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INVESTIGATION OF THE OPTICAL COATINGS ON THE DKDP SINGLE CRYSTALS BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Magnesium fluoride and tellurium oxide were used for fabrication of the protective and antireflective coatings on the DKDP crystals. The variation of the technology of coating deposition leads to changes of surface composition of coatings which was studied by using the X-ray photoelectron spectroscopy (XPS). The XPS data allow us to conclude that carbon and its compounds, as well as oxygen resulting in the oxide formation, are the main impurities introduced at the different stages of coating deposition. The results of paper testify the fact that the ion beam processing of the DKDP single crystals with film coatings deposited onto their working surfaces facilitates the recovery of the initial composition of the film under deposition, the removal of impurities from the film surfaces that, in turn, contributes to the improvement of mechanical properties of the coating and its consolidation.

INTRODUCTION

Di-deuterium potassium phosphate (DKDP) single crystals have found wide practical application in the different-purpose optical and laser device production. This is due to high optical homogeneity of the above crystals which provides laser harmonics generation, parametric frequency tuning and laser emission amplification [1]. The disadvantage of the above crystals includes their relatively high hygroscopicity leading to the thickening of polished crystalline element surfaces under the influence of atmospheric humidity. This deterioration of crystal surface could be eliminated only partially using special polymer coatings [2] which, unfortunately, do not demonstrate enough strength to the action of laser emission. More promising are the multi-layer inorganic coatings. However the choice of material and technology of deposition onto crystal surface is a complicated tech-nical task caused mainly by such DKDP properties as high fragility in combination with low melting tem-perature. This eliminates the possibility of application of thermal heating of sample under surface cleaning and improvement of adhesion of the deposited film.

Here we report the results of investigation of the deposition conditions of double-layer protective and antireflective TeO_2 and MgF_2-based coatings onto the DKDP elements. In Tab. 1 we present the characteristics of obtained coatings which allow achieving the value of reflectance of the working crystal surfaces of 0,1% at the emission wavelength of Nd laser.

Table 1

Calculated values of coating layer thickness for the emission at the wavelength of Nd laser

Material of coating	Coating thickness, μm		Refractive index	
	$\lambda = 1{,}06$	$\lambda = 0{,}53$	$\lambda = 1{,}06$μm	$\lambda = 0{,}53$μm
TeO_2	0,0199 0,220	0,012 0,103	2,208	2,295
MgF_2	0,254 0,149	0,125 0,067	1,313	1,380

EXPERIMENTAL TECHNIQUES

We have studied three series of samples (A, B, C) differing by the method of coating deposition by using the thermal evaporation at 10^{-6} Torr pressure using the ВУ-2M vacuum setup. There were investigated three types of coatings deposited on the surface of DKDP single crystals. The A series samples were produced by serial deposition of the TeO_2 and MgF_2 layers of preset thickness onto the crystal with no vacuum chamber depressurizing. To produce the samples of series B, after the deposition of the TeO_2 layer the chamber was depressurized with further pumping out and deposition of the MgF_2 layer. The

C series samples were produced by simultaneous deposition of both layers onto the crystal with preset deposition cycle period.

The X-ray photoelectron spectroscopy (XPS) technique was applied to analyze the elemental composition of both coating and crystal surfaces. XPS spectra were recorded using a home-made high-vacuum installation. Al_{K6} ($h\nu$ = 1486,6 eV) line was used as the X-ray source and cylindrical mirror analyzer operated at constant pass energy of 100 eV as an electron analyzer. The surface of crystals before and after coating deposition was cleaned by the Ar^+-ion beam bombardment for 20 minutes at the beam current density of 10 μA/cm^2 and ion energy of1 keV. The XPS spectra taken from the DKDP single crystal surface with deposited coatings show the lines of the main coating material elements and an intense carbon line. Tab. 2 presents the relative intensities of the observed lines for different samples before and after ion beam cleaning.

violation of stoichiometric composition of such films due to the rise of anionic vacancies in the films. The influence of atmosphere leads to neutralization of the above indicated vacancies by the OH^- ions and the production of the complex composition $MgF_{2x}OH_x$.

Analysis of the XPS spectra for the B series samples measured immediately after the deposition of the coatings also indicates the presence of the magnesium, fluoride, oxygen and carbon lines of almost the same intensity as for the A series samples. However in this case ion cleaning of the surface leads to essentially different results: the carbon line intensity decreases only twice, whereas the oxygen line undergoes almost no changes. Probably, in this case oxygen-containing compounds are not only adsorbed at the surface but are also involved in the bulk of film. This is confirmed, in particular, by the behavior of the fluoride line, the intensity of which increases slightly after the ion cleaning.

Table 2

XPS line intensities (relative units) of surface coatings prepared by different technological procedures and subjected to ion beam cleaning

Sample series	Element	C	O	Te		Mg	F
	Electron configuration	$1s_{1/2}$	$1s_{1/2}$	$3d_{5/2}$	$3d_{5/2}$	$2s_{1/2}$	$2s_{1/2}$
	Binding energy, E (eV)	285	532	573	583	91	686
A	Before ion cleaning	35	40	–	–	5	28
	After ion cleaning	7	8	–	–	7	98
B	Before ion cleaning	23	53	–	–	3	17
	After ion cleaning	12	45	–	–	8	5
B	Before ion cleaning	24	40	50	30	8	90
	After ion cleaning	12	16	25	15	7	10

EXPERIMENTAL RESULTS AND DISCUSSION

Surface cleaning of A series samples by the Ar^+ ion beam results in almost total vanishing of the carbon line and considerable reduction of the oxygen line intensity. This indicates not only the high efficiency of ion cleaning for elimination from the crystal surface of compounds of organic origin, but also testifies the formation of oxides on the MgF_2 film surface. This result agrees well with the data [3] on the

At the simultaneous deposition of both TeO_2 and MgF_2 layers onto the crystal (C series samples) the XPS spectra demonstrate the lines of the deposited elements: magnesium (binding energy of 54 and 95 eV), fluorine (685 eV), carbon (286 eV), oxygen (535 eV) and tellurium (580 and 590 eV). Fig. 1 shows the XPS spectra for the C series samples within the 500–750 eV energy range. In this energy interval, the observed Te line has double shape and is sensitive to the further ion beam processing, while

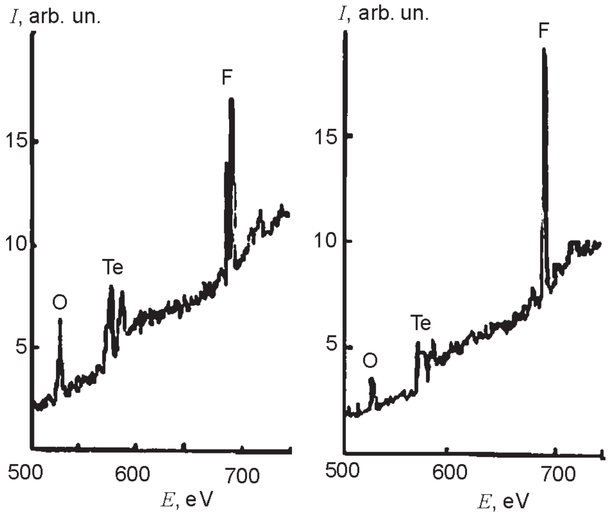

Fig. 1. XPS spectra of the C series of samples: (a) – prior to the ion-beam cleaning, (b) – after the ion-beam cleaning.

its main maximum shifts towards the higher energies by 10 eV with respect to the previous sample series. After ion cleaning the intensity of these maxima is decreased, and the maxima at 573 and 583 eV, typical for the clean TeO_4 film spectrum, are revealed more distinctly. One may assume that at the simultaneous deposition of both TeO_2 and MgF_2 layers onto the crystal the formation of TeF_4-like compounds occurs. This assumption is confirmed, in particular, by the behavior of the fluoride lines in the observed XPS spectrum. Ion cleaning of the deposited film results in a slight increase (by 1,3 times) of the fluorine line intensity, while the oxygen and carbon lines intensities decrease by 2,3 and 2,0 times, respectively. In this case the coating surface reveals the properties similar to those of the MgF_2 films.

For the oxygen lines the energy shift from 532 eV to 535 eV is also observed allowing, thus, one to as-sume the presence of the MgO-like oxides in the MgF_2 film or that of other combination of oxygen compounds. In the case of C series samples, the ccurrence of oxygen could be caused by its presence in the residual gas of the deposition chamber.

The authors of [4] have shown that MgF_2 film processing by plasma discharge in the carbon tetra fluoride atmosphere increases the mechanical durability and enhances film resistance against the influence of climatic conditions. that could be explained by disappearance of anionic vacancies. This could be explained by anionic vacancies "curing" and the recovery of the stoic-geometric composition of pro-duced film. The results of the present paper testify the fact that the ion beam processing of the DKDP single crystals with film coatings deposited onto their working surfaces facilitates the recovery of the initial composition of the film under deposition, the removal of impurities from the film surfaces that, in turn, contributes to the improvement of mechanical pro-perties of the coating and its consolidation. The des-tructive effect of ion cleaning could be relatively easy prevented by choosing the relevant regime in each particular case.

Thus, our investigations allow us to conclude that carbon and its compounds, as well as oxygen resulting in the oxide formation, are the main impurities introduced at the different stages of coating deposition. One may not exclude the possibility of oxygen production at the thermal decomposition of tellurium dioxide used as one of the coatings. This indicates the necessity of further search for the coatings of optimal composition. At the same time, the results obtained in this work allow to produce optical elements of DKDP with protective and antireflective coatings that possess high enough technical characteristics and to develop the most optimal regimes of the coating deposition.

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ДОСЛІДЖЕННЯ ОПТИЧНИХ ПОКРИТТІВ НА DKDP МОНОКРИСТАЛАХ МЕТОДОМ РЕНТГЕНІВСЬКОЇ ФОТОЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ

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Для одержання захисних і просвітляючих покриттів кристалів ДКДР використовувалися фторид магнію та оксид телуру. Модифікація технології нанесення покриттів призвела до зміни складу поверхні покрить, що досліджувалися методом рентгенівської фотоелектронної спектроскопії (РФС). Дані РФС дозволяють зробити висновок, що вуглець та його сполуки, а також кисень, що призводить до утворення оксидів, є основними домішками, які вводяться на різних етапах нанесення покриттів. Результати роботи свідчать на користь того, що обробка монокристалів ДКДР з плівками, осадженими на їх робочі поверхні, за допомогою іонного пучка сприяє відновленню вихідного складу осаджуваної плівки, вилученню домішок з її поверхні, що, в свою чергу, покращує механічні властивості покриття і його експлуатаційні характеристики.

ИССЛЕДОВАНИЕ ОПТИЧЕСКИХ ПОКРЫТИЙ НА DKDP МОНОКРИСТАЛЛАХ МЕТОДОМ РЕНТГЕНОВСКОЙ ФОТОЭЛЕКТРОННОЙ СПЕКТРОСКОПИИ

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Для получения защитных и просветляющих покрытий кристаллов ДКДР использовались фторид магния и оксид теллура. Модификация технологии нанесения покрытий привела к изменению состава поверхности покрытий, исследуемых методом рентгеновской фотоэлектронной спектроскопии (РФС). Данные РФС позволяют заключить, что углерод и его соединения, а также кислород, приводящий к образованию оксидов, являются основными примесями, вводимыми на различных этапах нанесения покрытий. Результаты работы свидетельствуют в пользу того, что обработка монокристаллов ДКДР с пленками, осажденными на их рабочие поверхности, с помощью ионного пучка способствует восстановлению исходного состава осаждаемой пленки, удалению примесей с ее поверхности, что, в свою очередь, улучшает механические свойства покрытия и его эксплуатационные характеристики.