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Anisotropy of sapphire properties associated with chemical-mechanical polishing with silica

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The chemical-mechanical polishing of sapphire with (0001), $(10\bar{1}2)$, $(11\bar{2}0)$ crystal orientations at use of aqueous suspension of silica as a polishing means has been studied. It has been established that the polishing removal rate and optical quality of sapphire surface depends on its crystal orientation and a deviation angle of the geometrical sample surface from crystallographic plane. Sapphire samples with an optical surface quality 20/10-10/5 by USA MIL-O-13830 standard and a roughness R_a ~ 2–3 Å have been obtained.

Изучен процесс химико-механической полировки сапфира кристаллографических ориентаций (0001), $(10\bar{1}2)$, $(11\bar{2}0)$ при использовании водной суспензии диоксида кремния в качестве полировального раствора. Установлена анизотропия скорости съема и оптического качества поверхности сапфира в зависимости от его кристаллографической ориентации и угла отклонения геометрической поверхности образца от кристаллографической плоскости. Получены образцы сапфира с поверхностью класса оптической чистоты 20/10-10/5 по стандарту USA MIL-O-13830 и шероховатостью R_a ~ 2–3 Å.

1. Inroduction

Sapphire is used widely as a constructional material in many both science and practical applications, in particular, in microelectronics and optics for manufacturing of integrated microcircuits based on silicon-on-sapphire structures, as substrates for gallium nitride and indium nitride films in preparation of light emitting diodes. Sapphire substrates with different crystallographic orientations are used to obtain epitaxial films. The (0001) plane is used to produce light emitting diodes, whereas for "silicon-on-sapphire" structures, $(10\bar{1}2)$ one is used. High technical requirements are made to the substrate functional surface such as lack of defect near-surface layer; roughness level R_a<3 Å; flatness $L \le 5$ μm; the surface should be mirror polished; optical surface quality 20/10 by USA MIL-O-13830 standard; high accuracy of surface orientation.

The use of chemical-mechanical polishing (CMP) as the finish surface treatment technology provides high-quality surfaces of some materials such as semiconductors, crystals, glasses, plastics [1, 2]. This polishing technique has some advantages over other ones. It provides high optical quality surfaces without surface defects, high material removal rate, high efficiency along with low manufacturing costs. The sapphire CMP usually is carried out using aqueous silica suspension as the polishing means [3, 4]. However, sapphire is highly wear- and corrosion-resistant due to its high chemical and thermal stability and hardness, therefore, its polishing is a complicated task. The CMP mechanism combines interdependent chemical and mechanical processes which are poorly studied to date. Moreover, the polishing process depends heavily on crystallographic orientations of the article surface. In literature, there are only disembodied and poorly comparable experimental data on the matter [5, 6]. The CMP conditions and the results obtained by all the authors are different because they are defined by numerous individual treatment parameters such as the design and material of polishing devices, technological regimen, the polishing mix composition, as well as the structural perfection of crystals being polished. Obtaining of the surface with high parameters of optical quality and roughness is complicated when the surface area to be treated increases.

The aim of the present work was to reveal the regularities in the influence of CMP parameters on polishing rate and surface optical quality of sapphire articles depending on their crystallographic orientations and deviation angles from those, as well as to develop the complex of polishing technological conditions necessary to manufacture sapphire substrates with required technical parameters.

2. Experimental

The sapphire CMP was done using a "Camerton-500D-1" polishing machine (Lugansk), developed by Institute for Single Crystals, NAS of Ukraine. The polishing pad diameter was 500 mm, its surface was covered by kapron fabric. The polishing was carried out at regulated pressure of the sample to pad pressing P from 0.017 up to 0.080 MPa, the polishing pad rotation speed 25 rpm and frequency of driving holder double oscillations 25 min^{-1}. Silica (Aerosil-380, specific surface area 380 m^2/g) and deionized water in proportion 1:20 were used to prepare the polishing suspension. The suspension was homogenized using a mechanical stirrer. The polisher and polishing solution temperature was kept in the range of 15 to 54°C ±0.5°C by means of thermal control unit. The experimental samples (diameter 70 mm, thickness 4.5 mm) with crystallographic orientations (0001), $(10\bar{1}2)$, $(11\bar{2}0)$ and deviation angles $\varphi=9'$, 1°, 4° were made of sapphire of 99.996 % purity and high structural perfection, grown by horizontally directional crystallization according to technology developed in Institute for Single Crystals. The mechanochemical polishing of the samples was carried out on a special face-plate, which provided independent simultaneous treatment of three samples under similar conditions.

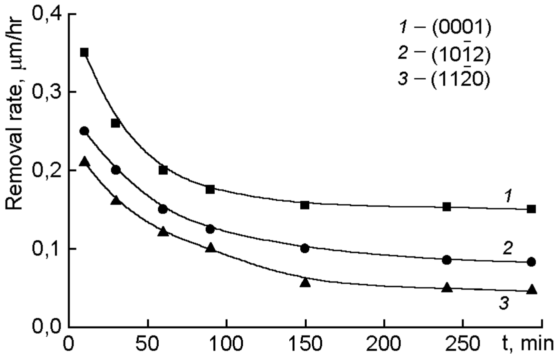


Fig. 1. Removal rate as a function of polishing time ($\varphi=9'$, $T=25$°C, $P=0.017$ MPa).

For quantitative estimation of CMP efficiency, the sapphire removal rate V was used measured by the sample mass loss using an "Axis ANG 200C" analytical balance and was calculated as

$$V = \frac{4\Delta m}{\rho\pi d^2 t},$$

where Δm is the mass loss; ρ, sapphire density (3.98 g/cm^3); t, the polishing duration; d, the sample diameter. To enhance the mass loss measuring accuracy of weight loss, not absolute mass but the mass difference between the experimental sample and reference one was determined at every measurement. The reference sample was prepared of sapphire of the same size and mass and left unchanged during the investigation. The use of reference sample made it possible to increase the mass loss measurement reproducibility and provided the measurement accuracy of ±0.1 mg, what corresponds thickness variation by ±60 Å for our samples. The structural perfection of near-surface layer was studied using the triple-crystal high resolution X-ray diffractometry [7]. The optical quality and roughness of sapphire was evaluated using a MII-4 optical microscope and an Solver P47H PRO atomic-force microscope (AFM) (Russia).

3. Results and discussion

Fig. 1 presents the polishing time dependence of sapphire removal rate at CMP of samples with different crystallographic orientations the samples being preliminary mechanically polished using the ACM-28/20 diamond paste). At the initial stage, the

Table. Mechanical (MP) and chemical-mechanical polishing (CMP) removal rates and microhardness for different crystallographic sapphire planes

Crystallographic plane	Removal rate (MP), μm/hr	Removal rate (CMP), μm/hr	Microhardness [8], GPa
(0001)	21.61	0.151	19.4
(10$\bar{1}$2)	20.31	0.083	23.15
(11$\bar{2}$0)	23.92	0.046	22.0

material removal rate is higher and then it decreases to certain constant values. Such character of the curves can be explained by presense of a defect near-surface layer formed during the mechanical polishing (MP) [8]. The CMP rate becomes constant and time-independent after removal of this layer. For further investigations, the samples were used where the defect near-surface layer has been removed by preliminary CMP.

The maximum removal rate is observed for (0001) crystallographic plane, the minimum, for (11$\bar{2}$0) one. Such relationship between the rates is kept during the whole process of sample treatment. The removal rate anisotropy observed at polishing of different planes is due to the anisotropy of sapphire physicochemical properties [9].

In literature, there are several assumptions concerning the causes of corrosion resistance anisotropy of sapphire surface. The authors [8] pay attention to the nature of atomic bonds of crystallographic planes, their electron structure and energy, considering the number of dangling bond per unit surface as an approximate measure of surface energy. The maximum number of such bonds has (0001) plane, that causes its maximum surface activity. Also only in (0001) plane, the flat grids of aluminium and oxygen atoms lay in the Al–Al–O–Al–Al–O sequence. The Al–Al bond is weaker than Al–O one, that is why its breakdown energy is minimal.

The data on mechnical and chemical-mechanical polishing removal rates along with the microhardness values for different crystallographic sapphire planes are presented in the Table. It is seen that the CMP rate does not correlate with MP data for the same samples: for (11$\bar{2}$0), the CMP rate is minimum, while the MP rate is maximal. There is also no correlation with the of microhardness values for these planes. This shows obviously that the nature of chemical-mechanical polishing process cannot be described from the purely mechanic standpoint, it includes a more complex mechanism. Also the fact that silicon dioxide with Mohs hardness of 7 may remove sapphire layer with the hardness is 9 [4] is hard to be explained. The mechanism of this process is not completely cleared up till now. The authors mentioned assume that an ultrathin hydrated AlO(OH) layer is formed at the (0001) plane only. The Mohs hardness of AlO(OH) is 6.5–7, therefore, this layer can be removed at abrasive treatment by SiO_2 particles. Then regeneration of hydrated layer occurs and the polishing process continues.

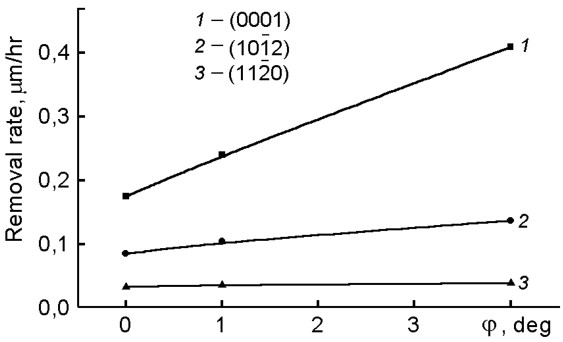


Fig. 2. Deviation angle φ dependence of the removal rate (T=25°C, P=0.017 MPa).

The study results of the CMP removal rate for (0001), (10$\bar{1}$2), (11$\bar{2}$0) planes with deviation angles of geometric surface from crystallographic plane $\varphi=9'$, 1°, 4° are presented in Fig. 2. The angular anisotropy of removal rate is observed for all planes. It is most pronounced for (0001) plane where the rate increases almost three times at deviation on 4°. A lower angular anisotropy occurs for (10$\bar{1}$2) and (11$\bar{2}$0) planes (by a factor of 2 and 1.15, respectively).

Perhaps the increase of removal rate with change in φ is caused by increasing amount of extended surface defects. In the sites where the defects exit to a surface, the position of surface atoms does not correspond to the minimum free energy. As a result, the surface areas with excess surface energy interact chemically and physically with components of polishing suspension

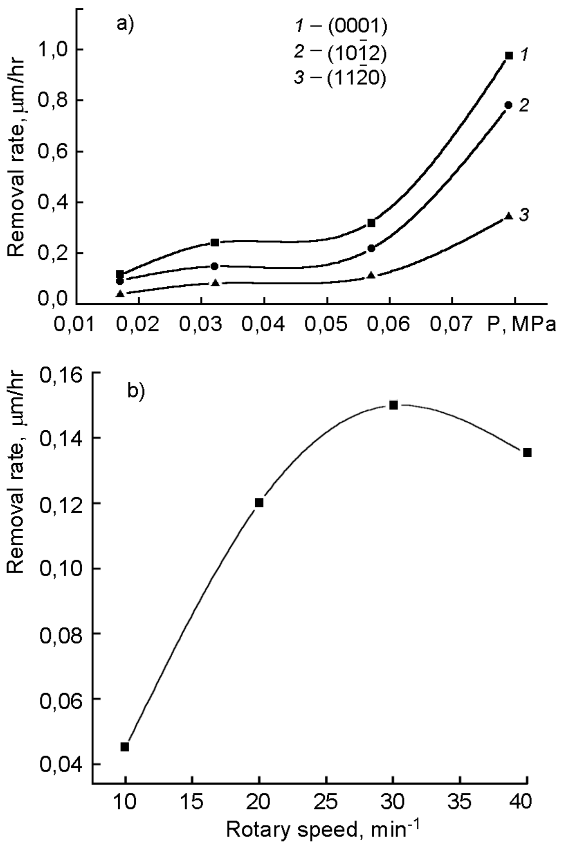


Fig. 3. Removal rate as a function of: application pressure (a) and the polishing pad rotation speed (b) (T=25°C).

more actively. The CMP process in such places is more efficient, while polishing of the samples with small deviation angles demands more time.

The increase of removal rate at increasing sample pressing pressure evidences the presence of mechanical component in the CMP process (Fig. 3, a). The sample surface quality is considerably improved in this case. The pressure dependence of the CMP removal rate was studied in [10], too. In our polishing conditions, we succeed to obtain similar removal rates at 4–5 times lower pressures. The results obtained are of a considerable practical value because the high pressing pressures results usually in vibrations; to eliminate the latter, more complex and high-priced polishing equipment is required.

The traverse speed of the sample being polished relatively to the polishing pad considerably influences the polishing efficiency. It is specified by several parameters: polishing pad rotation speed, the oscillation speed of driving holder and the sample position on the driving holder. It is established that at increase of traverse speed (in this experiment, the polisher pad rotation speed increases, other two parameters being fixed), the CMP removal rate increases too, but after attainment of a certain maximal value it starts to decrease (Fig. 3, b). The optimum traverse speed depends on the pressing pressure and on the polishing suspension viscosity. The dependence character is identical for samples of all orientations and deviation angles, the maximum position being displaced only. Perhaps it is caused by hydrodynamic effect which results in a worsened mechanical contact of the sample with polisher at a high traverse speed.

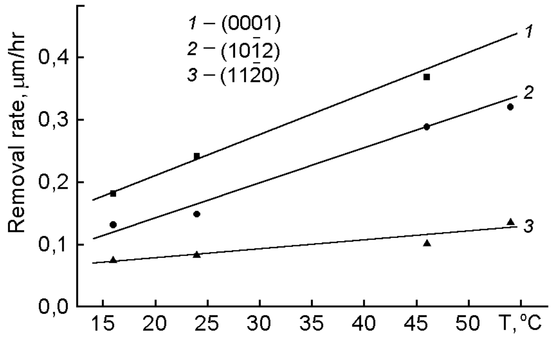


Fig. 4. Polishing temperature dependence of the removal rate (P=0.032 MPa).

As the polishing temperature rises, the removal rate grows, that evidences indirectly a chemical component in the mechanism of abrasive-substrate interaction at the sapphire CMP by silica (Fig. 4).

The removal of distorted near-surface layer (formed at previous stage of diamond-abrasive sapphire MP) after CMP treatment was confirmed by examination of the near-surface layer structural perfection by triple-crystal high resolution X-ray diffractometry. The formation of the areas with increased dislocation density in the near-surface layers due to the sample treatment was fixed stepwise by change of integral reflection power when removing of defect layer by CMP. It is shown that presence of defect textured surface layer results in the rocking curve extension of diffraction reflection and in its integral power increasing (Fig. 5, curves *1*). After the CMP, the halfwidth of rocking curve β reduces by a factor of 2–4 (Fig. 5, curves *2*) and makes 6.7 and 8.4 angular seconds for (0001) and (10$\bar{1}$2) planes, respectively. The X-ray examinations have shown that the distorted layer thickness after MP may attain 1.2–1.5 µm.

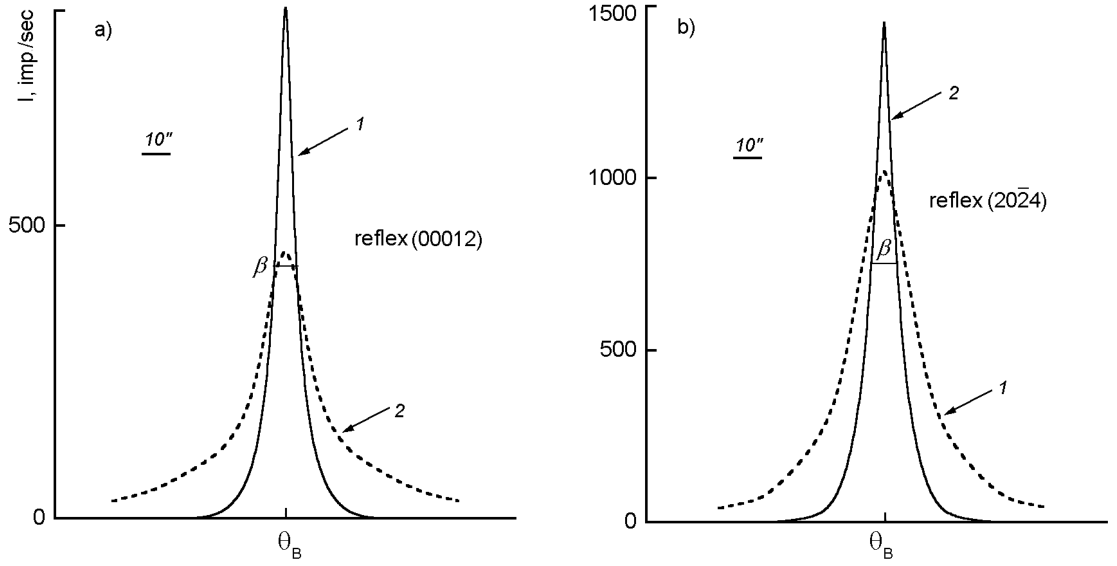
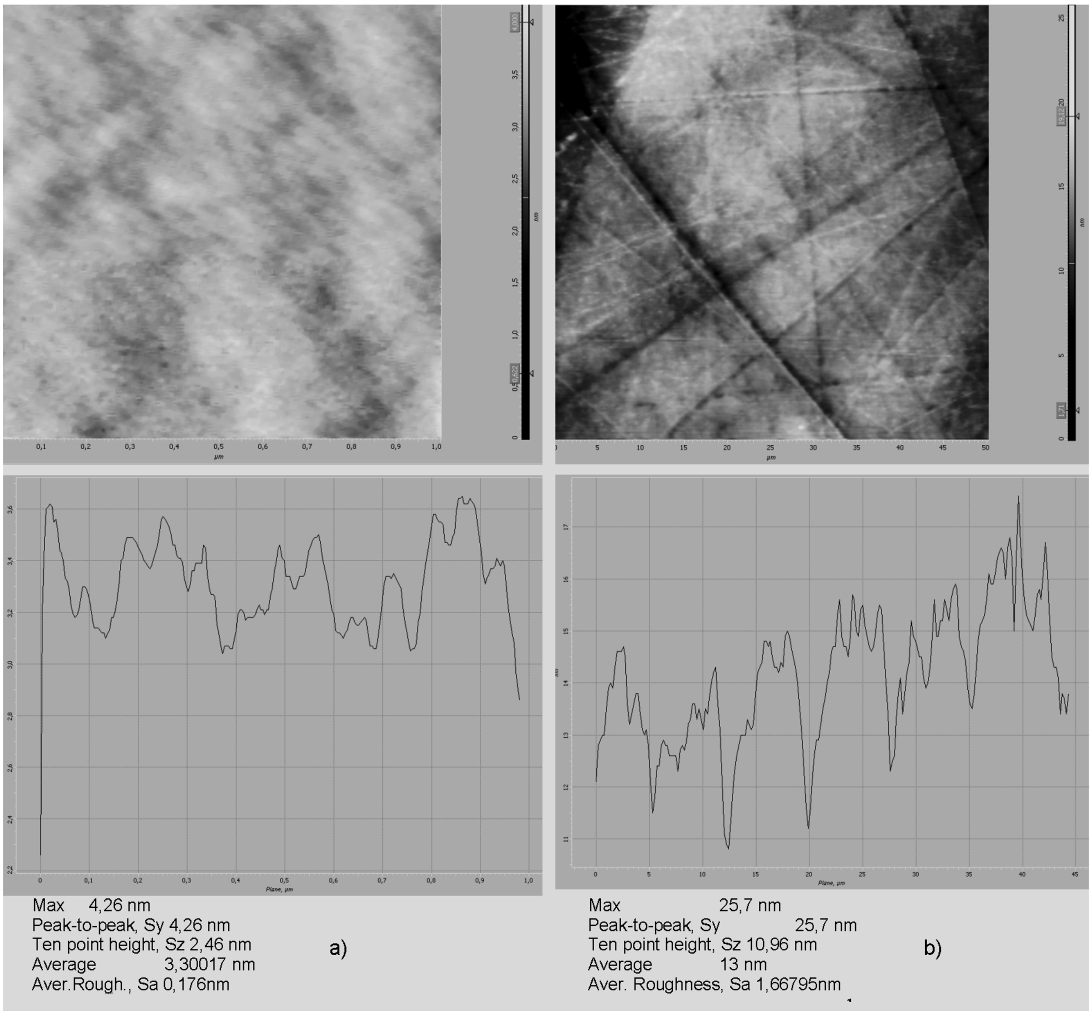


Fig. 5. The diffraction reflection curve shape for sapphire (0001) plane (a) and (10$\bar{1}$2) plane (b) (after MP (*1*) and CMP (*2*)).



Max 4,26 nm
Peak-to-peak, Sy 4,26 nm
Ten point height, Sz 2,46 nm
Average 3,30017 nm
Aver.Rough., Sa 0,176nm

a)

Max 25,7 nm
Peak-to-peak, Sy 25,7 nm
Ten point height, Sz 10,96 nm
Average 13 nm
Aver. Roughness, Sa 1,66795nm

b)

Fig. 6. AFM analysis of (0001) plane sapphire surface: a) φ=4°, b) φ=9′.

To select the optimum conditions of sapphire CMP, the topographic surface studies characterizing the optical purity and roughness were carried out besides quantitative characteristics of the process describing the near-surface layer removal rate. At increasing deviation angle φ from crystallographic plane, a general trend to surface quality improvement and decrease of roughness is observed. At φ=4°, for all crystallographic planes after 1 h. of CMP (T=25°C, P=0.017 MPa) the surface characterizes by class of optical quality 20/10-10/5 according to USA MIL-O-13830 standard. The roughness attains the values R_a ~ 2–3 Å. At reduction of φ, the polished surface quality becomes worse, the optical quality does not exceed values 80/50, roughness is $R_a \approx 50 \div 200$ Å. The surface studies at different CMP stages has revealed that more scratches are observed at (0001) sapphire surface. A particularly worsened surface quality appears at low deviation angles, the grid of scratches and damages with $R_a \approx 100 \div 200$ Å remaining after CMP (Fig. 6). The study of (0001) plane topography with φ=9′ at different CMP conditions (temperature, pressure, traverse speed of polisher pad) has shown that these parameters variation does not significantly influence the surface quality.

Examination of the (0001)9′ sample surface at different CMP stages has shown that etching of diamond abrasive scratches takes place initially. The narrow scratches become wider and more visible. Then they are finally polished and their relief become smooth. Further, they disappear; new ones arise, repeating the evolution of the disappeared ones. Thus, a certain dynamical concentration of scratches is retained on the surface, which does not change over a long time. The described effect is not observed on other crystallographic planes. New scratches also arise and disappear thereon, but the etching effect (worsening significantly the surface optical purity and its roughness) is not observed. Perhaps this is due to observed higher angular anisotropy of removal rate for (0001) plane than for $(10\bar{1}2)$ and $(11\bar{2}0)$ (see Fig. 2). Really, the relief of mechanically polished surface consisting of scratches and digs realizes set of disorientation angles where the removal rate anisotropy exists. Obviously the conditions of high angular anisotropy of removal rate can imitate the selective etching effect.

4. Conclusion

Thus, the CMP of sapphire with different crystallographic orientations and deviation angles has studied. The removal rate anisotropy is found: the removal rate is maximum for (0001) plane and minimum for $(11\bar{2}0)$ plane; it increases with increasing φ angle. Dependences of the CMP removal rate on the polishing slurry temperature, sample pressing pressure, traverse speed of polishing pad are determined. As a result of developed CMP technology, sapphire samples have been obtained with the optical surface quality 20/10–10/5 by USA MIL-O-13830 standard at the roughness R_a ~ 2–3 Å (for φ=4°). The optical properties and surface quality have been found to worsen at reduction of deviation angle, that is why further development of CMP technology is needed.

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Анізотропія властивостей сапфіру при хіміко-механічному поліруванні діоксидом кремнію

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Досліджено процес хіміко-механічного полірування сапфіру кристалографічних орієнтацій (0001), $(10\bar{1}2)$, $(11\bar{2}0)$ при використанні водної суспензії діоксиду кремнію як полірувального розчину. Встановлено анізотропію швидкості знімання та оптичної якості поверхні сапфіру в залежності від його кристалографічної орієнтації та кута відхилення геометричної поверхні зразка від кристалографічної площини. Одержано зразки сапфіру класу оптичної чистоти 20/10–10/5 за стандартом USA MIL–O–13830 з шорсткістю $R_a \sim 2$–3 Å.