Atomic force microscopy studies of $SrTiO_3$ (001) substrates treated by chemical etching and annealing in oxygen

WANG Xu[1], FEI Yiyan[1], LU Huibin[1], JIN Kui-juan[1], ZHU Xiangdong[1,2], CHEN Zhenghao[1], ZHOU Yueliang[1] and YANG Guozhen[1]

1. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100080, China;
2. Department of Physics, University of California, Davis, California, USA

Correspondence should be addressed to Yang Guozhen (email: yanggz@iphy.ac.cn)

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Abstract The $SrTiO_3$ (001) substrates treated by chemical etching in NH_4F-buffered HF solution and annealing in oxygen ambient have been studied by an atomic force microscopy (AFM). The $SrTiO_3$ substrates with TiO_2-termineted and atomically smooth surfaces and single unit cell steps have been obtained. The surface morphologies of $SrTiO_3$ substrates strongly depend on the treated conditions and the quality of the substrates.

Keywords: SrTiO3, AFM, Surface morphology, Surface defects.

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Thin films and heterostructures of perovskite oxide have attracted much interest in recent years from both scientific and technical viewpoints. The fabrication of artificial crystalline materials through layer-by-layer epitaxial growth with full control over the composition and structure at an atomic level has become one of the most exciting areas of research in condensed matter physics and material sciences. The substrate with atomically smooth surface is very important to obtain high-quality thin film and in favor of device application. $SrTiO_3$ is one of the most often used substrates for depositing perovskite oxide films because of the compatible lattice constants and thermal expansion coefficients between $SrTiO_3$ and those oxide materials. $SrTiO_3$ has a stacked structure with two alternative kinds of SrO and TiO_2 and perpendicular to the [001] direction. Generally, the topmost surface of the as-received $SrTiO_3$ substrates is a mix-terminated surface of SrO and TiO_2. The termination of $SrTiO_3$ substrate surface affects the epitaxial growth of perovskite thin films. It is well known that the single-terminated surfaces of SrO or TiO_2 can greatly improve the quality of the thin films[1,2]. Therefore, $SrTiO_3$ substrates with single-terminated surface is also necessary to obtain high-quality films and heterostructures.

The effective treatments of the $SrTiO_3$ surface have been found recently. One of the methods is chemically etching in NH_4F-buffered HF solution (BHF)[3]. The single-terminated surface depends strongly on the pH value of the BHF and the etching time. The BHF-treated substrates have been applied in the epitaxial growth of oxide films such as $BaTiO_3$, $PrGaO_3$, $YBa_2Cu_3O_7$ and BaO to obtain the high-quality thin film of the materials[4,5]. The persistent intensity oscillation of reflection high-energy electron diffraction (RHEED) has been observed during the laser MBE of oxide films by using the BHF-treated substrates[2]. Another treatment of $SrTiO_3$ substrate is thermal annealing in oxygen only. But a mix-terminating of SrO and TiO_2 is always existent in the topmost surface of $SrTiO_3$ if the treatment of thermal annealing is used[6−9]. However, if the chemical etching is combined with the thermal annealing, the control of the BHF pH value and etching time would become less difficult and the $SrTiO_3$ substrates with nearly perfect and atomically flat surface would have been obtained[10].

In this paper, $SrTiO_3$ (001) substrates treated by BHF chemical etching and annealing in oxygen ambient have been studied by atomic force microscopy (AFM). The TiO_2-terminated $SrTiO_3$ substrates with the surface of single unit cell steps were obtained. It was also found that there are some defects in the substrate surfaces and the surface morphologies depend strongly on $SrTiO_3$ substrate quality.

1 Experiments

The as-received $SrTiO_3$ (001) substrates were used in our experiments. There are lots of protuberances in the substrate surface of the as-received $SrTiO_3$, and in practice the substrates have widely varying surface morphology. Fig. 1(a) shows a typical three-dimensional (3D) AFM image (5 μm×5 μm) of an as-received $SrTiO_3$ (001) substrate. The root mean square (Rms) roughness is about 1.0 nm. The Rms roughness was decreased to 0.4 nm (5 μm×5 μm) after the as-received substrate was treated in flowing oxygen (1 atm) at 950℃ for two hours. The thermal annealing process is referred to as pre-annealing. The 3D AFM image of the $SrTiO_3$ surface after per-annealing is shown in Fig. 1(b). The protuberances in the substrate surface of the as-received $SrTiO_3$ disappeared and the step line-forms were formed in the $SrTiO_3$ surface as shown in Fig. 1(b).

After pre-annealing, the substrate was ultrasonically soaked in ~~deionised~~ water for 10 minutes so that the SrO in the topmost surface of $SrTiO_3$ reacted with water and formed Sr-hydroxide, while the chemically stable TiO_2-termineted terraces were remained. Then, the substrate was dipped into a homemade BHF (pH≈5.4) for 25 seconds so that the Sr-hydroxides were dissolved and the TiO_2-terminated terraces were left. After BHF etching, the substrate was annealed again at 950 °C in flowing oxygen (1atm) for eight hours so that atoms diffused and formed the regular TiO_2-termineted terraces in the $SrTiO_3$ surfaces. The annealing-etching-annealing process is referred to as full-treating process.

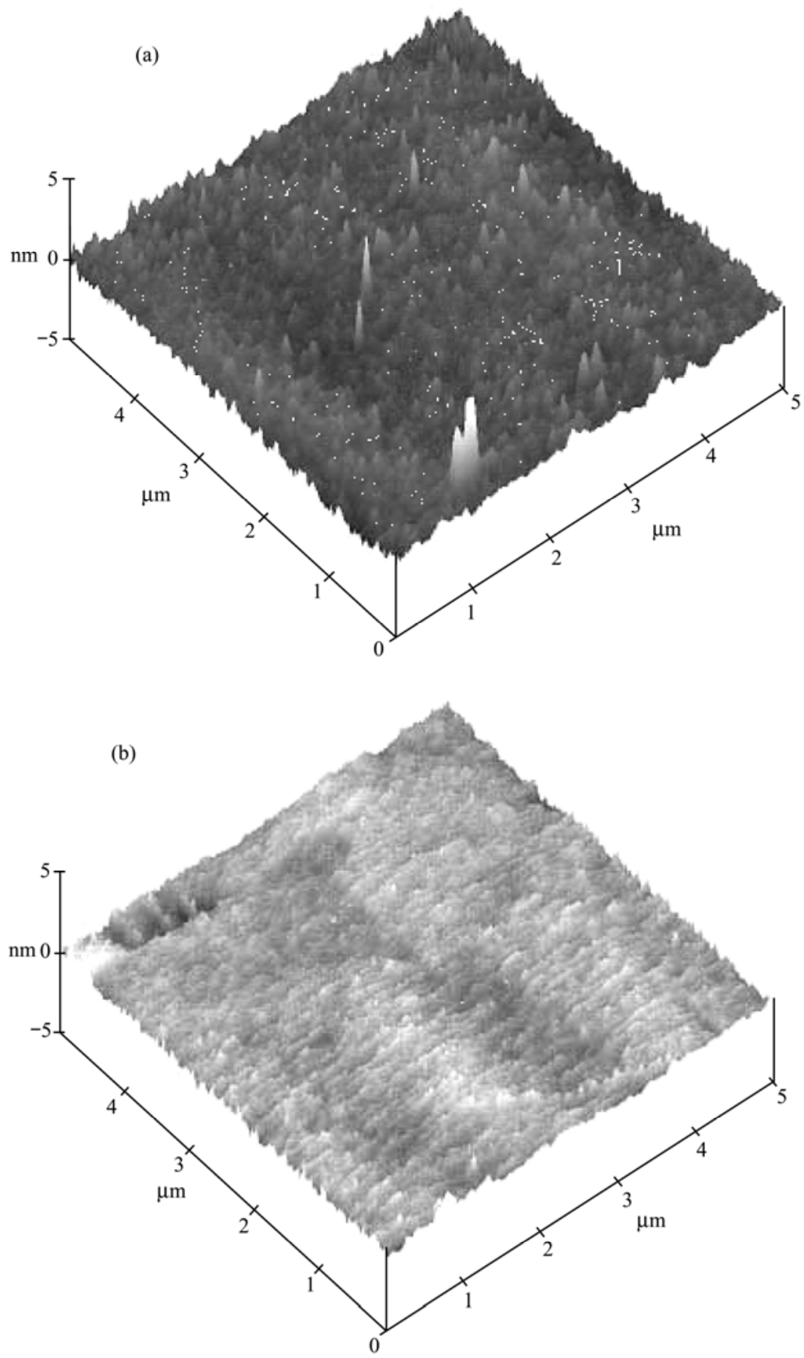

Fig. 1. 3D AFM images: (a) the $SrTiO_3$ surface of an as-received substrate, (b) the $SrTiO_3$ surface annealed in flowing oxygen at 950℃ for 2 hours.

After all the steps of the treatment, the substrates were studied by an AFM in contact mode.

2 Results and discussion

We have obtained the substrates of atomically smooth surface by using the full-treating method. Figure 2(a) shows a 2D AFM image (1 μm×1 μm) of an full-

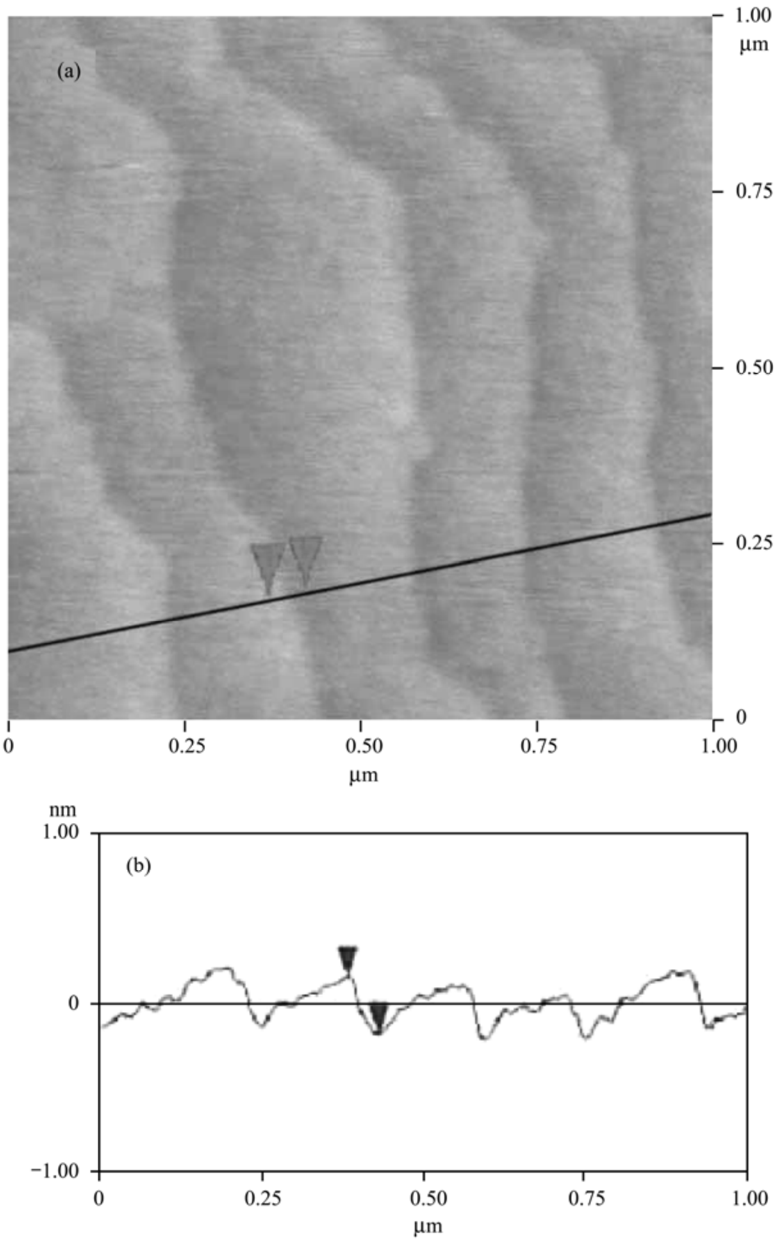

Fig. 2. (a) 2D AFM image of a fully-treated substrate, (b) the height profile along the diagonal of the 2D image.

treated $SrTiO_3$ substrate. The surface consists of flat terraces and steps with an averaged width of about 200 nm. The Rms roughness is only 0.04 nm. The average width of the steps was determined by the miscut angle of the substrate. From the averaged width of the steps, we can get the miscut angle of the substrate of ~0.1°, which is consistent with the value determined by x-ray diffraction. The height profile taken along the diagonal of the 2D AFM image as shown in Fig. 2(b) reveals that the height of the steps is ~0.39 nm or one $SrTiO_3$ unit cell. From the etching treatment described above, these terraces are TiO_2-termineted.

Both the treating conditions and the substrate quality play important roles to obtain the substrates of TiO_2-terminated surface with unit cell steps. The best annealing temperature is 950℃ and the annealing time is one of the most important parameters. There will be some pillars of Ti oxides in the substrate surface when the annealing time is too long, and some holes in the substrate surface when the annealing time is too short.

The experimental results show that Ti surface segregation will be gained if the annealing temperature is higher than 900℃ for longer time[11,12]. Fig. 3(a) and 3(b) show the 2D and 3D AFM images of a SrTiO3 substrate which was annealed at 950℃ for 10 hours. Obviously, there are some pillars with the height of ~2—8 nm on the surface even if the surface is with terraces. Kazimirov et al. studied the treatment of $SrTiO_3$ substrate in a similar way and found that there were pillars on the surfaces. They thought that the pillar compositions were mainly Ti oxides because the Sr got concentrated toward the surface in the region of 4—6 nm at the beginning of the annealing process, subsequently the Sr oxides were evaporated and the micro-crystallites of Ti oxides remained in the surface[12].

Figure 4 shows the 2D AFM image of a treated $SrTiO_3$ substrate which was annealed at 950℃ for 6 hours in oxygen ambient. The substrate surface is atomically flat with the unit cell high steps, but there are some quadrate holes in the surface. The quadrate holes were mostly located near or at the step edges. Similar square holes have been observed by Lippmaa et al. when the $SrTiO_3$ substrate was annealed in a ultra high vacuum[11], and by Stauble-Pumpin et al. when the $SrTiO_3$ substrate was annealed in oxygen[13]. The four circles marked with A, B, C and D show the different shapes of the holes in Fig. 4. Circle A represents a hole located in the middle of the step and B denotes a larger hole in the step edge. C shows a broken hole and D shows a hole which is disappearing. The four holes may indicate a dynamic process of the thermal annealing because these holes will disappear if the annealing time is longer. Most of the holes generated in the middle of the steps and moved toward the step edges or were filled by the migrating atoms during the annealing treatment. Lippmaa et al. observed the holes in the terraces being filled gradually by a scanning tunneling microscopy (STM)[11].

In fact, the surface morphologies of fully treated substrates still exhibit different qualities. We have observed some defects in the surfaces of fully treated substrates. Fig.

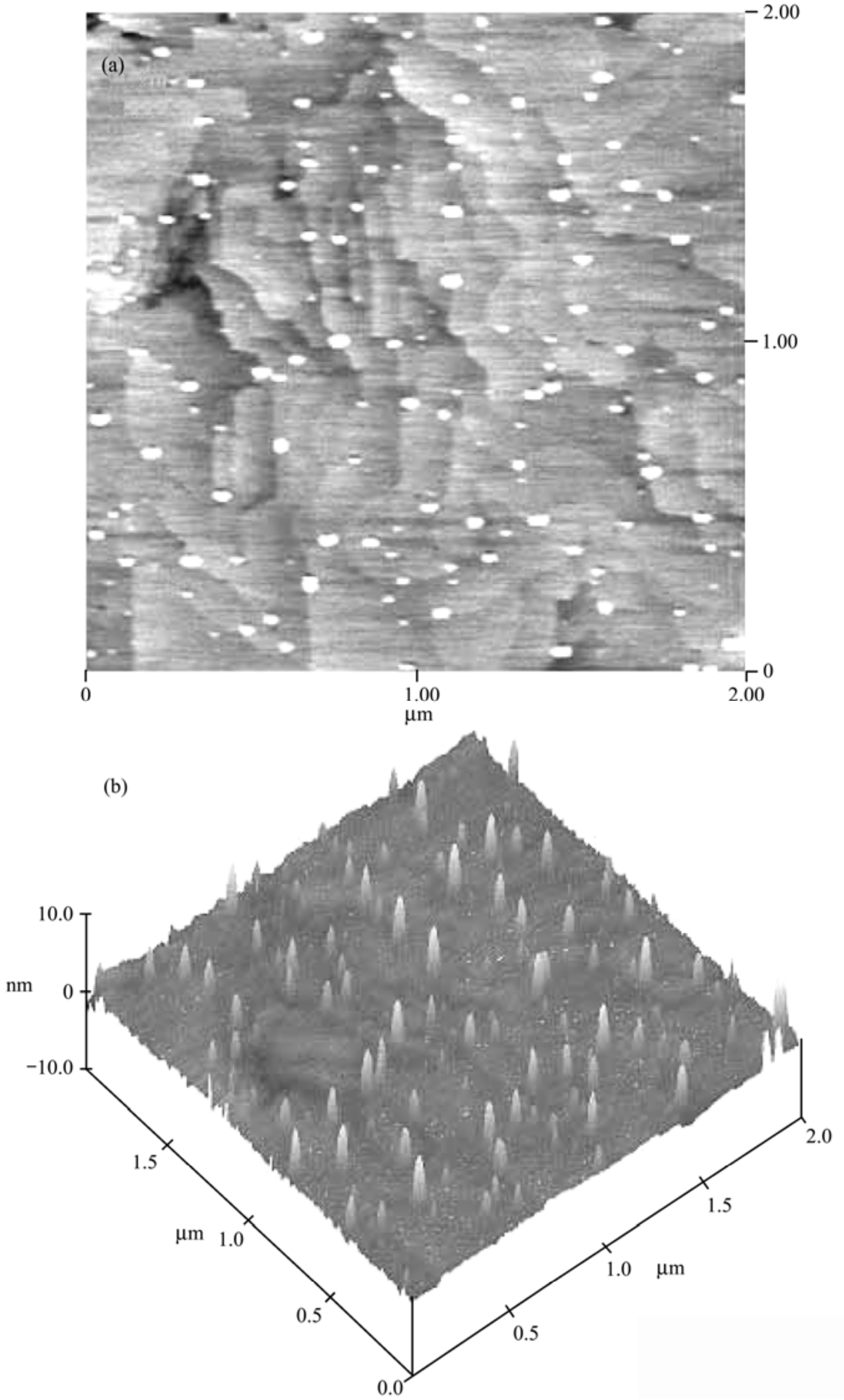

Fig. 3. The AFM images of a fully-treated substrate annealed for 10 hours at 950℃. (a) 2D AFM image, (b) 3D AFM image.

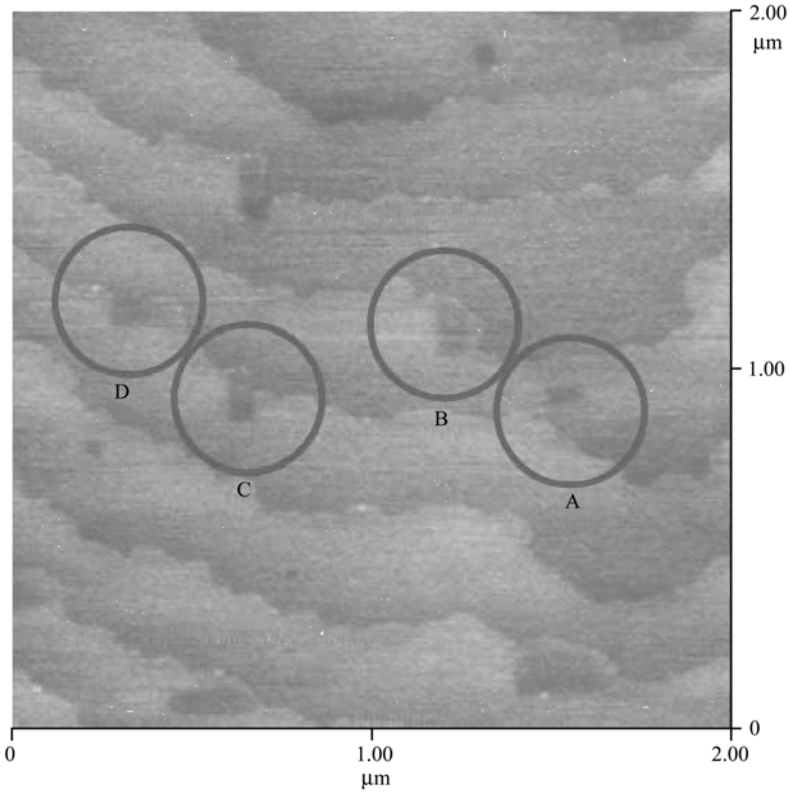

Fig. 4. 2D AFM image of a fully-treated substrate annealed for 6 hours at 950℃.

5(a) and 5(b) show the 2D and 3D AFM images of a fully-treated substrate and there is a layer dislocation marked by a circle in the surface. It seems that the layer dislocation was caused by the intrinsic crystal defects. Moreover, the 2D surface morphology with many defects in Fig. 6 is very different from the images in Figs. 2(a) and 5(a) though the $SrTiO_3$ substrates were treated in the same condition. Obviously, there are so many defects in Fig. 6 because the singlecrystal $SrTiO_3$ substrate itself is not good enough. It will be very difficult to obtain good epitaxial growth for films if the substrate as shown in Fig. 6 was used.

3 Conclusions

We have studied the $SrTiO_3$ (001) substrates treated by the chemical etching and thermal annealing in oxygen by AFM. The $SrTiO_3$ substrates with atomically smooth and TiO_2-termineted surface have been obtained. The surface morphologies of fully-treated substrates strongly depend on the treated conditions and the quality of the substrates. The experimental results have proved that treating method of the chemical etching and the thermal annealing in oxygen is valid not only in getting high-quality $SrTiO_3$ substrates but also in judging the quality of the $SrTiO_3$ substrates.

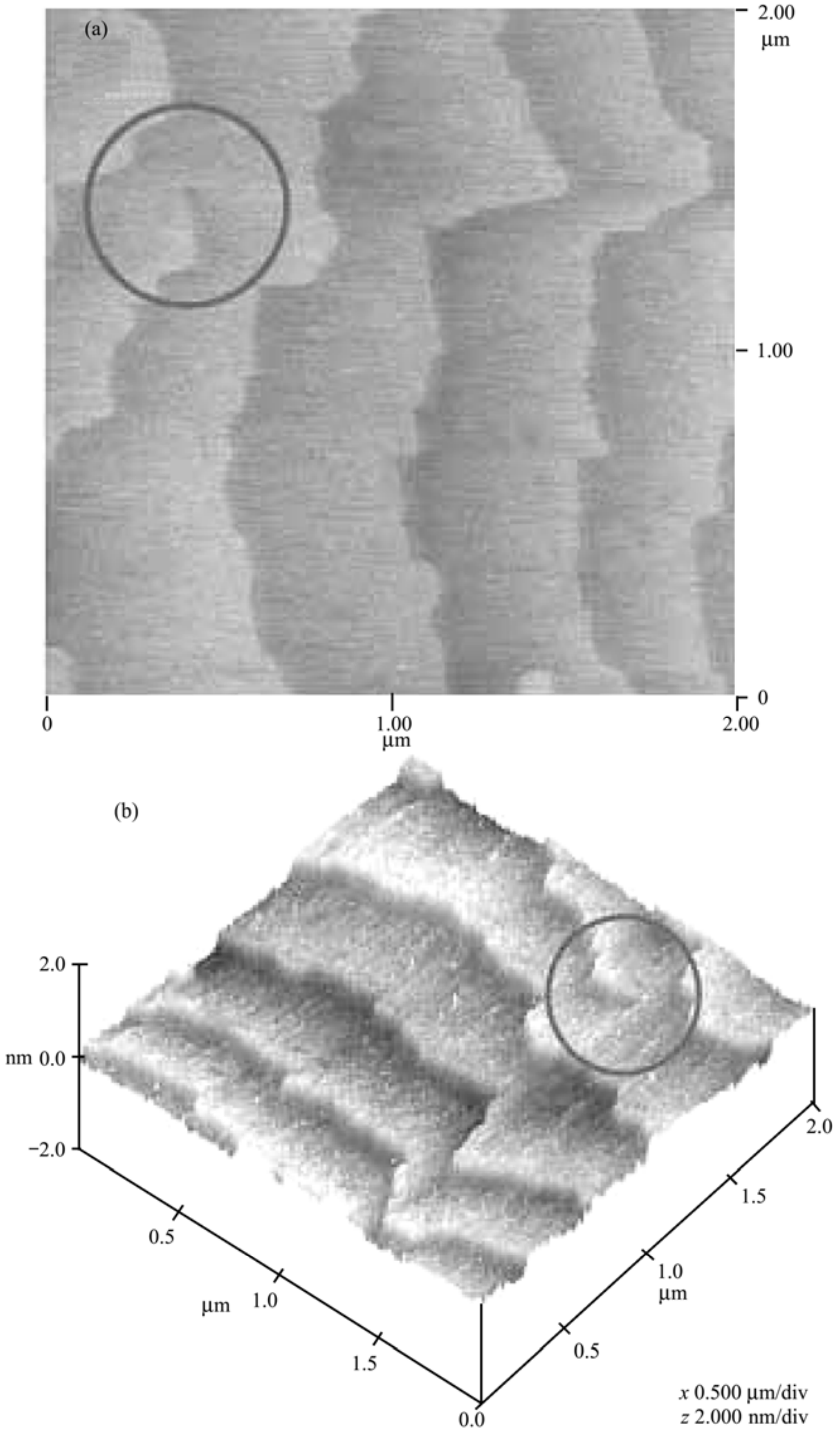

Fig. 5. AFM images of a layer dislocation. (a) 2D image, (b) 3D image.

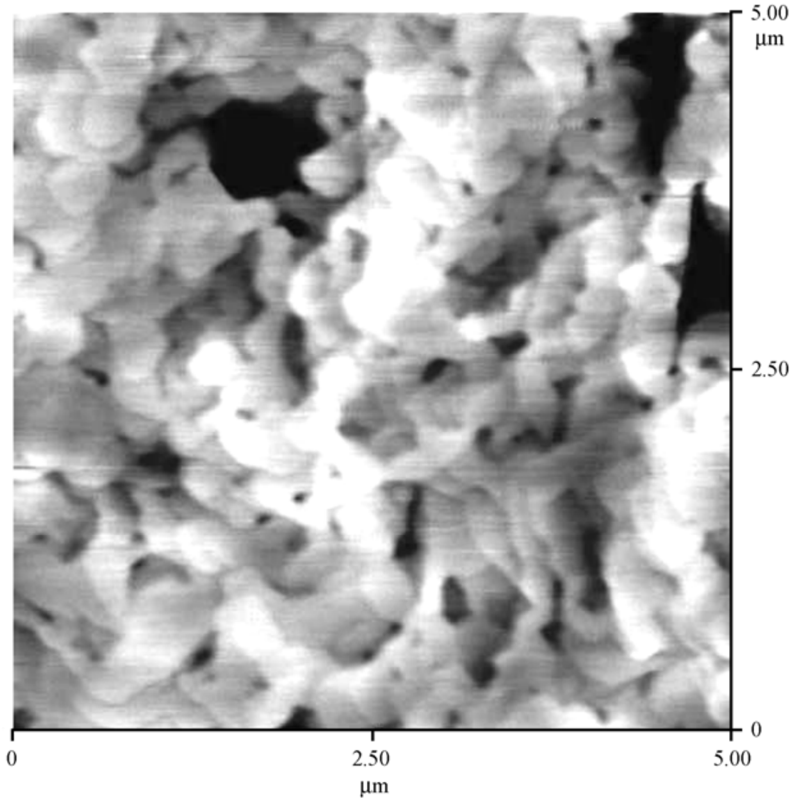

Fig. 6. 2D AFM image of a fully-treated substrate with many defects.

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