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ФОТОИНДУЦИРОВАННЫЕ ПОЛИКОНДЕНСАЦИОННЫЕ ПРОЦЕССЫ В ТОНКИХ ПЛЕНКАХ СМЕШАННОГО ОКСИДА МОЛИБДЕНА И ВАНАДИЯ: ПЕРСПЕКТИВЫ СОЗДАНИЯ НОВЫХ ФОТОЛИТОГРАФИЧЕСКИХ МАТЕРИАЛОВ

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На основе использования фрактального анализа атомно-силовых изображений исследован механизм УФ-стимулированной поликонденсации в пленках V_2O_5 : MoO_3 (мольное соотношение оксидов 3 : 2), полученных из соответствующих оксокислот. Установлено, что твердофазная полимеризация смешанно-оксидных олигомеров протекает по 3D-механизму, результатом действия которого является увеличение среднего арифметического отклонения профиля поверхности оксидного слоя при одновременном уменьшении фрактальной размерности. Показано, что поликонденсация сопровождается эффектами упорядочения, приводящими к образованию агломератов зерен в виде псевдокристаллитов нанометрового размера, которые можно наблюдать на атомно-силовых изображениях после проявления в растворе кислоты. Такое упорядочение является одним из факторов, обеспечивающих размерную стабильность фотолитографических рисунков, генерированных при помощи пленок MoO_3 : V_2O_5, и сохранение у них ровного края.

Ключевые слова: фотополимеризация; смешанный оксид молибдена и ванадия; фоторезисты.

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PHOTOINDUCED POLYCONDENSATION PROCESSES IN MOLYBDENUM AND VANADIUM MIXED OXIDE THIN FILMS: TOWARDS NOVEL PHOTOLITHOGRAPHIC MATERIAL

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Investigation of the mechanism of UV-induced polycondensation in the oxoacid-derived mixed oxide V_2O_5 : MoO_3 (molar ratio of oxides was 3 : 2) films employing fractal analysis of AFM images has evidenced that solid-state polymerisation process *via* 3D-mechanism resulting in the increased roughness of the microrelief of the film accompanied, however, with decrease of the fractal dimension. The polycondensation is accompanied with ordering yielding nuclei agglomerates built of nanometer-sized faceted pseudocrystals which become visible after development in the acid solution. These alignment effects, that result in the recovery of the photoresist film microrelief and the increase of the fractal dimension to the initial value ensures the dimension stability and sharp edges in the case of patterns generated with MoO_3 : V_2O_5 photoresist films.

Keywords: photopolymerisation; molybdenum and vanadium mixed oxide; photoresists.

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Introduction

The inorganic oxides have attracted much attention in recent years as the promising photoresist materials due to excellent radiation-, plasma- and thermostability inherent in them [1; 2]. These materials enable generation of highly stable masks for deep reactive-ion etching without using sophisticated multilayered masking assembles comprising both thermostable and photosensitive layers [3] that opens new avenues in microelectronics and micromachining. Thin films of molybdenum and vanadium oxides derived from corresponding oxoacids were successfully used as the negative photoresists which can be readily developed in the acid-containing aqueous solutions [4; 5]. The employment of oxoacids as the precursors of photosensitive oxide-hydroxide materials permits one to exert an effective control over the photoresist film formation by choosing proper concentration of oxoacid and acidity of the medium where polycondensation occurs [6]. Under UV-exposure, initially oligomeric vanadium and molybdenum acids exhibit further polymerisation in condensed state yielding (after acid development) the oxide patterns with rather sharp edges [5]. Of special interest for photolithographic applications are highly uniform films of molybdenum and vanadium mixed oxide derived from diluted aqueous solutions of mixed molybdenum and vanadium acid which demonstrate so smooth surface at the nanoscale that their morphology and surface relief features cannot be effectively studied with scanning electron microscopy. In this work, the structure and morphology of molybdenum and vanadium mixed oxide films were investigated employing the fractal analysis of atomic-force images with special emphasis on the effects associated with photoinduced polycondensation of oligomers in the photoresist material.

Materials and methods

Thin films of molybdenum and vanadium mixed oxides were deposited *via* centrifugation onto the surface of silica wafers employing 0.2 mol/L solution of mixed Mo – V acid obtained by acidification of corresponding metallates on a resin [6]. The composition of mixed oxoacid corresponds to the composition of mixed oxide V_2O_5 : MoO_3 (molar ratio of oxides was 3 : 2). After air drying thus prepared hydrated V_2O_5 : MoO_3 films (ca. 6 μm in thickness) were exposed to UV-light through quartz mask using Philips TUV 15 W lamp (*Philips Lighting B. V.*, Belgium) (wavelength 253.7 nm, intensity 1.5 mW/cm^2).

The exposed films were processed in 0.005 mol/L acetic acid; the development time needed to obtain oxide pattern was 20 min. The developed pattern was thoroughly washed with triply distilled water and air dried.

The investigation of the surface morphology of V_2O_5 : MoO_3 at different stages of photolithographic process (before exposure, after exposure, after development) was performed employing atomic force microscopy (AFM) with the use of TT2 microscope (*AFMWorkshop*, USA). For fractal analysis of AFM images the *Gwyddion* package was used. The fractal dimension values were obtained by cube counting method.

Results and discussion

Thin films derived from mixed Mo – V acid which demonstrate a pronounced tendency to the spontaneous oligomerisation [7] yields defect-free V_2O_5 : MoO_3 films with very smooth surface (the roughness average (R_a) is below 12 nm) as evidenced by AFM. The UV-exposure induces the process of polymerisation and resultant film becomes insoluble in the acid solution (the rate of etching of non-exposed areas at V_2O_5 : MoO_3 film is 52 times larger than the rate of etching of the exposed ones) that opens the possibility of pattern generation. During development in the acid solution the exposed areas remain almost untaken (the rate of the etching of the exposed areas is below 0.014 μm/s).

To reveal the exact microgeometry of the oxide film surface and to trace the changes in the surface morphology upon exposure and further development *via* treatment in acid solution the polynomial background subtraction was performed resulting in flattering of the AFM images. Thus corrected images given in fig. 1 evidence that freshly prepared V_2O_5 : MoO_3 films demonstrate wave-like oscillations of the relief along definite directions (this regular variations of the surface relief become observable only in some cross-sections). The observed relief is a manifestation of directional alignment of oxide-hydroxide nuclei in the photoresist film during its formation. Note that similar wave-like relief oscillations were reported previously for sol-gel derived titania films employed as the photosensitive material for photocatalytic lithography [8].

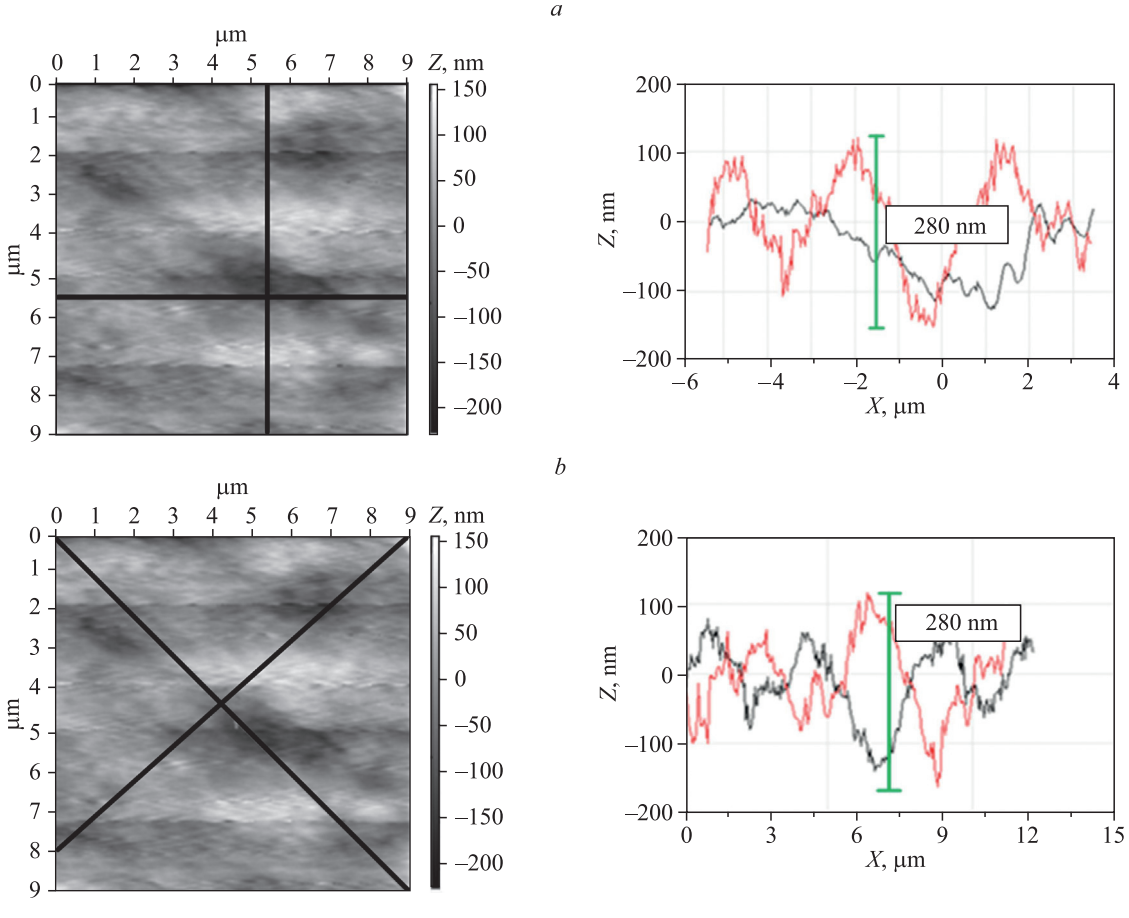

Fig. 1. AFM images and surface relief profiles of as-prepared V_2O_5 : MoO_3 films.
The profiles were obtained in the normal directions (*a*) and in the diagonal directions (*b*)

Upon UV-exposure, the microgeometry of V_2O_5 : MoO_3 films surface becomes much more complicated (fig. 2) and loses the anisotropy: the cross sections reveal the lack of directions along which exhibits any regular oscillations. In general, the relief becomes more rough (R_a = 30.15 nm). It is also seen from fig. 3 that there exists a pronounced asymmetry in the position of the structural elements at the surface of as-prepared V_2O_5 : MoO_3 photoresist film (one distance between structural elements appears to be smaller than others (see fig. 3, *a*)), this asymmetry disappearing upon exposure (see fig. 3, *b*) shows, however, recovery after development in the acid solution (see fig. 3, *c*). The exposure thus changes the localisation of structural features at the photoresist surface, these elements being now equidistant from each other that can be considered as a strong indicative of solid-state 3D-polycondensation.

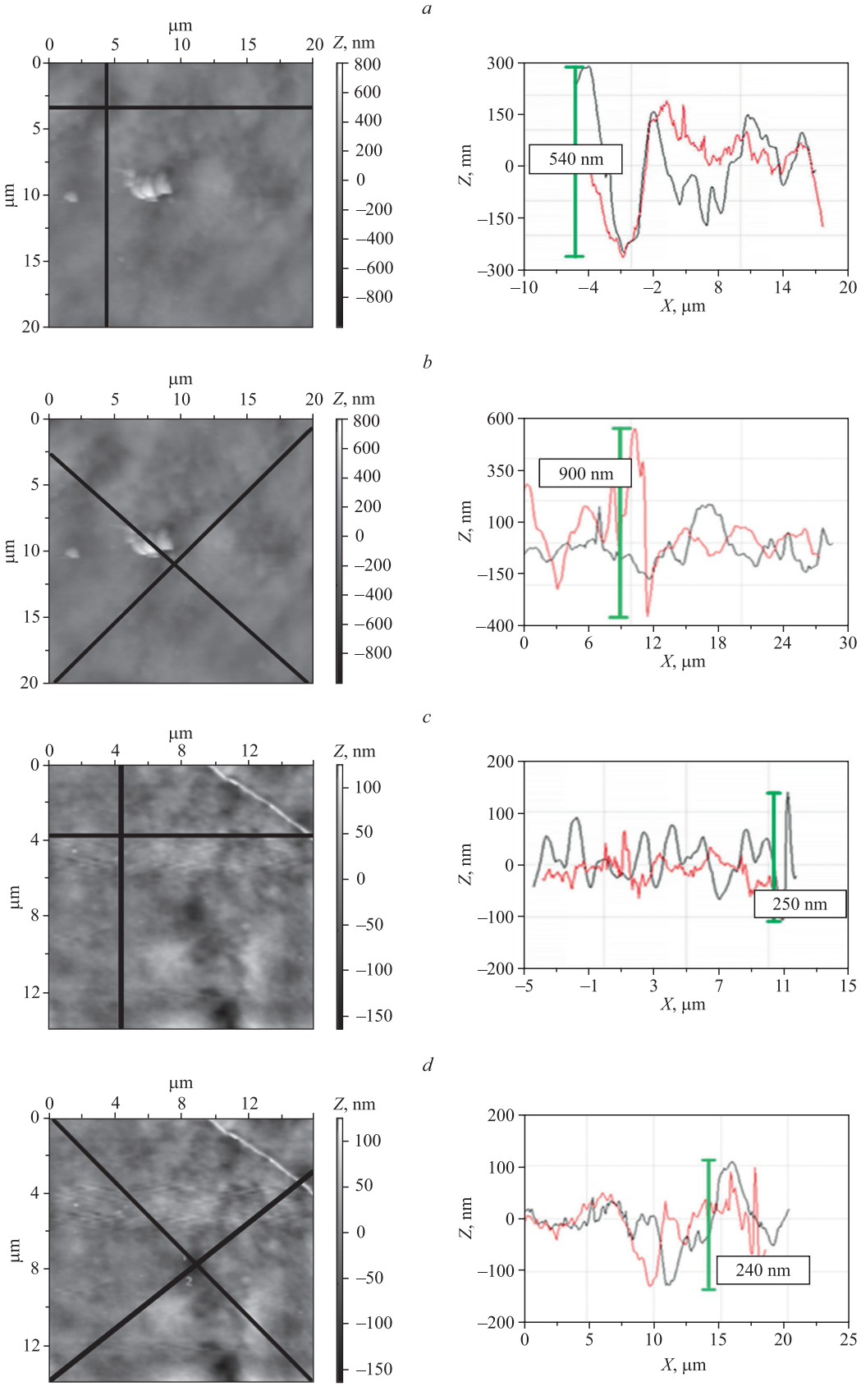

Fig. 2. AFM images and surface relief profiles of V_2O_5 : MoO_3 filmsexposed to UV-light (*a*, *b*) and exposed to UV-light and etched in acid solution for 6 min (*c*, *d*). The profiles were obtained in the normal directions (*a*, *c*) and in the diagonal directions (*b*, *d*)

During the course of UV-illumination, the roughness average increases 3-fold. The observed increase of the surface roughness in nanoscale can be attributed to the agglomeration of nuclei forming the mixed oxide film. The latter effect appears to be compensated to large extend as the result of acid etching that occurs as the selective process. The etching of the exposed V_2O_5 : MoO_3 film in the acid solution, however, results in a pronounced smothering of the relief as evidenced by fig. 3, suggesting that dissolving process localised mostly at the surface defects and stepwise structures.

The analysis of the surface relief of V_2O_5 : MoO_3 film reveals the nuclei which are visualised in fig. 4 that makes it evident that the medium size of nuclei (R_N) exhibits increase when coming from as-prepared mixed oxide films to the exposed ones; the etching in the developing solution results in the decrease of R_N value.

The nuclei observed in the AFM images at the surface of V_2O_5 : MoO_3 film (fig. 5) are non-uniform and possess inner structure. The analysis of the AFM image provide an evidence that nuclei consist of the faceted structural elements which can be considered as pseudocrystallites, the number of crystallites increasing drastically upon exposure and especially after etching. It can be thus suggested that solid-state photoinduced polycondensation is accompanied with recrystallisation of amorphous oxide-hydroxide film leading to the formation of inner (latent) structure which becomes visible upon etching.

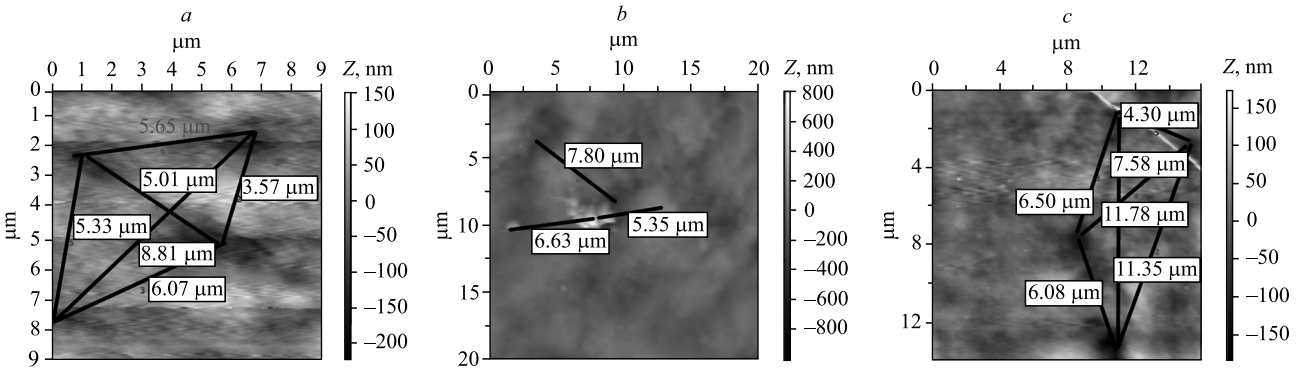

Fig. 3. The surface relief of V_2O_5 : MoO_3 films: *a* – as-prepared film; *b* – the film exposed to UV-light; *c* – the film exposed to UV-light and etched in acid solution for 6 min

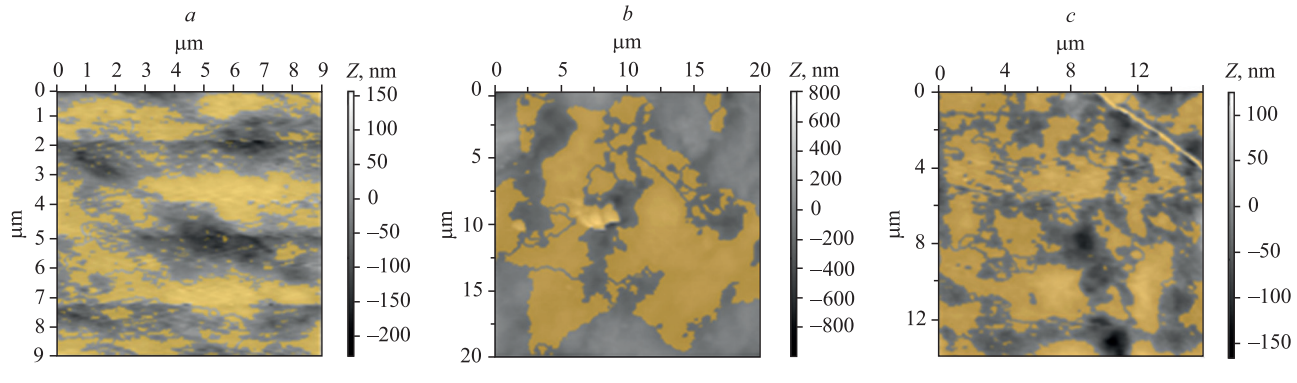

Fig. 4. The nuclei (shown in yellow) at the surface of V_2O_5 : MoO_3 films: *a* – as-prepared film, R_N = 63.14 nm; *b* – the film exposed to UV-light, R_N = 275.8 nm; *c* – the film exposed to UV-light and etched in acid solution for 6 min, R_N = 198.1 nm

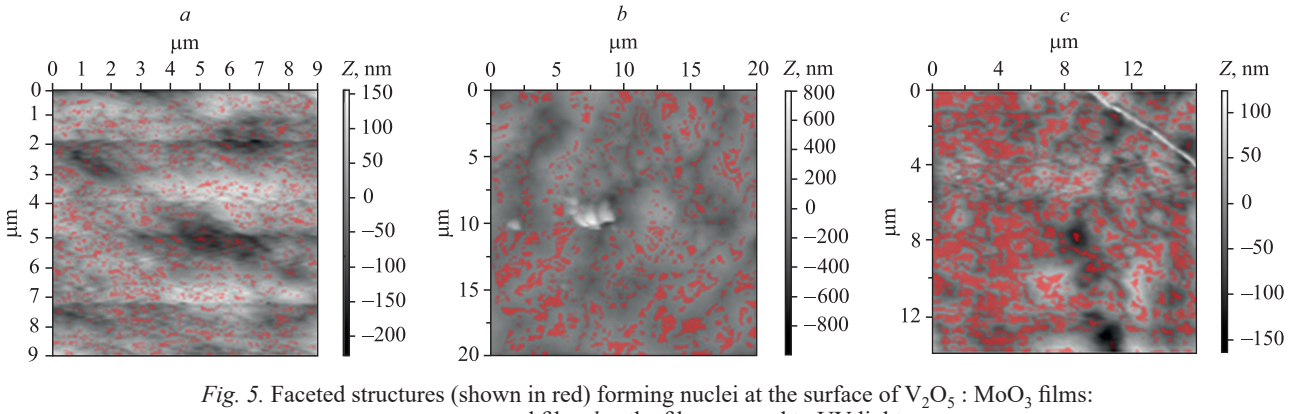

Fig. 5. Faceted structures (shown in red) forming nuclei at the surface of V_2O_5 : MoO_3 films: *a* – as-prepared film; *b* – the film exposed to UV-light; *c* – the film exposed to UV-light and etched in acid solution for 6 min

The AFM investigation of the V_2O_5 : MoO_3 mixed oxide films used as the photoresist material evidenced that their relief demonstrates pronounced asymmetry due to directional alignment of oxide nuclei. The exposure results in the degeneration of the structural elements in the film due to further binding of nuclei *via* three-dimensional photopolycondensation. The latter process manifests itself in the decrease of fractal dimension of the film surface (i. e. the entropy of the microgeometry diminishes whereas the geometric deviation of the relief increases) and homogenity of the structural elements at the surface of the mixed oxide film exhibits an increase. On the contrary, the acid etching of the exposed film is localised at the surface defects making pseudocrystallites visible; as the result the medium size of structural elements which contribute into surface relief diminishes while the number of these elements exhibits increase. The selective etching leads to the increase of the fractal dimension of the film surface to the initial value (see table) and also to the recovery of the initial relief of the photoresist film. These effects ensure the dimension stability of patterns generated with V_2O_5 : MoO_3 photoresist and permit one to expect formation of oxide masks with regular edges.

Structural characteristics of the surface of V_2O_5 : MoO_3 mixed oxide films

Parameters	As-prepared V_2O_5 : MoO_3 film	V_2O_5 : MoO_3 film exposed to UV-light	V_2O_5 : MoO_3 film exposed to UV-light and etched in acid solution for 6 min
Roughness average, nm	11.75	30.15	10.80
The Shannon differential entropy	15.45	14.73	15.76
Fractal dimension	2.3	2.1	2.3

References

1. Liu Boyang, Ho Sengtiong. Sub-100 nm nanolithography and pattern transfer on compound semiconductor using sol-gel-derived TiO_2 resist. *Journal of the Electrochemical Society*. 2008;155(5):57–60. DOI: 10.1149/1.2883730.

2. Chudnovskii FA, Stefanovich GB. Metal-insulator transition in disordered VO_2. *Journal of Solid State Chemistry*. 1992;98(1): 137–145. DOI: 10.1016/0022-4596(92)90079-B.

3. van Zant P. *Microchip fabrication*. New York: McGraw-Hill; 1997. 611 p.

4. Baraboshina AA, Sviridova TV, Tsybulskaja LS, Kokorin AI, Sviridov DV. Inorganic photoresists based on mixed oxides of molybdenum and vanadium. *Doklady of the National Academy of Sciences of Belarus*. 2015;59(4):68–71. Russian.

5. Sviridova TV, Sadovskaya LYu, Kokorin AI, Lapchuk NM, Sviridov DV. Photoinduced processes in thin films of MoO_3 and mixed V_2O_5 : MoO_3 oxides. *Russian Journal of Physical Chemistry B: Focus on Physics*. 2016;10:561–565. DOI: 10.1134/S1990793116040126.

6. Sviridova TV, Stepanova LI, Sviridov DV. Nano- and microcrystals of molybdenum trioxide and metal-matrix composites on their basis. In: Ortiz M, Herrera T, editors. *Molybdenum: characteristics, production and applications*. New York: Nova Science Publisher; 2012. p. 147–179.

7. Livage J, Henry M, Sanchez C. Sol-gel chemistry of transition metal oxides. *Progress in Solid State Chemistry.* 1988;18(4): 259–341. DOI: 10.1016/0079-6786(88)90005-2.

8. Byk TV, Sokolov VG, Gaevskaya TV, Skorb EV, Noh Chang Ho, Song Ki Young, et al. Photochemical selective deposition of nickel using a TiO_2 – Pd^{2+} layer. *Journal of Photochemistry and Photobiology A: Chemistry*. 2008;193(1):56–64. DOI: 10.1016/j.jphotochem.2007.06.007.

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