06

Study of the surface and subsurface layer of CVD- grown substrates after ultrafine polishing

© V.E. Kan,[1,2] A.L. Khudoley,[3] D.V. Irzhak,[4] M.A. Knyazev,[4] T.B. Teplova[1]

[1]FREZART SV,
117587 Moscow, Russia
[2]sk Scientific Center, Siberian Branch, Russian Academy of Sciences,
644024 Omsk, Russia
[3]A.V. Lykov Heat and Mass Transfer Institute of National Academy of Sciences of Belarus,
220072 Minsk, Belarus
[4]tute of Technological Problems of Microelectronics and Ultrapure Materials, Russian Academy of Sciences,
142432 Chernogolovka, Moscow oblast, Russia
e-mail: vasiliy_kan@mail.ru

Received October 24, 2024
Revised October 24, 2024
Accepted October 24, 2024

Diamond substrates have been polished with different techniques. The results of the investigation of substrate surface after treatments are presented. It is shown that the magnetorheologic treatment is promising technique for ultrafine polishing. The data obtained with atomic-force microscopy, optical profilometry and X-ray reflexometry confirm the smoothing of diamond surface and thinning of subsurface layer after the ultrafine treatment.

Keywords: Diamond, polishing, superhard materials, subsurface layer.

DOI: 10.61011/TP.2025.02.60834.357-24

Introduction

Single-crystal diamond has a unique set of physical properties, therefore it is one of the most promising materials for microelectronic, optical and other applications [1].

Despite the in-depth theoretical analysis of diamond-based instrument engineering fundamentals, a source of large amounts of high quality stable diamond raw materials is required for practical application of the new material. Until recently, the use of diamond raw materials for high-tech products was limited by the natural diamond recovery and quality. This prevented from intense development and mass production of microelectronic, optoelectronic, lighting and other diamond-based equipment.

Single-crystal and polycrystal diamond synthesis methods have been widely developed in recent years. Synthetic diamonds are widely known as HPHT-diamonds and CVD-diamonds that are named after the production techniques — High Pressure High Temperature and Chemical Vapor Deposition, respectively. Modern technologies are used to synthesize diamonds with desired doping level and structural perfection, in volumes sufficient to start their practical utilization.

Microelectronic and optical component technologies impose high requirements for substrate and final product surface treatment. For example, atomic surface smoothness (about 0.1−0.2 nm) must be achieved for X-ray optical components. At the same time, it is necessary to ensure controlled removal of the damaged subsurface layer that is formed during surface machining and forming. The quality of surface and subsurface layers of substrates affects the performance of instrument structures to be formed on them. Dislocations and defects contained in the substrate surface layers affect the structural perfection of homoepitaxial and heteroepitaxial layers to be grown.

Traditional semiconductor (e.g. silicon) wafer technology involves multistage surface treatment. After boule cutting into substrate workpieces, loose-abrasive and fixed-abrasive machining is performed. Such machining provides workpieces with surface roughness of about 200 nm and damaged surface and subsurface layer [2]. Next surface treatment stages are designed to remove the damaged layer and provide a smooth (up to atomically smooth) surface. For precision surface treatment of products made of superhard materials, one of the following techniques is most often used [2]:

- chemical-mechanical polishing,
- thermochemical polishing,
- laser treatment,
- ion-beam etching,
- plasma-enhanced chemical etching,
- electrical discharge treatment.

The polishing methods listed above not often may be used for precision treatment of natural and synthetic diamond surfaces due to specific properties of this material. Chemical inertness of diamond limits the efficiency of chemical-mechanical polishing, which is the most widespread final polishing technique for semiconductor wafers. Moreover, chemical surface treatment results in diffusion of uncontrolled impurities into the subsurface layer of the material to be polished, which considerably

Table 1. Test samples

Sample No. sample	Manufacturer’s initial polishing	Additional manual polishing	MRP
894	+	+	+
994	+	−	+
933	+	−	−
977	+	+	−

hinders further use of polished wafers in microelectronic applications. Other methods are hard-to-do and expensive.

Magnetorheological polishing (MRP) is one of the promising high quality diamond surface treatment techniques [3]. This is ultraprecision loose-abrasive surface treatment with formation of an adaptive polisher from magnetically controlled magnetic microparticles. MRP is successfully used to produce supersmooth surfaces with angstrom-scale roughness, substrate planarization and microelectronic thin film treatment, and is also extensively used for defective layer removal and surface cleaning [3].

This method is based on magnetic field-assisted changing rheological properties of magnetorheological polishing liquid [3,4] and showed high efficiency in treatment of metals and synthetic crystal materials (leucosapphire, silicon carbide, etc.). Study of the MRP applicability for final surface treatment of synthetic single-crystal diamond products is of interest. In addition, post-treatment study of diamond wafer surface and subsurface layer is of major importance.

To manufacture products from single-crystal diamonds, quality control of machined surface and subsurface layer is of special importance. Development of a surface condition control method is important for investigating surface treatment techniques and conditions for superhard and transparent materials as well as for routine quality control in mass production process. The objective of this work was to study the surface and subsurface layers of single-crystal synthetic diamond wafers after MRP treatment.

1. Experimental procedure

Single-crystal synthetic diamond wafers were the objects of study. The material was synthesized by Bhojal Corporation (India) using the CVD technique. Initial wafers had dimensions of $7.00 \times 7.00 \times 0.42$ mm and were polished by the manufacturer.

The following samples (Table 1) were prepared for the study.

Additional polishing was performed using the „Gran-1“ polishing machines. Cast-iron polishing disc speed — 2700 rpm, disc diameter — 305 mm. Charging with 10 μm powder was performed in the area of about 50 mm from the external disc edge (rough treatment). A 20−30 mm wide area towards the center of the disc from the edge of rough treatment area was charged with diamond powder, grain size 1−0.5 μm (final treatment).

MRP treatment of wafers was carried out using the Polimag laboratory system developed by Lykov Heat and Mass Transfer Institute of National Academy of Sciences of Belarus. Magnetorheological liquid was made according to an original procedure using the UDA-SP ultrafine diamond powder (detonation synthesis, grain size 40 nm). Sample travel rate with respect to the treatment area was 1 m/s. To increase the treatment uniformity, the sample was rotated axially at a constant speed of 100 rpm. Treatment was performed in 1 h cycles. Maximum total treatment time was 17 h max.

Optical interference profilometry was performed using MicroXAM-800 (KLA Tencor, USA) 3*D*- optical profilometer with $\times 5$ and $\times 50$ lenses (1.52×1.16 mm and $152 \times 116\,\mu$m test areas, respectively). In accordance with ISO 4287, the following quantitative roughness parameters were determined: average surface roughness R_a, ten-point height of irregularities R_z, root-mean-square roughness R_q, maximum height of profile PV with topography and middle surface profile recording in horizontal direction.

Surface roughness was also examined using the NTEGRA atomic-force microscope (AFM) in semi-contact scanning mode and the X-ray reflectometry method using the Bruker D8 Discover diffractometer.

2. Results

According to the optical profilometry data, the substrate surface has clearly pronounced directional wear marks caused by the tribological property anisotropy of diamond. Single-crystal diamond surface has so-called hard and soft directions. Visible linear wear marks show soft polishing direction and occur along the direction of abrasive particles implanted in the polishing disc with respect to the polished surface. Depth of these marks is up to 18 nm for surfaces with manufacturer’s initial polishing (samples 994 and 933) and up to 8 nm for surfaces after additional polishing (samples 894 and 977).

Initial surface roughness parameters of the substrates vary within:

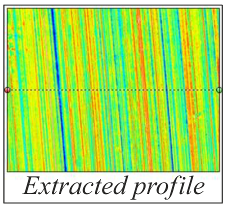
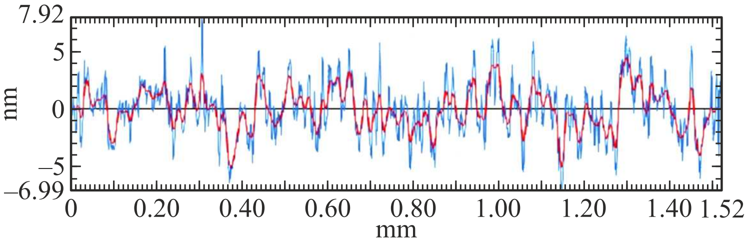
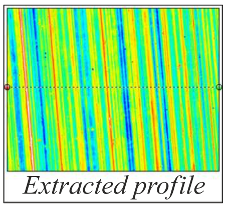
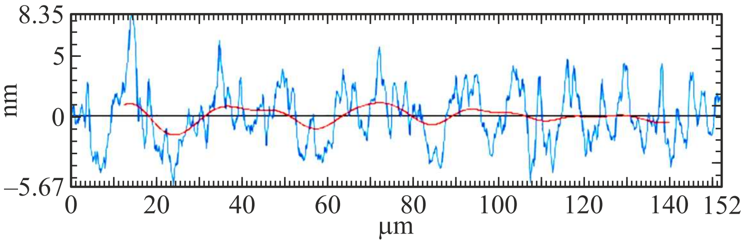
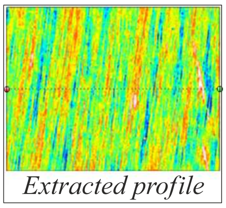
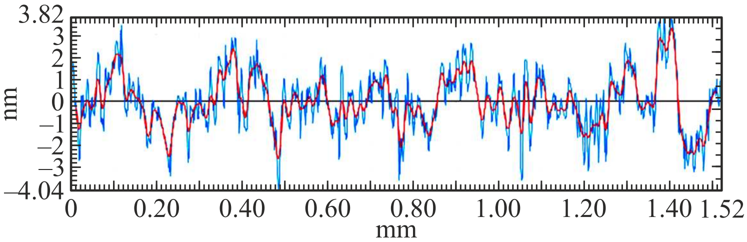
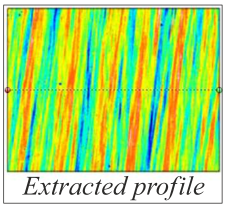
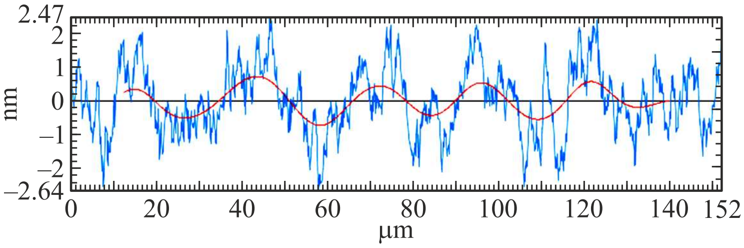
$$R_z = 3.72{-}14.40\,\text{nm}, \quad R_a = 0.63{-}2.31\,\text{nm},$$

$$R_q = 0.78{-}2.94\,\text{nm}, \quad PV = 5.39{-}17.60\,\text{nm}.$$

Minimum values refer to sample 894 after additional polishing, maximum values refer to sample 994 (Table 2).

Table 3 contains surface profilometry data for samples 994 and 894 after 6 h MRP treatment. Compared with surface properties of the initial samples, roughness has decreased. The most significant changes occurred at the surface of sample 994 that had the initial developed surface. After MRP polishing, the resultant surface roughness was at a suitable level for samples 994 and 894. According to the

Table 1. Results of pre-MRP optical profilometry of samples

Обозначение образца	Изображение, объектив	Профиль сечения срединной поверхности и параметры шероховатости, nm
994	 ×5	 $R_z = 11.00$; $R_a = 1.68$; $R_q = 2.12$; $PV = 14.90$
	 ×50	 $R_z = 8.76$; $R_a = 1.63$; $R_q = 2.01$; $PV = 14.00$
894	 ×5	 $R_z = 5.17$; $R_a = 0.82$; $R_q = 1.02$; $PV = 7.86$
	 ×50	 $R_z = 3.66$; $R_a = 0.61$; $R_q = 0.76$; $PV = 5.11$

data obtained on the ×50 lens, sample 994 has R_z decreased by a factor of 4.8, R_a — by a factor of 6.0, R_q — by a factor of 5.9, PV — by a factor of 4.1.

Comparison of surface topography and roughness control results during polishing of samples 894 and 994 indicates that the surface quality is gradually improved due to smoothing of previous treatment defects. However, after 6 h polishing, the treatment rate decreases rapidly and after 12 h no any significant change of the parameters takes place.

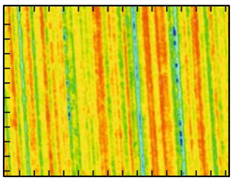
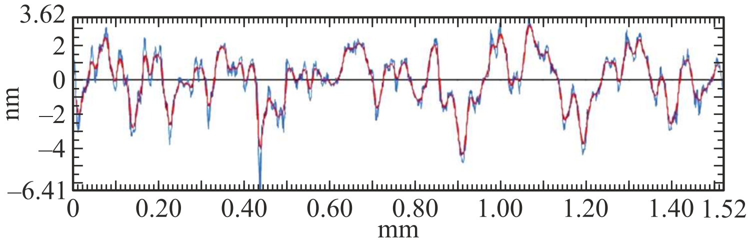
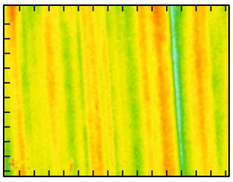
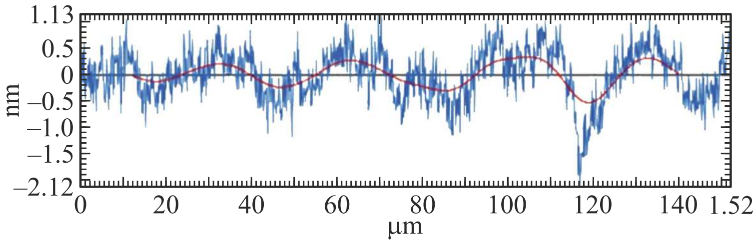
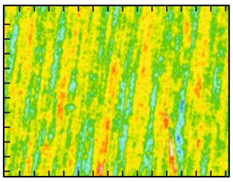
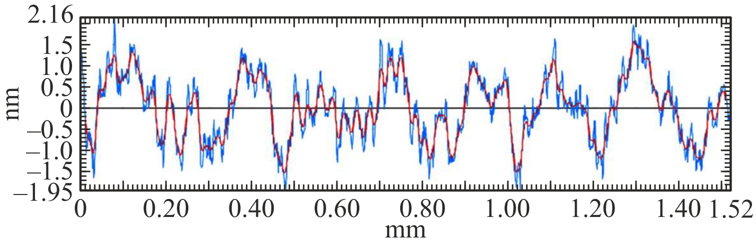
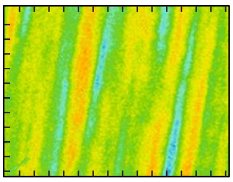
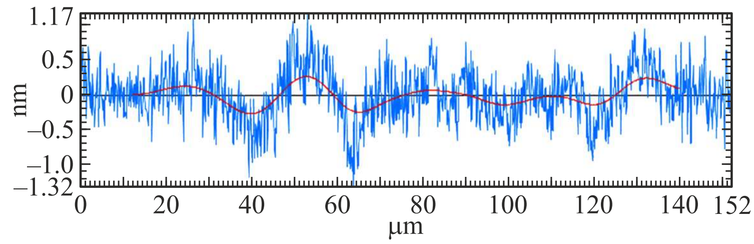
Figure 1 shows the surface roughness variation curves for CVD-diamond substrates depending on the total MRP time.

Quantitative parameters measured during MRP are affected by the initial surface condition. For manually polished sample 894 and sample 994 with the same treatment conditions, the roughness measurements differ by a factor of 2.2 to 2.5 in the 1.52 × 1.16 mm test area, by a factor of 0.8 to 0.9 in the 152−116 μm area, while the initial substrate surface roughness measurements differed almost equally by a factor of 2.2 to 2.7 (larger differences referred to the 152 × 116 μm area). This means that the MRP method first removes small defects. Longer treatment time is needed to remove macroirregularities.

AFM and X-ray reflectometry surface roughness data of the samples [5] agree well with the optical profilometry data.

The initial sample (sample 933) was examined by the AFM method. Surface roughness was more than 20 nm,

Table 2. Results of optical profilometry of samples after 6 h MRP

Обозначение образца	Изображение, объектив	Профиль сечения срединной поверхности и параметры шероховатости, nm
994	 ×5	 $R_z = 5.93$; $R_a = 0.99$; $R_q = 1.25$; $PV = 10.10$
	 ×50	 $R_z = 1.82$; $R_a = 0.27$; $R_q = 0.34$; $PV = 3.41$
894	 ×5	 $R_z = 3.03$; $R_a = 0.51$; $R_q = 0.63$; $PV = 4.80$
	 ×50	 $R_z = 1.60$; $R_a = 0.24$; $R_q = 0.30$; $PV = 2.46$

which prevents from X-ray reflectometry of the damaged layer depth. The samples after additional machining were examined by both methods. The degree of surface irregularities on the post-MRP samples is about 1−2 nm. X-ray reflectometry measurements showed the change of density profile near the post-MRP sample surface, which, together with the AFM surface roughness measurements, makes it possible to determine the damaged subsurface layer thickness. The AFM sample surface profile measurements are shown in Figure 2.

Figure 3 shows the dependences of reflected X-ray radiation intensity on the diamond crystal surfaces with various surface treatment options (Table 1). This figure also shows simulated density variation data over the sample depth that provides the best coincidence between the experimental and calculated reflection curves.

For the sample subjected to initial polishing and additional manual polishing (sample 977), it is not possible to evaluate separately the damaged layer thickness and surface roughness using X-ray measurement. The density variation area is ~ 15 nm. In the post-MRP samples (samples 994 and 894), the damaged layer thickness is ~ 1.5 nm, however, the damaged layer has minor changes of density. Surface roughness varies from 1.5 nm for sample 894 to 2.5 nm for sample 994, which coincides with the AFM measurements. This indicates both the damaged

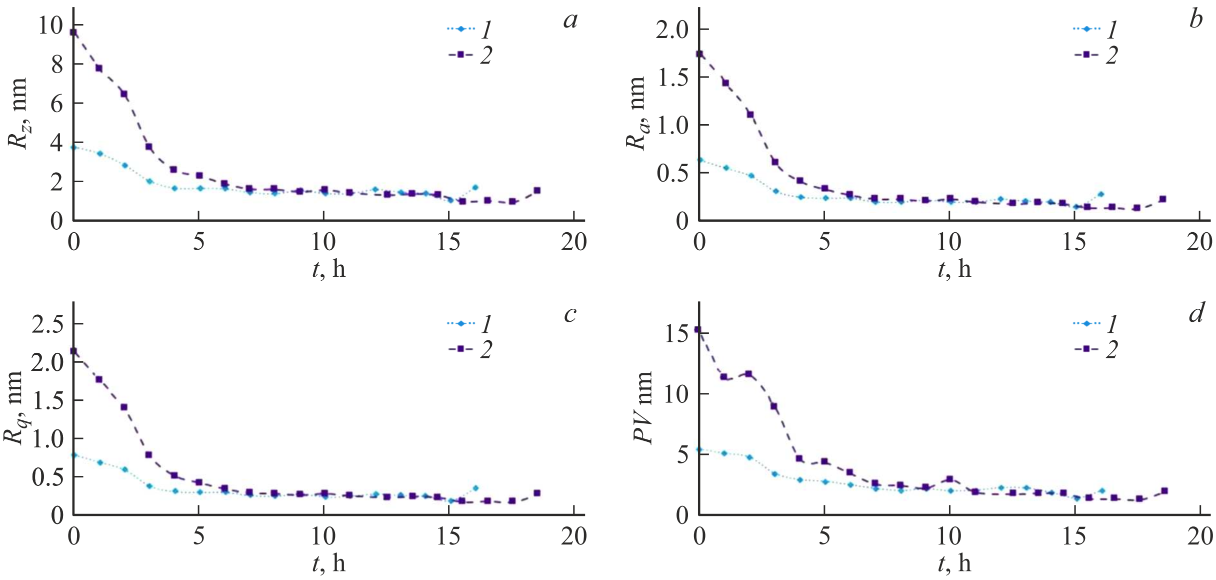


Figure 1. Substrate surface roughness variation during MRP (×50 lens): *a* — R_z, *b* — R_a, *c* — R_q, *d* — PV. *1* — sample 894; *2* — sample 994.

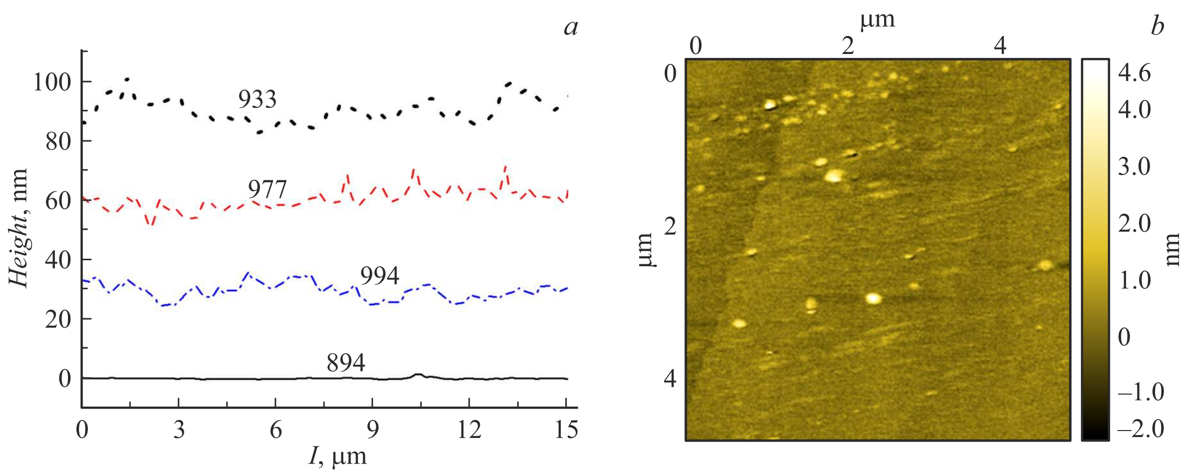


Figure 2. AFM surface examination: *a* — test sample surface profiles; *b* — AFM surface image of sample 894.

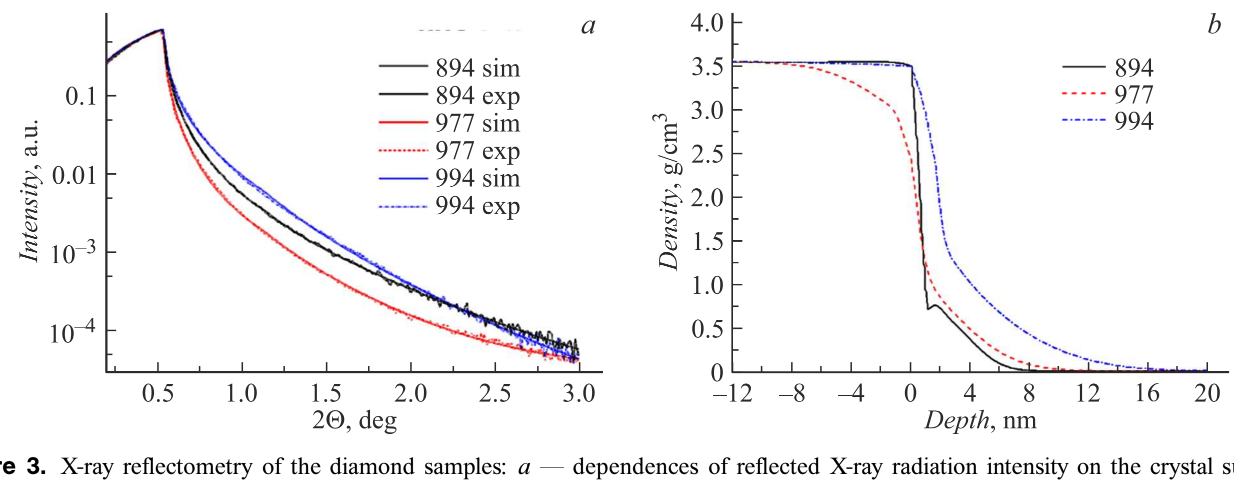


Figure 3. X-ray reflectometry of the diamond samples: *a* — dependences of reflected X-ray radiation intensity on the crystal surfaces. Designations: sim — simulation, exp — experimental curve; *b* — simulation of density variation over the depth of samples.

layer thickness variation and considerable surface roughness reduction after MRP surface treatment of the samples.

Conclusions

The studies suggest that the surface treatment quality of the single-crystal diamond samples after MRP is improved compared with the samples after surface polishing.

The X-ray reflectometry data are indicative of a considerable decrease in the damaged subsurface layer thickness after diamond surface MRP.

MRP firstly removes large irregularities. Surface shape correction of diamond products by the MRP method is possible, but requires long treatment period.

The employed set of studies (AFM, optical profilometry, X-ray reflectometry) ensures surface treatment quality control of single-crystal diamond products.

Funding

D. Irzhak and M. Knyazev carried out the studies under state assignment № 075-00296-24-00.

Conflict of interest

The authors declare no conflict of interest.

References

[1] R.A. Khmel’nitskii, N.Kh. Talipov, G.V. Tchucheva. *Sintetichesky almaz dlya elektroniki i optiki* (IKAR, M., 2017) (in Russian).
[2] T.B. Teplova. *Pretsizionnaya obrabotka poverkhnostnogo sloya tverdykh i sverkhtverdykh khrupkikh materialov v rezhime kvaziplastichnosti.* (Tekhnosfera, Moskva, 2023) (in Russian)
[3] A.L. Khudoley, V.L. Kolpashchikov, G.R. Gorodkin. *Tez. dokl. II Rossiisko-Belorusskoy nauchno-tekhnicheskoy konferentsii imO.V.Lozeva „Elementnaya baza otechesvennoy radioelektroniki: importozameshchenie i primenenie“* (Nizhny Novgorod, Rissiya, 2015), t. 1, s. 283–286 (in Russian).
[4] V.I. Kordonsky, S.R. Gorodkin. Opticheskoe materialovedenie i tekhnologiaya, **79** (9), 81 (2012) (in Russian).
[5] V. Holý, U. Pietsch, T. Baumbach. *High-Resolution X-Ray Scattering from Thin Films and Multilayers* (Springer Berlin, Heidelberg, 1999), DOI: 10.1007/BFb0109385

Translated by E.Ilinskaya