Modification of Atomic Structure of Thin Amorphous V\textsubscript{2}O\textsubscript{5} Films under UV Laser Irradiation

A B Cheremisin\textsuperscript{1}, S V Loginova\textsuperscript{1}, A A Velichko\textsuperscript{1}, V V Putrolaynen\textsuperscript{1}, A L Pergament\textsuperscript{1} and A M Grishin\textsuperscript{2}

\textsuperscript{1} Petrozavodsk state university, 185910 Petrozavodsk, Russia
\textsuperscript{2} Condensed Matter Physics, Department of Microelectronics and Information Technology, Royal Institute of Technology, SE-164 40 Stockholm-Kista, Sweden

E-mail: alexiii1982@mail.ru, velichko@psu.karelia.ru

Abstract. Influence of ultra-violet radiation of the KrF laser (wave length 248 nm, pulse duration 20 ns) on atomic structure of amorphous vanadium pentoxide thin films, prepared by the pulsed laser deposition method, is studied. Calculations of the short-range order characteristics (radii and diffusiveness of coordination spheres, coordination numbers) were performed by the Finbak -Warren method. It is established that minimal structure unit of amorphous V\textsubscript{2}O\textsubscript{5} film before and after irradiation is a strongly deformed oxygen octahedron. Distortions of tetragonal pyramids in the initial and modified film are different. Also, oxygen deficiency in a tetragonal pyramid is observed.

Investigation of the influence of laser radiation on the properties of transition metal oxide (TMO) amorphous films is of importance due to the applied potentiality [1]. It is known that TMO can be exposed to structural and phase transformations under the action of laser radiation. Modification is always accompanied by significant changes in physical and chemical properties of a material. Influence of ultra-violet (UV) radiation of the ArF laser (wavelength 193 nm) with on the titanium oxide amorphous thin films prepared by CVD method was investigated in work [2]. It has been shown that the UV irradiation of amorphous TiO\textsubscript{2} film leads to crystallization in anatase structure, and then in rutile structure at a pulse energy of 40-50 mJ/cm\textsuperscript{2} and a doze more than 3 J/cm\textsuperscript{2}. In our works [3-5], influence of laser radiation (wavelengths 1.06 \textmu m, 0.53 \textmu m and 0.26 \textmu m) on the properties of amorphous oxide thin films of V, Ti, Ta, and Nb, prepared by electrochemical oxidation, was investigated. In [3], with amorphous V\textsubscript{2}O\textsubscript{5} film as an example, the opportunity of optical recording of the information (diffraction grating) using standard laser holographic system was shown. In [5], the opportunity of e-beam lithography with the submicron resolution using anodic amorphous V\textsubscript{2}O\textsubscript{5} and VO\textsubscript{2} thin films as inorganic resists was presented.

Thus, modification of the properties of TMO due to laser irradiation is usually connected with the process of crystallization of initially amorphous films and partial reduction to the lower oxides [5, 6], and dozes for initiation of phase transformations do not exceed \textasciitilde1-10 mJ/cm\textsuperscript{2} [5]. The detailed analysis of structure modification after laser treatment for the films of amorphous V\textsubscript{2}O\textsubscript{5}, which possess the greatest sensitivity to laser radiation [3], was not performed so far. Therefore, the main purpose of the present work was to investigate the atomic structure modification of amorphous V\textsubscript{2}O\textsubscript{5} thin films, prepared by pulsed laser deposition (PLD) method, subject to ultra-violet laser radiation.
Thin films of amorphous V$_2$O$_5$ were synthesized by the PLD technique described in detail in [7]. Thickness of as-grown films was ~100 nm.

Modification of amorphous oxide films was performed with a KrF excimer laser (COMPEX-102) at a wavelength of 248 nm, pulse duration 20 ns, and energy density in a pulse ~ 75 mJ/cm$^2$. X-ray diffraction study of initial and modified films on glass substrates was performed using an automated diffractometer DRON-3.0 with MoK$_\alpha$ radiation in the angle range from 5° to 50° in asymmetrical configuration. Samples were set at angle of 5°.

Using a technique described in [8] for the films not separated from a substrate, the contribution brought by a substrate has been deducted, and X-ray patterns of the V$_2$O$_5$ films thus has been obtained.

Normalization of the distribution curves of amorphous oxide film intensity dispersion was made, as well as calculations of an s-weighted interference function and the pair function distribution were made by means of an approved method described in detail in [9-10].

Comparison of curves of intensity of dispersion I(s) for initial (dashed line) and modified (solid line) film is shown in figure 1. Curves of dispersion intensity for the studied films are similar, but there is the increase in intensity of second maximum for the initial film. The absence of sharp peaks indicates that the films both before and after UV laser irradiation are amorphous.

Curves of pair functions D(r) for initial (1) and modified (2) amorphous V$_2$O$_5$ thin film are showed in figure 2. Fluctuations on the D(r) curves fade at values of r ~ 2.4 nm and r ~ 1.2 nm for initial and modified films, respectively, and these values represent the size of short-range order.

Calculations of the short-range order characteristics (radii and diffusiveness of coordination spheres, coordination numbers) were performed by the Finbak -Warren method [9-12]. Setting values of the radii of coordination spheres $r_{ij}$ and diffusiveness $\sigma_{ij}$, coordination numbers $N_{ij}$ were calculated by the least squares method [13, 14]. Values of $r_{ij}$, calculated for crystal phase of vanadium pentoxide, were used as initial value of the radii of coordination spheres. Then $r_{ij}$ and $\sigma_{ij}$ were selected by the method of consecutive approximation so that the degree of discrepancy for an experimental curve of pair functions distribution and the theoretical curve (received using the given set of $r_{ij}$, $\sigma_{ij}$ and $N_{ij}$) was less 4÷5 % [14].

The calculated characteristics of the short-range order for initial and modified V$_2$O$_5$ thin film in comparison with crystalline vanadium pentoxide are presented in table 1. V-O$^1$ and V-O$^2$ are the distances in the first coordination polyhedron representing a tetragonal pyramid. V-O$^1$ is the association of distances 0.157 nm and 0.175 nm. In V-O$^2$, it is given the contribution of the atoms located on distances 0.177 nm, 0.184 nm and 0.203 nm. Coordination numbers for a crystal phase on spheres V-O$^3$, V-V$^1$ and V-V$^2$ are calculated in view of contributions of spheres O-O by a method described in [15]. Also, it was taken into account that the values of coordination numbers on first and second V-V spheres give the contribution to coordination numbers of some spheres V-O.
Table 1. The calculated characteristics of the short-range order for initial and modified V$_2$O$_5$ thin film in comparison with crystalline vanadium pentoxide

| Sphere type | Initial film | Modified film | Crystalline phase V$_2$O$_5$ [16] |
|-------------|--------------|---------------|---------------------------------|
|             | $r_{ij}, \text{nm}$ | $\sigma_{ij}, \text{nm}$ | $N_{ij}, \text{at}$ | $r_{ij}, \Delta r_{ij}, \text{nm}$ | $\Delta r_{ij}, \text{nm}$ |
| V–O$^1$    | 0.174        | 0.001         | 0.56±0.06 | 0.170        | 0.000         | 3.11±0.14 | 0.166±0.009 | 2.0 |
| V–O$^2$    | 0.196        | 0.001         | 4.30±0.47 | 0.187        | 0.006         | 1.60±0.07 | 0.188±0.010 | 3.0 |
| V–O$^3$    | 0.270        | 0.001         | 2.84±0.31 | 0.259        | 0.000         | 2.47±0.12 | 0.267±0.022 | 2.95 |
| V–V$^1$    | 0.303        | 0.001         | 4.38±0.48 | 0.300        | 0.010         | 3.75±0.19 | 0.320±0.018 | 3.98 |
| V–V$^2$    | 0.372        | 0.035         | 10.64±1.16| 0.362        | 0.040         | 9.98±0.48 | 0.358±0.004 | 3.28 |

Deviation of values of radii and diffusiveness of coordination spheres for the initial and modified film: $\Delta r_{ij}^*=±0.001 \text{ nm}; \Delta \sigma_{ij}^*=±0.002 \text{ nm}$.

The comparative analysis of the values of radii and coordination numbers of the first and second V–O spheres shows that, in tetragonal pyramids, four distances up to an oxygen atom are longer in comparison with the fifth one for initial vanadium pentoxide, while three distances up to atom of oxygen shorter, than others two for initial vanadium pentoxide.

Calculation of total coordination number of oxygen atoms on the first coordination sphere of vanadium (in the coordination polyhedron representing a tetragonal pyramid) gives the values of 4.86 and 4.71 for initial and exposed vanadium pentoxide, respectively, which is a little bit lower than the corresponding value in a crystal (5.0). Hence, the small part of pyramids in the studied films of amorphous vanadium pentoxide is not completed (there is no one of tops).

After UV modification of amorphous V$_2$O$_5$ thin film, the reduction of radius of the third V–O spheres and numbers of atoms on this sphere from 2.84 to 2.47 is observed. This could be understood as both radius of sphere, and coordination number, apparently, are connected to shortage of oxygen in tops of tetragonal pyramids.

Thus, distortion of tetragonal pyramids in the initial and modified film is various.

Radius of the first V–V sphere for initial and modified films is almost equal. Nevertheless, UV modification of a V$_2$O$_5$ film lead to a decrease of coordination number (amount of vanadium atoms on this sphere) from 4.38 to 3.75. The value of coordination number of the initial and modified film for second V–V sphere is strongly overestimated due to the contribution of the subsequent spheres which not used in calculation of the short order characteristics. Hence, results for this sphere are not significant.

Thus, the analysis of the structure of vanadium oxide thin films, prepared by PLD method, has shown that before and after the ultra-violet laser irradiation, the V$_2$O$_5$ films are amorphous. UV modification of an initial vanadium pentoxide film lead to a decrease of the short order range sizes from 2.4 nm to 1.2 nm. A minimum structure unit of the studied amorphous oxide films is a strongly distorted oxygen octahedron. The character of tetragonal pyramid distortions in initial and modified films is different, and it also differs from the V$_2$O$_5$ crystalline phase. Also, the small part of pyramids in the studied films of amorphous vanadium pentoxide is not completed (there is no one of tops).

Acknowledgments
This work was supported by Svenska Institutet (Dnr: 01370/2006), US CRDF grant (award No. RUX0-000013-PZ-06) and by Government of Russian Federation (federal program “Research and Development in Priority Directions of Science and Technology Complex of Russia 2007-2012”, application No. 2007-3-1.3-00-02-058).
References
[1] Bugaev A A, Zakharcheny A P and Chudnovskii F A 1979 Metal–Semiconductor Phase Transition and Its Application (Leningrad: Nauka)
[2] Mitrev P, Benvenuti G, Hofman P, Smirnov A, Kaliteevskaya N and Seisyan R 2005 Tech. Phys. Letters Vol.31 p.908
[3] Chudnovskii F A, Pergament A L, Schaefer D A and Stefanovich G B 1995 J. Solid state chemistry. 118 417
[4] Chudnovskii F A, Kikalov D O, Pergament A L and Stefanovich G B 1999 Physica Status Solidi A. 172 391-5
[5] Stefanovich G B, Pergament A L, Velichko A A and Stefanovich L A 2004 J. Phys.: Condens. Matter. 16 4013–4024
[6] Smith D J, McCartney M R and Bursill L A 1987 Ultramicroscopy. 23 299–303
[7] Putrolainen V V, Cheremisin A B, Velichko A A, Pergament A L, Stefanovich G B and Grishin A M 2006 Proc. V Int. Conf. on Amorphous and Microcrystalline semiconductors (St. Petersburg) p 285
[8] Aleshina L A, Malinenko V P and Fofanov A D 1991 Zavodskaya laboratoriya. 57 39
[9] Mozzi R L and Warren B E 1970 J. Appl. Cryst. 3 251
[10] Warren B E 1969 X-ray diffraction. (New York)
[11] Finbak C and Borgen O 1954 Acta Chem. Scand. 8 829
[12] Aleshina L A and Fofanov A D 1987 X-ray diffraction method of amorphous materials: textbook (Petrozavodsk)
[13] Forsiet G, Malkolm M and Mowler K 1980 Computer’s methods of mathematic calculations (Moscow: Mir)
[14] Lowson Ch and Henson R 1986 Numerical task solutions by technique of least squares (Moscow: Nauka)
[15] Aleshina L A, Malinenko V P, Phoupahanov A D and Jakovleva N M 1986 J. Non-Cryst. Solids 87 358
[16] Ozero R P 1955 Uspekhi khimii 24 951