РАЗДЕЛ II.
ФИЗИКА

УДК 537.635+537.9

DOI: 10.18384/2310-7251-2016-2-29-36

ELECTRON PARAMAGNETIC RESONANCE OF SILICA GLASS IMPLANTED WITH TUNGSTEN

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Abstract. One-millimeter thick discs of Russian commercial silica glasses of KV type are implanted with W^+ ions at an energy of 200 keV and a fluency density from 10^{15} to 2×10^{17} ions/ cm^2. RBS shows a Gaussian distribution of W ions with a maximum concentration at 80 nm from the surface. In the optical spectrum of the silica glass studied in the present work, the absorption bands at 710 nm and 1100 nm are observed. They can be assigned to W^{5+} ions as well as the EPR spectrum consisting of the asymmetric line with $g_{\parallel}$ =1.593 and $g_{\perp}$=1.754. TEM data indicate the formation of almost spherical particles about 3 nm in diameter for the sample implanted at 10^{16} ions/cm^2.

Keywords: electron paramagnetic resonance, optical spectra, silica glasses, implantation with W^+ ions.

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ЭЛЕКТРОННЫЙ ПАРАМАГНИТНЫЙ РЕЗОНАНС КВАРЦЕВОГО СТЕКЛА, ИМПЛАНТИРОВАННОГО ВОЛЬФРАМОМ

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Аннотация. В диски из российских коммерческих кварцевых стекол KV-типа толщиной 1 мм были имплантированы ионы W^+ с энергией 200 кэВ и плотностью потока от 10^{15} до $2{\cdot}10^{17}$ ионов/см^2. Данные RBS свидетельствуют о гауссовом распределении ионов W при максимальной их концентрации в 80 нм от поверхности. В оптическом спектре исследованного в настоящей работе кварцевого стекла наблюдаются полосы поглощения на 710 и 1100 нм. Они могут быть приписаны, также, как и спектр ЭПР из асимметричной линии с параметрами $g_{\parallel}$ =1,593 и $g_{\perp}$=1,754, иону W^{5+}. Данные TEM указывают на образование почти сферических частиц около 3 нм в диаметре в образце, облученном потоком плотностью 10^{16} ионов/см^2.

Ключевые слова: электронный парамагнитный резонанс, оптические спектры, кварцевые стекла, имплантация ионов W^+.

1. Introduction

It is expected that an implantation of transition metal (TM) ions which have partially filled d-electron shells can be used to modify optical, magnetic and electric properties of near-surface layers of glasses. These properties are determined by valence and coordination states of implanted ions as well as of their local environment (for example, [1]).

In this work silica glasses implanted with W^+ ions are studied. Earlier the properties of W^+-implanted silica glasses (E = 200 keV) have been investigated in Ref [2]. It has been shown by means of X-ray photoelectron spectroscopy that in these glasses metallic W, WO_2 and mixed WO-SiO_2 oxides are formed. The present work aims to study the evolution of W states depending on the fluence (F) of implanted ions and heat treatment of the samples. We investigated silica glasses implanted with W^+ by means of electron paramagnetic resonance (EPR), optical absorption spectroscopy, Rutherford backscattering (RBS) spectroscopy and transmission electron microscopy (TEM).

The information concerning the valence and coordination states of TM, their local environment, concentration and cluster formation in implanted layers can be extracted from EPR spectra. Optical absorption spectroscopy is useful in the determination of valence state of TM.

2. Experimental procedures

Disks 1 mm thick of Soviet commercial silica glasses of KV type, obtained by gas-flame fusion of natural quartz crystal and contained ~23 ppm metallic impurities (Al, Ge and alkali) and approximately 82 ppm of OH groups, were irradiated with W^+ ions at the energy E = 200 keV to fluences (F) from 10^{15} to $2 \cdot 10^{17}$ ions/cm^2. Current densities were about 0.3 μA/cm^2. The EPR spectra of samples co-implanted with W^+ (E = 200 keV) and O^+ (E = 25 keV at different fluences) were also studied. The temperature of substrates during the implantation process measured by a thermocouple was about 330 K. Some samples were annealed at 800^{0}C for 1h in the H_2–Ar atmosphere.

Optical spectra in wavelength region from 200 to 1200 nm were measured with an SP-8 spectrophotometer.

After implantations and optical measurements some slabs were crushed and used for EPR measurements which were performed using a modified spectrometer RE-1306 operating at X-band frequency. EPR spectra were recorded at room temperature (RT) and 77K (LNT).

Concentration and depth profiles of implanted ions were determined by means of RBS using 2 MeV He^+ ions at scattering angle 160°. Scanning TEM with bright field imaging was used for the study colloids produced in implanted layer.

3. Results and Discussion

Fig 1 shows the EPR spectrum recorded at LNT and microwave power P = 40 mW for the sample implanted with W^+ at energy E=200 keV. This spectrum contains the narrow intense signal. Its g-values (g_1 = 2.069, g_2= 2.0074 and g_3 = 2.0009) are similar to those for peroxyradical (POR) in ion implanted glasses [3], i.e. this signal can be assigned to POR.

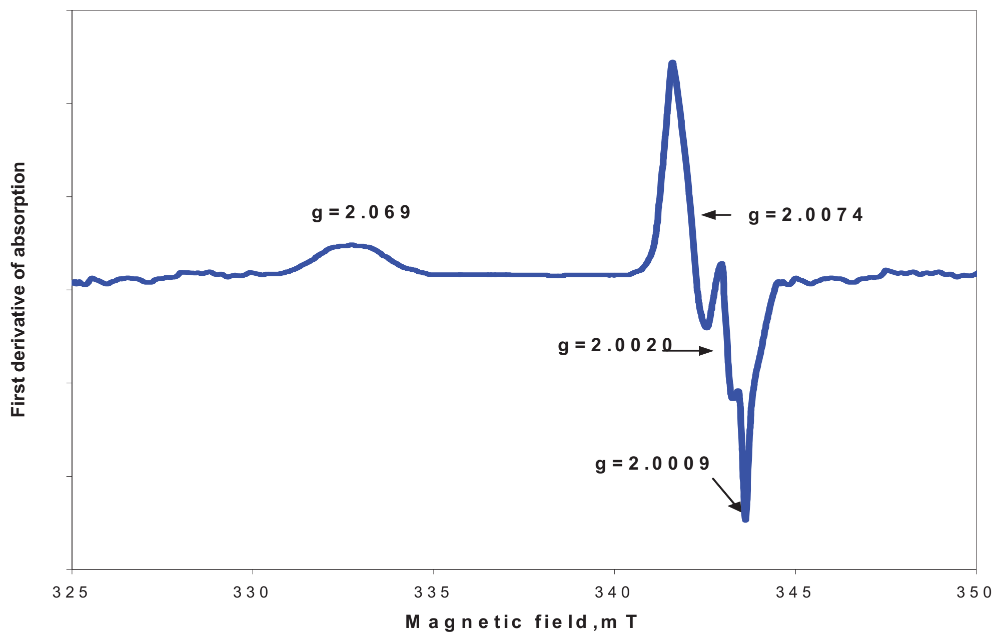

Fig. 1. EPR spectrum recorded at 77K and microwave power *P* = 40 mW for the sample implanted with W^+ at energy *E* = 200 keV.

The second signal with *g* ~ 2.0020 is presumably due to E'-type center. The structural defects (E'-center, E'-type center and POR) in ion-implanted silica glasses have been discussed in many papers (for example, [3–5]). Here, we consider only EPR signals related to W ions.

Depth profiles of W in the silica glass obtained by means of RBS indicates that W ions enters into implantation layer. However, no EPR spectra related to W were observed for the samples implanted to F ≤ 10^{16} ions/cm^2. In the sample firstly implanted with W^+ (F = 10^{17} ions/cm^2) and then O^+ optical spectrum (Fig. 2) at 295K contains absorption bands typical of W^{5+} ion (at 700 and 1100 nm) and EPR spectrum of W^{5+} appears for this sample (Fig.3).

The absorption bands at 213 and 236 nm are seen in Fig.2. They are typical for E' center and diamagnetic oxygen deficient defect, respectively [6]).

Fig.3 shows experimental (1) and calculated (2) EPR spectrum of W^{5+} recorded at room temperature for the sample implanted at F = 10^{17} ions/cm^2. This is asymmetric line. Computer calculation of this spectrum made under assumption of its axial symmetry [7] gives $g_{\parallel} = 1.593$ and $g_{\perp} = 1.754$. This line becomes more symmetric with base-crossing $g = 1.72 \pm 0.02$ and its width decreases from 40 to 15 mT with increasing fluence of O^+. Co-implantation of W and O can be accompanied by the appearance of tungsten in high valence states.

The W^{6+} ions with $5d^0$ configuration give no EPR spectra. The W^{5+} ($5d^1$) ions give an EPR signal due to their unpaired electrons. This signal centered at $g \sim 1.7$ is due to W^{5+} ions located in axially distorted octahedral position. These locations are characterized by short W–O bond. There is a large displacement of W atoms from the center of octahedron [8].

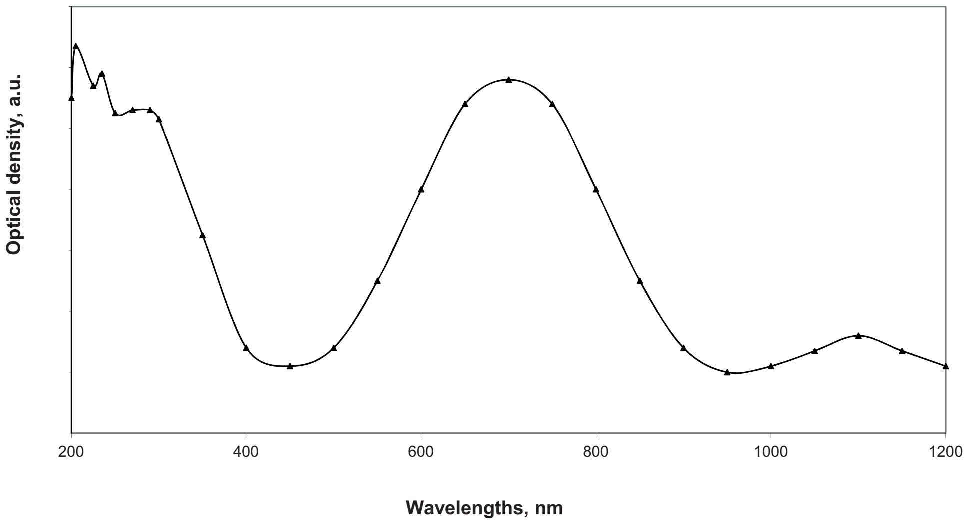

Fig. 2. Optical spectrum in the sample firstly implanted with W^+ ($F = 10^{17}$ ions/cm^2) and then O^+.

The free W^{5+} ion has ^2D ground state with fivefold orbital degeneracy which in octahedral field splits into $^2T_2$ ground state and ^2E excited state. In tetragonally distorted octahedron $^2T_2$ state is further split into $^2B_2$ Ixy> and (Iyz>, Izx>) states. Which of orbital doublet or singlet Ixy> is the lower is determined by whether the octahedron is elongated or compressed, respectively, along z-axis. For Ixy> ground state $g_{\parallel} = g_e - 8\Lambda/\Delta E_1$, $g_{\perp} = g_e - 2\Lambda/\Delta E_2$, where Λ is constant of spin-orbit interaction, g_e is g -value of free electron, ΔE_i are separations between the ground and exited states. The g -value obtained for W^{5+} correspond to ground state B_2 Ixy>.

Fig. 4 shows TEM micrograph of the sample implanted at F = 10^{16} ions/cm^2. Almost spherical particles are seen with diameter up to ~ 3 nm. They belong presumably to metallic W [2].

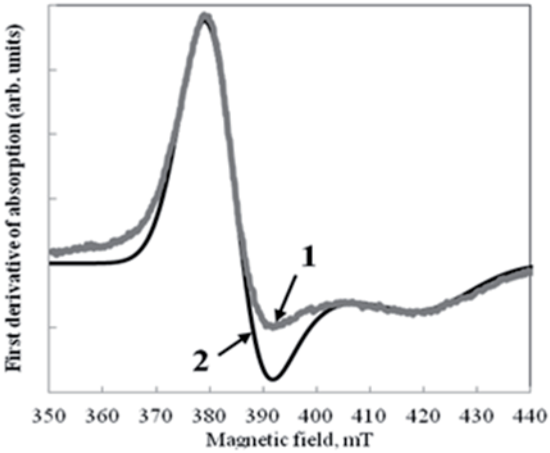

Fig. 3. Experimental (1) and calculated (2) EPR spectrum of W^{5+} recorded at 300 K for the sample implanted at F = 10^{17} ions/cm^2.

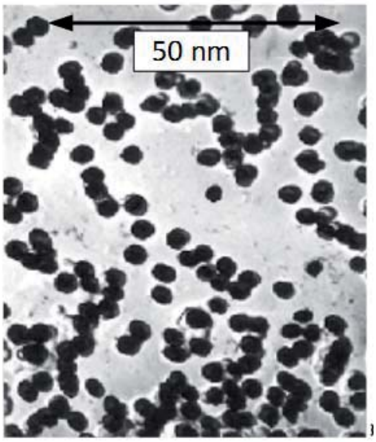

Fig. 4. TEM micrograph of the sample implanted at F = 10^{16} ions/cm^2.

Conclusion

The silica samples implanted by W^+ ions with energy E = 200 keV to fluence F ≤ 10^{16} ions/cm^2 give EPR spectra associated only with native defects of silica (POR, E'-type center). Heat treatment of these samples leads to formation of colloid metallic particles. EPR signals of W^{5+} are observed for the samples implanted to F > $5 \cdot 10^{16}$ ions/cm^2 and co-implanted with O^+. The ion W^{5+} is located in tetragonally compressed octahedral oxygen environment.

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БИБЛИОГРАФИЧЕСКАЯ ССЫЛКА

L. Bogomolova, V. Zhachkin. Electron paramagnetic resonance of silica glass implanted with tungsten // Вестник Московского государственного областного университета. Серия: Физика-математика. 2016. № 2. С. 29–36.
DOI: 10.18384/2310-7251-2016-2-29-36.

BIBLIOGRAPHIC REFERENCE

L. Bogomolova, V. Zhachkin. Electron paramagnetic resonance of silica glass implanted with tungsten // Bulletin of Moscow State Regional University. Series: Physics and Mathematics. 2016. no. 2. pp. 29–36.
DOI: 10.18384/2310-7251-2016-2-29-36.