed. J. H. Edgar, (British Institution of Electrical Engineers Publ. , London 1994)

[2]G. Nowak, in preparation

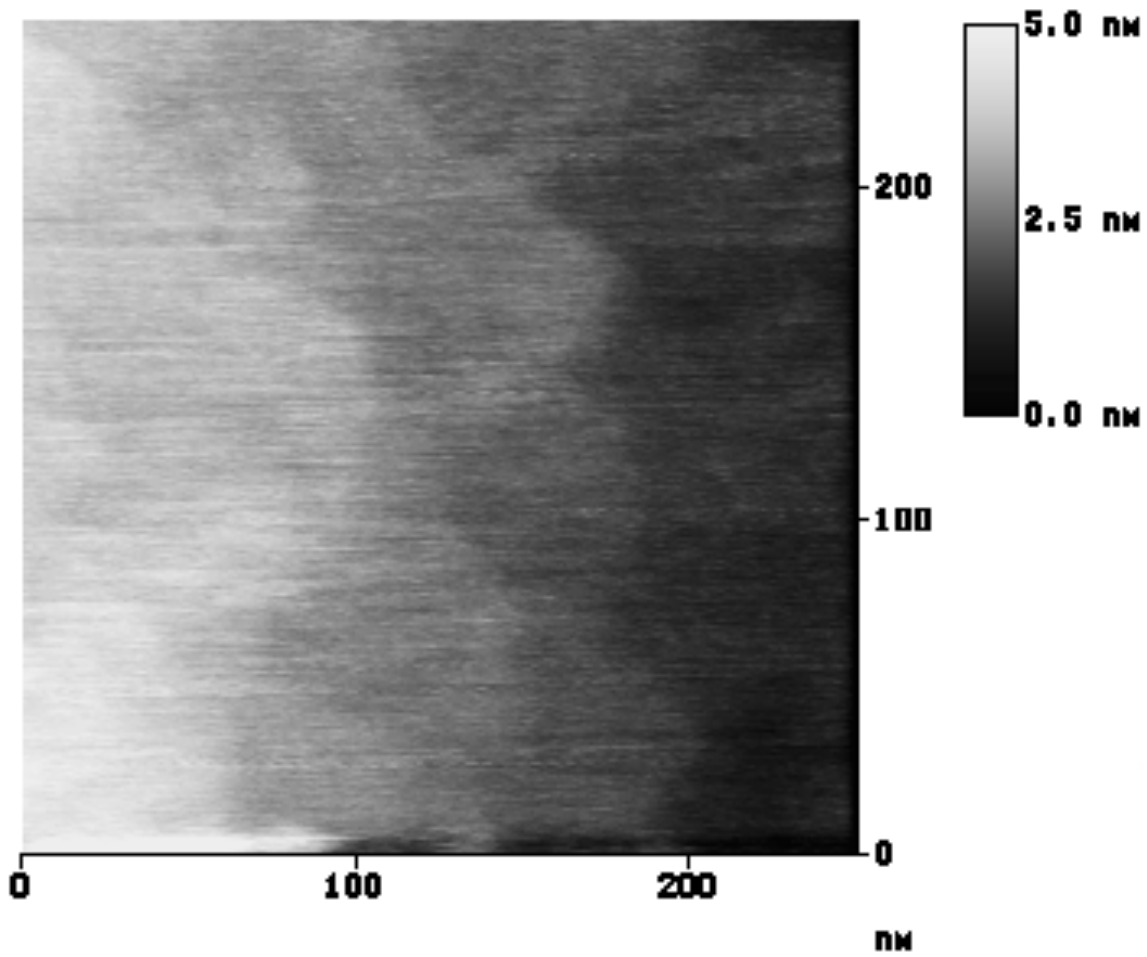


Figure 1a. Surface morphology of the face A

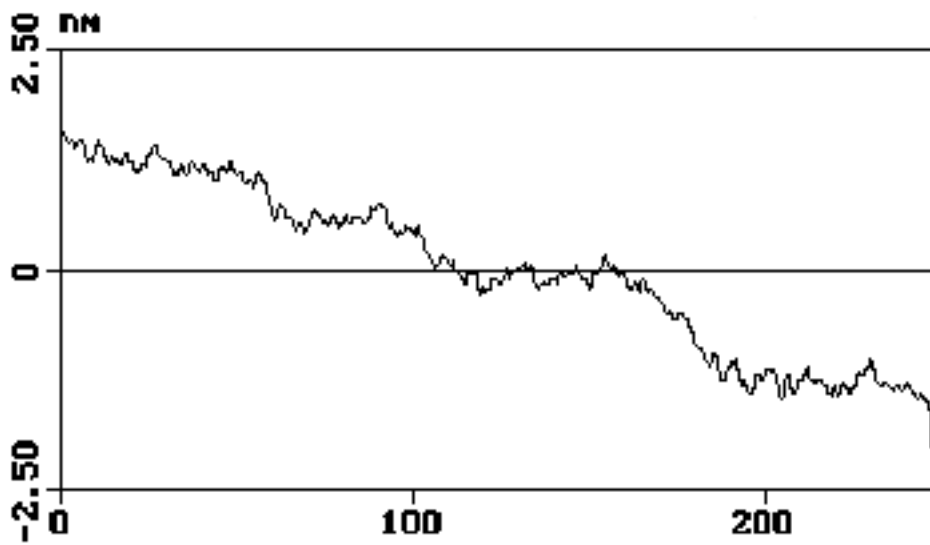


Figure 1b. Cross-section of the surface shown on [Figure 1a](#).

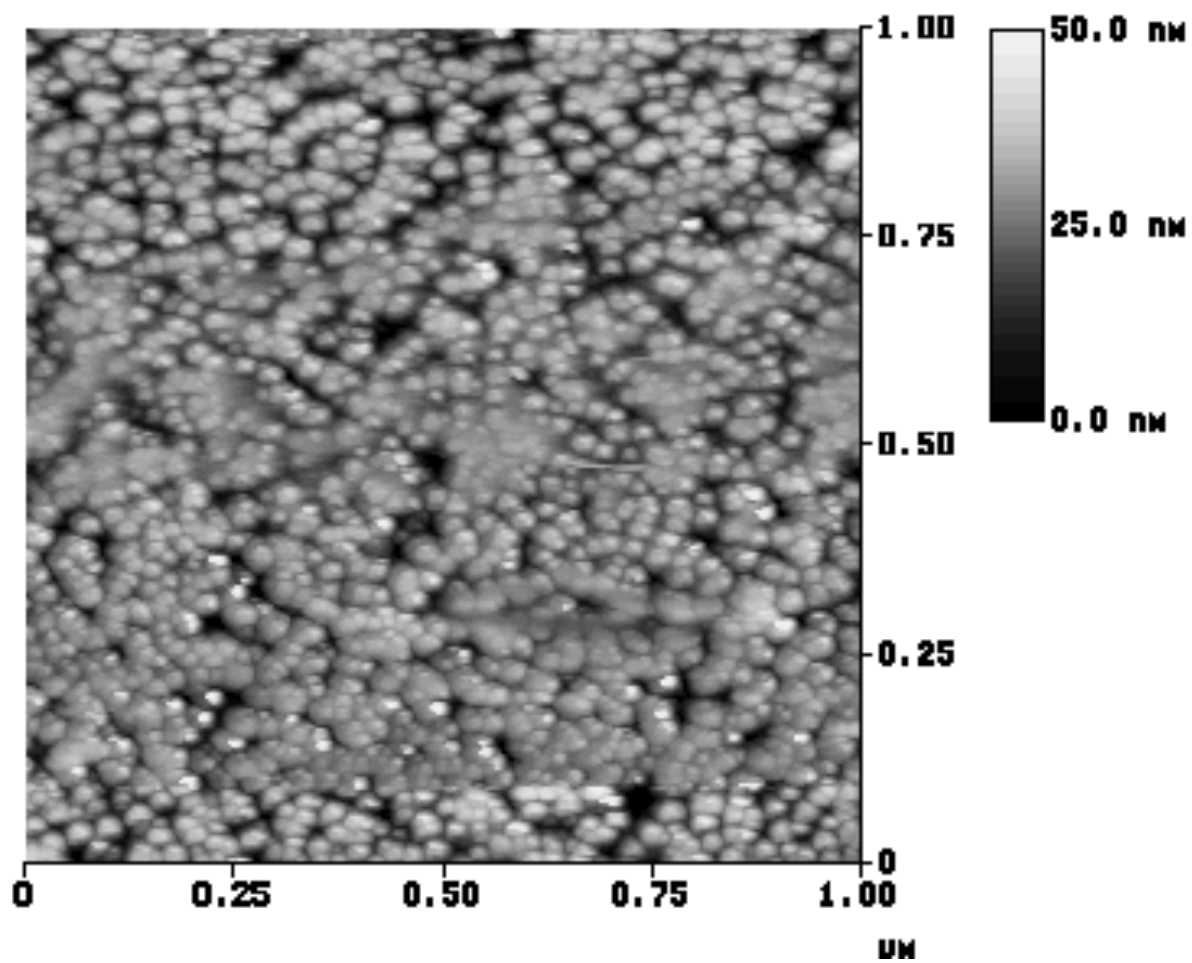


Figure 2a. Surface morphology of the face B.

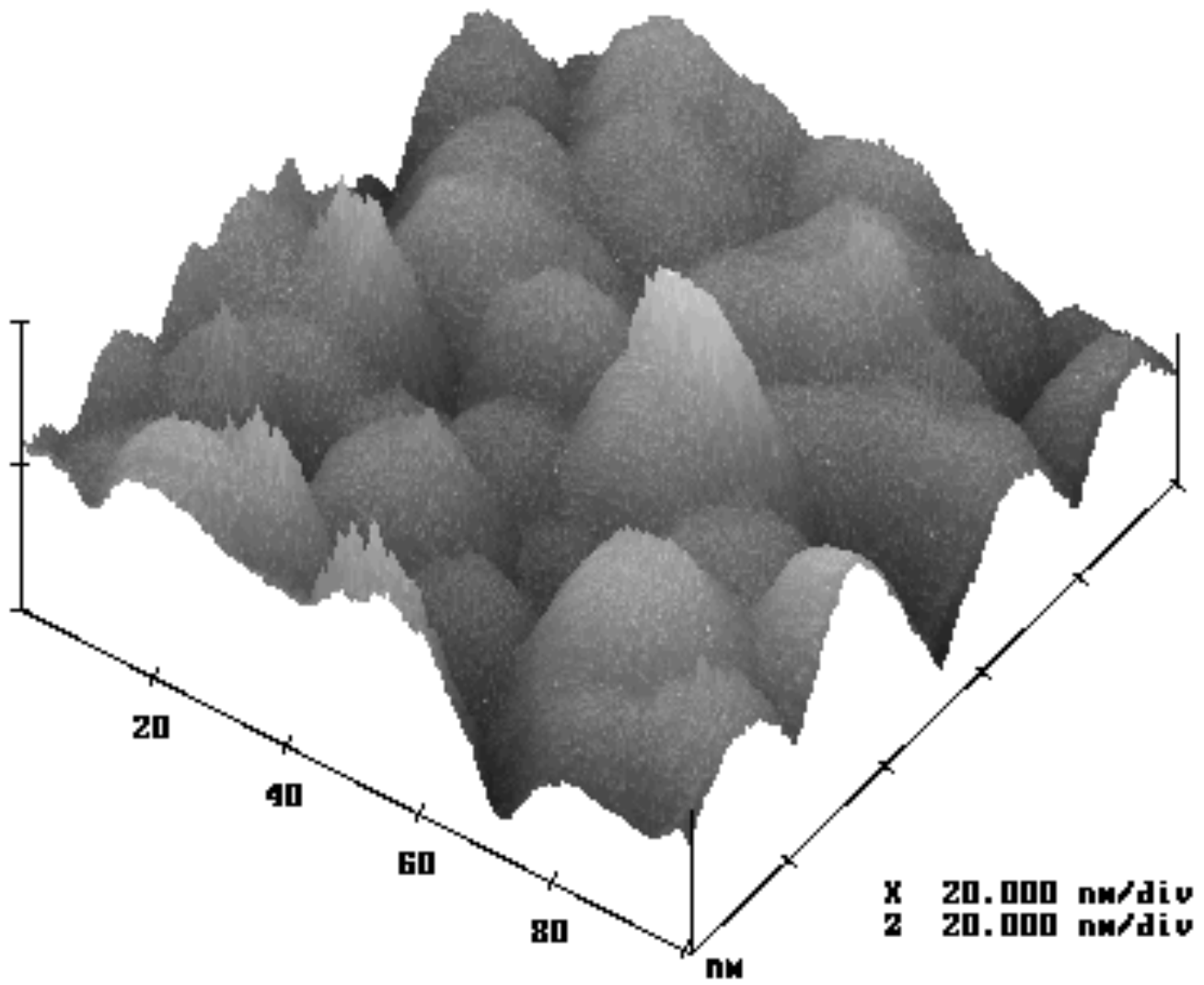


Figure 2b. Three-dimensional view of the surface shown on [Figure 2a](#).

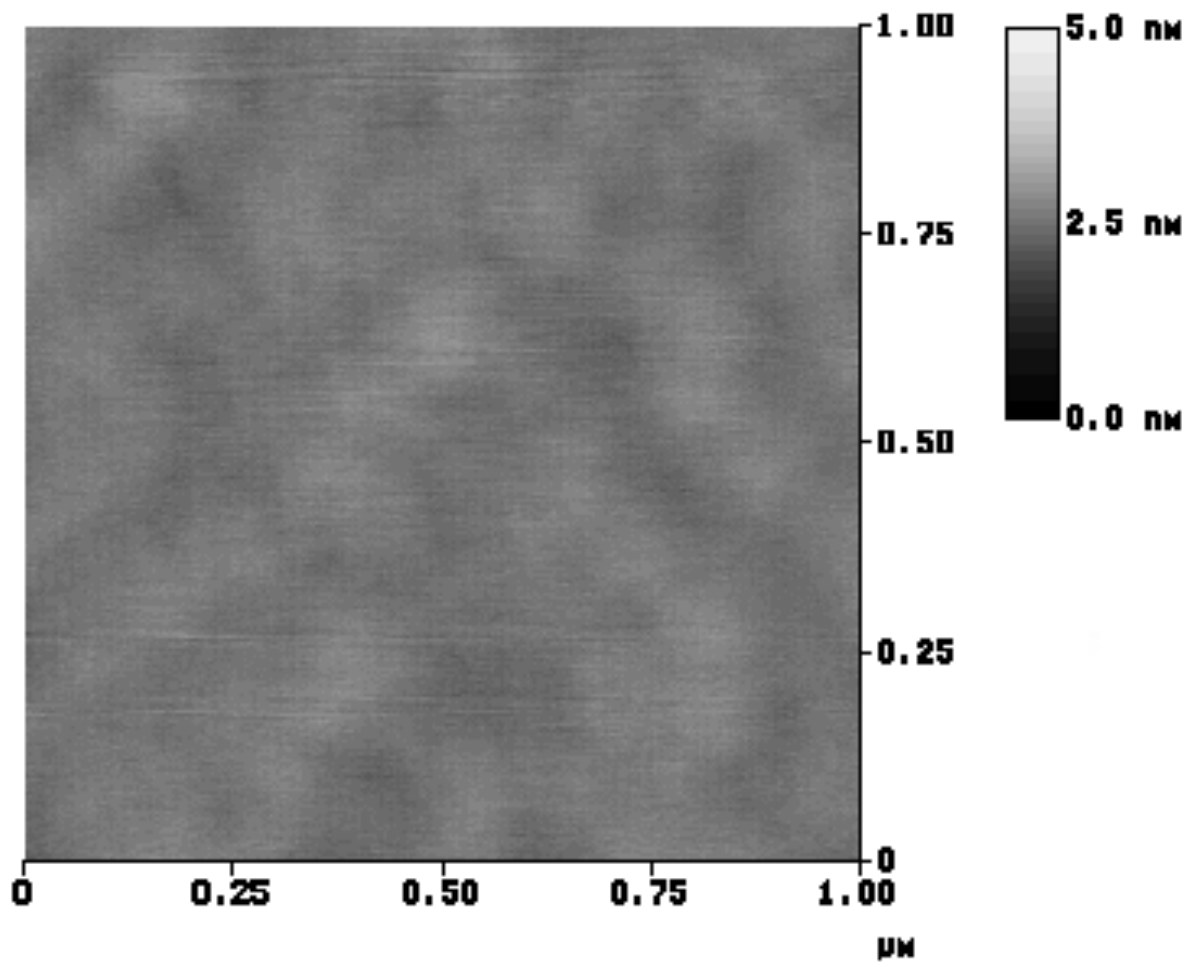


Figure 3a. Surface A - reference

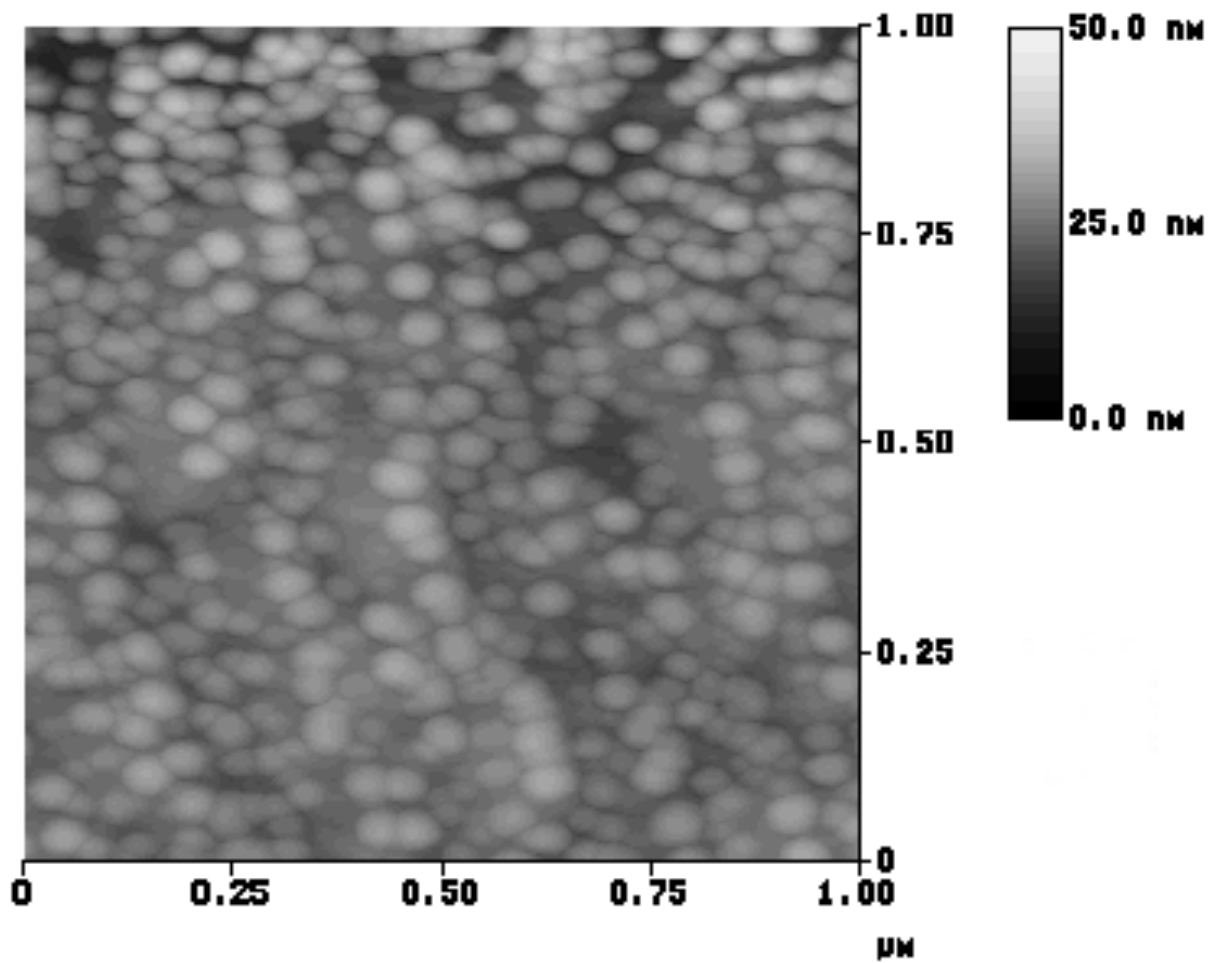


Figure 3b. Surface morphology of surface A after annealing at 700°C.

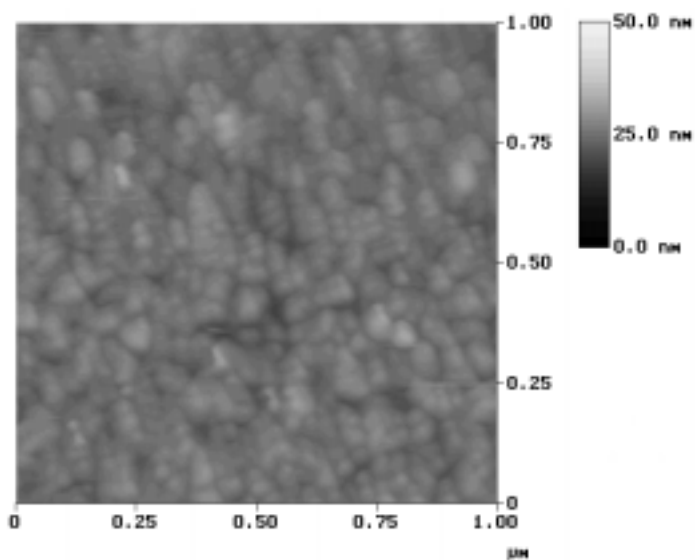


Figure 3c. Surface morphology of surface A after annealing at 800°C.

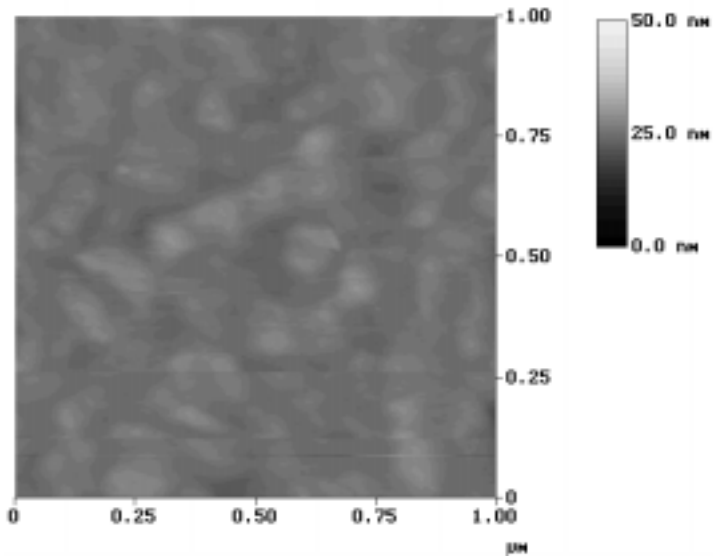


Figure 3d. Surface morphology of surface A after annealing at 900°C

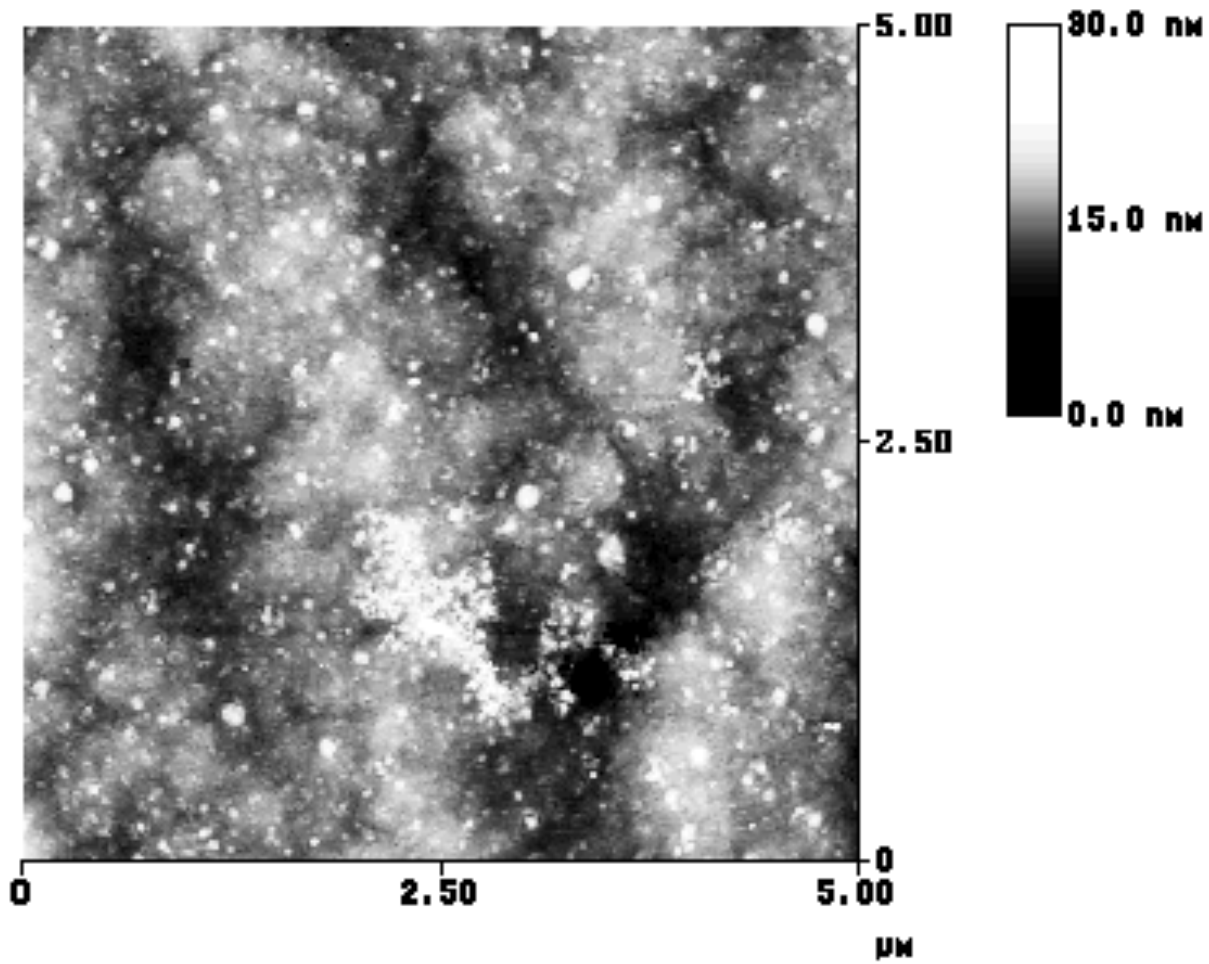


Figure 4a. Surface B - reference

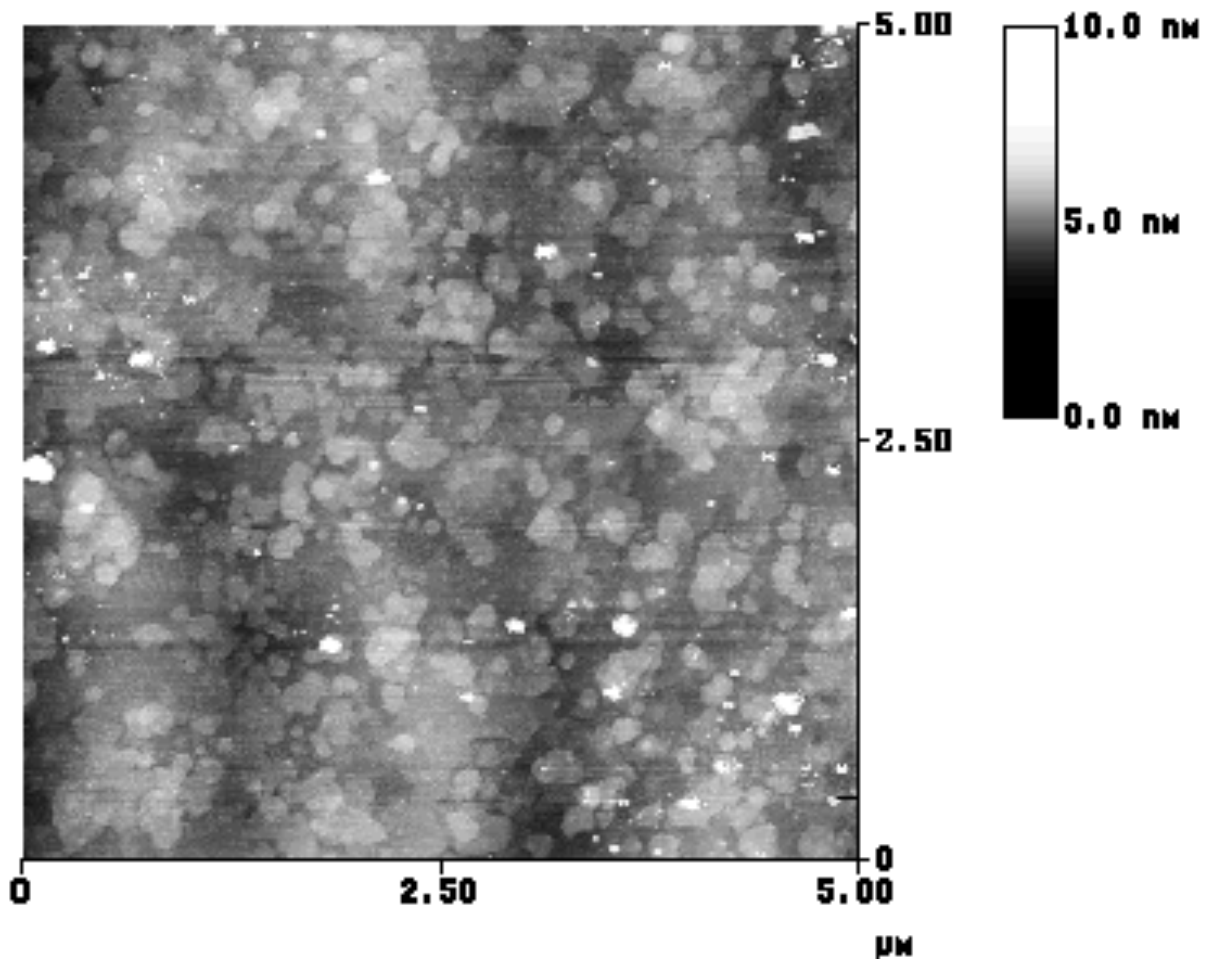


Figure 4b. Surface morphology of surface B after annealing at (b) -700°C, (c) - 800°C, (d) - 900°C

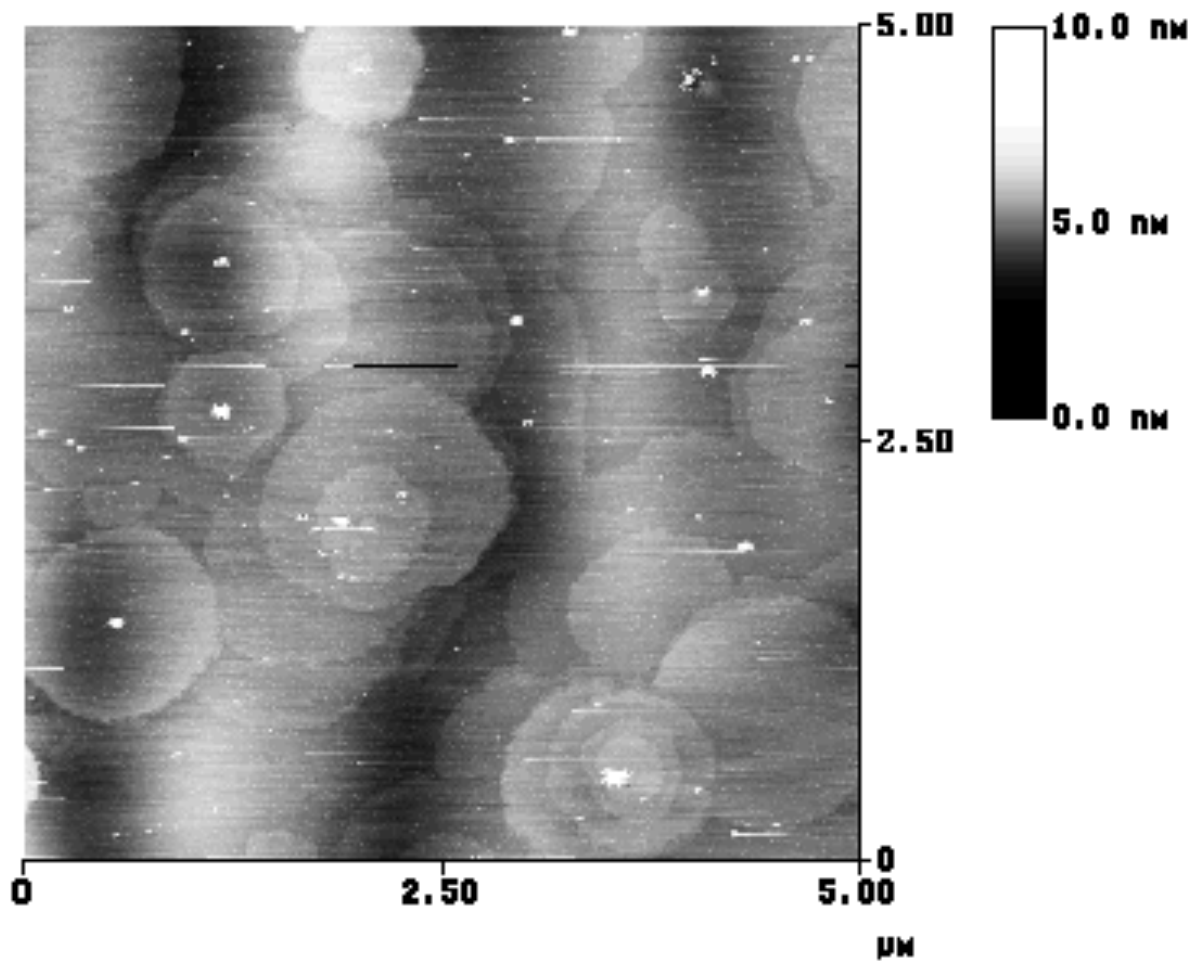


Figure 4c. Surface morphology of surface B after annealing at (b) -700°C, (c) - 800°C, (d) - 900°C

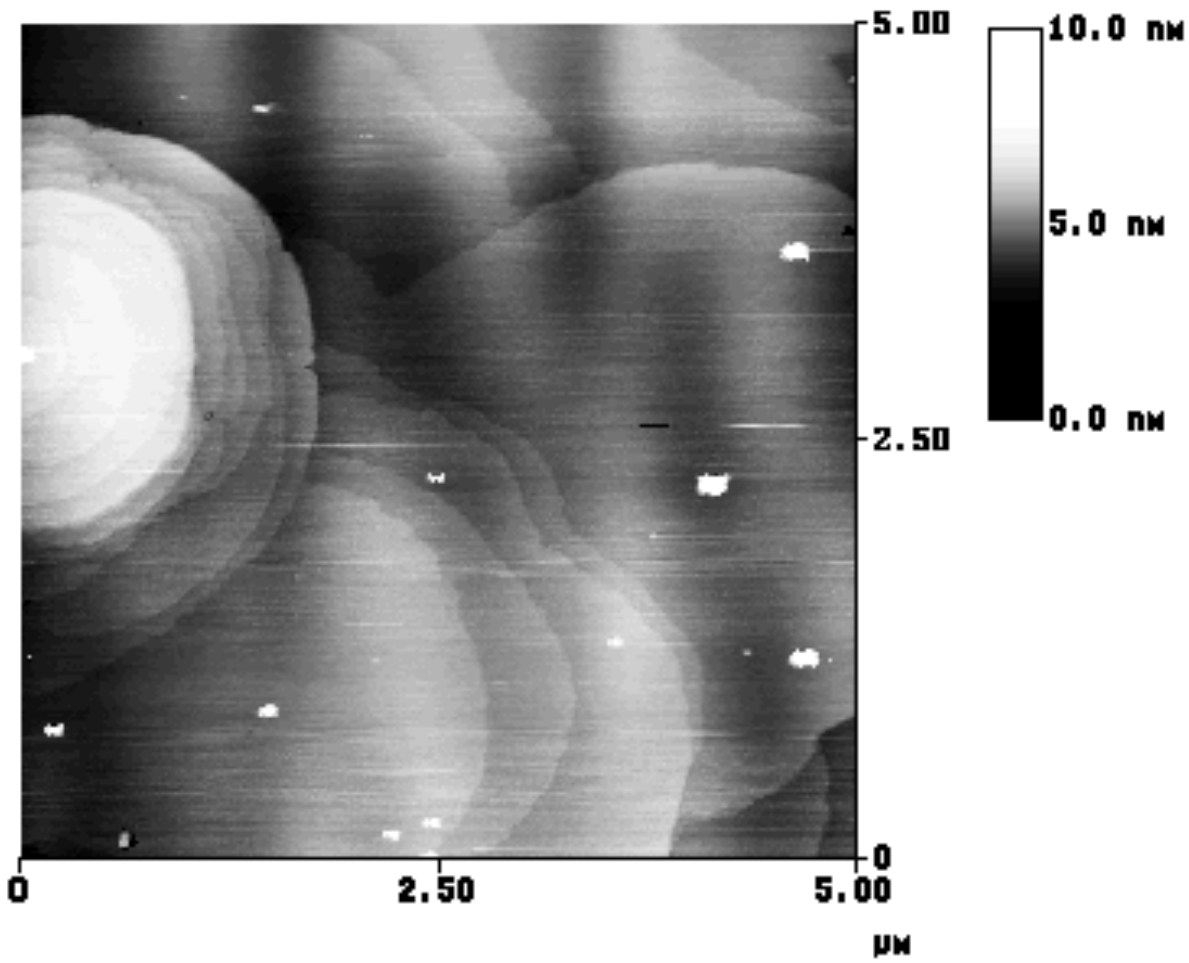


Figure 4d. Surface morphology of surface B after annealing at (b) -700°C, (c) -800°C, (d) -900°C

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