Functional Materials 12, No.2 (2005)

TMR, MRE, and X-ray photoelectron spectroscopy of $Fe–SiO_2$ granular films

V.G.Kravets[1,2], *L.V.Poperenko*[2], *K.L.Vinnichenko*[2]

[1]Laboratory of Solid State Physics,
Gerhard-Mercator-University Duisburg, Lotharstr. 1, D-47057, Germany
[2]Department of Physics, T.Shevchenko National Kyiv University,
6 Acad. Glushkov Ave., 03022 Kyiv, Ukraine

$Fe_x(SiO_2)_{1-x}$ magnetic granular films below the percolation threshold ($x < 0.45$) have been studied using tunneling magnetoresistance (TMR), magnetorefractive effect (MRE), and X-ray photoelectron spectroscopy. Maximum magnetoresistance ratio of 3.7 % at room temperature was observed for films of $Fe_{0.35}(SiO_2)_{0.65}$ composition. Both the experimental and theoretical analysis reveal a correlation between TMR and MRE, thus demonstrating the usage possibility of the MRE as a contactless method to measure the TMR. The chemical surface structure was analyzed by X-ray photoelectron spectroscopy (XPS) and compared to that of the corresponding SiO_2 and Fe surfaces. The XPS spectra of $Fe_x(SiO_2)_{1-x}$ granular films display two main peaks at 707 and 720 eV, which arise from Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, and a small peak appears around 710.5 eV due to Fe_2O_3.

Магнитные гранулированные пленки $Fe_x(SiO_2)_{1-x}$ с содержанием металла ниже порога перколяции изучены с помощью туннельного магнитосопротивления, магниторефрактивного эффекта и рентгеновской фотоэлектронной спектроскопии. Максимальное значение магнитосопротивления 3,7 % при комнатной температуре было обнаружено для пленок $Fe_{0,35}(SiO_2)_{0,65}$. Экспериментальные результаты и теоретический анализ показывают корреляцию между туннельным магнитосопротивлением (ТМС) и магниторефрактивным эффектом (МРЭ), что позволяет использовать МРЭ в качестве бесконтактного метода измерения ТМС. Химический состав поверхности пленок проанализирован с помощью рентгеновской фотоэлектронной спектроскопии (РФС) и проведено его сравнение с поверхностями SiO_2 и Fe. РФС спектры гранулированных пленок $Fe_x(SiO_2)_{1-x}$ характеризуются двумя полосами, локализованными при энергиях 707 и 720 эВ, которые связаны с Fe $2p_{3/2}$ и Fe $2p_{1/2}$ энергетическими уровнями. Также наблюдался незначительный пик при 710,5 эВ благодаря вкладу Fe_2O_3.

Nanocomposite materials consisting of ultrafine magnetic particles embedded in a metallic or insulating matrix have recently attracted a great attention. In particular, there is an extensive interest in the giant magnetoresistance (GMR) effect and the tunnelling magnetoresistance (TMR) effect [1, 2]. The TMR magnitude is defined by the spin polarisation of the conduction electrons at the Fermi energy EF. The optical and magneto-optical properties are known to be very sensitive to the electron state density near the Fermi level. Transport properties depend mainly on the intraband transitions of the conduction electrons, which dominate the dielectric properties in the infrared (IR) spectral region. Therefore, IR transmission/reflection spectroscopy in a magnetic field provides a direct tool for probing spin-dependent conductivity [3, 4].

In this work, the magneto-optical properties of metal-insulator $Fe–SiO_2$ granular films are studied at room temperature over a wide range of Fe concentrations. The reflection of $Fe–SiO_2$ granular films were investigated in IR spectral region in the magnetorefractive effect (MRE) geometry. The magnetorefractive effect probes the change of reflection and transmission in the IR spectral region due to the change in electri-

cal conductivity in a magnetic field [3, 4]. Since its discovery, the MRE has been measured at transmission and reflection for a limited range of systems including both multilayers and granular films [3–5]. It was shown that the shape of the MRE vs. wavelength curve is sensitive to the spin-dependent scattering parameters of Co–Ag granular magnetic films rather than just the magnitude of the GMR [4]. We have also examined the electron properties of Fe–SiO_2 granular films using X-ray photoelectron spectroscopy (XPS).

The granular Fe–SiO_2 films were prepared by rf magnetron sputtering at 20 mTorr Ar gas pressure. The films were deposited on glass substrates to a total thickness of about 170 nm using two targets of Fe and SiO_2. The composition of the film was determined by energy dispersion analysis using X-ray and the crystalline structure was investigated by X-ray diffraction. The electrical resistivity and TMR were measured by a conventional four-probe method.

IR reflection spectra were recorded between 2.5 and 25 μm using a Nicolet Nexus 670 Fourier transform IR reflection spectrometer with 4 cm^{-1} resolution and a liquid-nitrogen-cooled HgCdTe detector. The light incidence angle was 65° to the normal and MRE measurements were performed up to the field maximum of 12 kOe. To detect any small, magnetic field-dependent features, reflectance ratios [$\Delta R = (R(H = 0) - R(H))/R\ (H = 0)$] were calculated. The data were collected in several separate runs, which generally show the same field dependence, differing mainly in the noise level. Repetition of the experiment several times enables us to check the measurement reproducibility and the correction of the absorption peak positions determination. For comparison, Ag and Al reference mirrors were also measured and found to display no substantial field dependence.

A standard Mg K_α excitation source ($\hbar\nu$ = 1253.6 eV) was used for the XPS investigation. XPS analysis was carried out in an ultrahigh vacuum system at a background pressure of $5 \cdot 10^{-10}$ mbar. The spectrometer hemispherical analyzer was set to 44 eV constant pass energy and used to determine the kinetic energy of photoelectrons at the step size of 0.1 eV. The binding energy (BE) scale was calibrated by measuring reference peak of Au $4f_{7/2}$ (BE = 84.5 eV) using an Au film. The accuracy of the measured binding energies was ±0.3 eV. For three of our samples, the Fe 2*p*, O 1*s*, and Si 2*p* signals were recorded. All measurements were performed at angle $\varphi = 45°$ between the sample normal and the detection direction. At this angle the (elliptically-shaped) analyzed area was about 2.5×3 mm^2. The X-ray diffraction patterns for the $Fe_x(SiO_2)_{1-x}$ magnetic granular films show a broad peak at the Bragg angle corresponding to the <110> diffraction line at $2\theta = 44.5°$ of bcc Fe solid solution, indicating the nanocrystalline nature of the films. The average grain size of the ferromagnetic particles varying between 3 and 5 nm, as typical of metal-insulator granular films, was evaluated using the Scheller's formula.

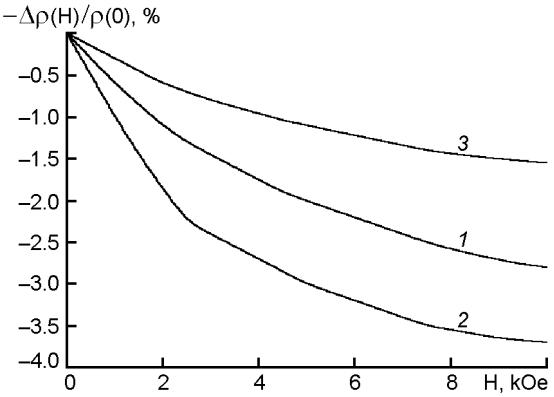

Fig. 1. TMR curves of $Fe_x(SiO_2)_{1-x}$ granular films measured at room temperature, for different Fe concentrations: (*1*) — $x = 0.29$; (*2*) — 0.35; (*3*) — 0.41.

The TMR ratio $(\rho_0 - \rho_H)/\rho_0$ values of the $Fe_x(SiO_2)_{1-x}$ granular films as a function of x measured at $H = 10$ kOe at room temperature are plotted in Fig. 1. It is seen that a maximum MR value of about 3.7 % is obtained for $x = 0.35$. For $x > 0.35$, the TMR ratio decreases rapidly with increasing x. The resistance changes occurs mainly at the magnetic field values below 5 kOe. Above 5 kOe, the film resistivity decreases slowly, but has not saturated for magnetic fields approaching 10 kOe. The electrical resistivity at $H = 0$ Oe is of the order of $10^5 \mu\Omega \cdot$cm for the film with large MR ratio. This value is extremely large as compared with the metal resistivities. The percolation threshold being around $x_P \approx 0.42$–0.45 where the electrical conductivity mechanism is changed. The granular films with low x are insulating, except for tunneling among metallic grains, while in samples with large x values, the metal granules form an infi-

nite network, exhibiting metallic conductivity and magnetic closure structure. The TMR curves are well proportional to $-(M/M_S)^2$ (where M, M_S are magnetization and saturation magnetization of the films). When Fe content decreases from 35 to 20 %, the TMR increases abruptly, because tunneling current is dominant at the Fe contents lower than the percolation threshold point x_P.

In insulating Fe–SiO_2 composites, the electrons are transferred from one grain to another by tunneling at an activation energy required to create electron-hole pairs in the grains [6, 7]. The hopping conductivity can be written as follows [8]:

$$\sigma \approx \exp(-2qs - E_c/k_BT), \quad (1)$$

where q is the tunneling parameter; s, the intergrain potential barrier height; E_c, the activation energy; k_B, the Boltzmann constant; $E_c \sim e^2/\ 4\pi\varepsilon_0\varepsilon_d r$; e is electron charge, ε_d is the dielectric constant, and r is the grain radius. For example, for grains of $r = 2.5$ nm and $\varepsilon_d = 4.5$ in SiO_2, the Coulomb ionization potential is $E_c = 0.13$ eV [6, 7]. The activation energy is lowered by mutual screening of grains beyond the percolation radius, i.e. the radius of grains providing an infinite percolation cluster [6, 7]. Similarly to the insulator-metal transition according to [6, 7], we get

$$E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_d r}\left[1 - \left(\frac{x}{x_p}\right)^{\frac{1}{3}}\right], \quad (2)$$

In our samples, E_c/k_B for $x = 0.35$ is about four times as high as compared to $x = 0.45$ [6]. One can notice that the resistivity of the $Fe_{0.37}(SiO_2)_{0.63}$ granular films is much larger than that for $x = 0.45$. The mean diameter of Fe grain $<d>$ decreases and the mean intergrain distance $<s>$ increases with increasing x. So, the potential height of insulating tunnel barrier for $x = 0.35$ is much higher than that for $x = 0.45$, indicating that E_c/k_B for $x = 0.35$ is also much higher than that at $x = 0.45$. Because of a broad distribution in grain size, it is highly probable that large grains are separated from each other due to their low number density. Taking into account the tunneling between large grains through intervening small ones, the relative magnetoresistivity is given by [2, 9]:

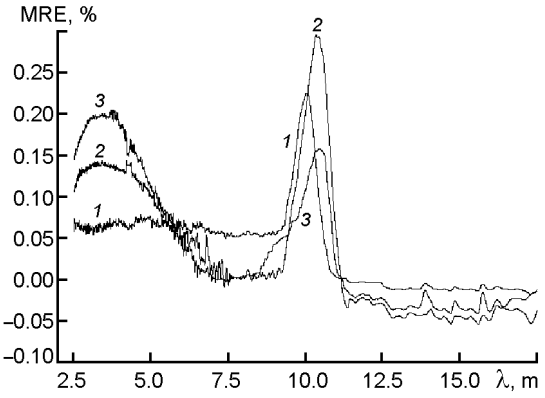

Fig. 2. MRE as a function of wavelength for different Fe concentrations x: (*1*) — $x = 0.29$; (*2*) — 0.35; (*3*) — 0.41.

$$\frac{\Delta\rho}{\rho} = \frac{2P^2m^2}{1 + P^2m^2} \cdot \exp(-2qs), \quad (3)$$

where $P = (N_F{}^{\uparrow} - N_F{}^{\downarrow})/(N_F{}^{\uparrow} + N_F{}^{\downarrow})$ and $q = (2m^*(V - E_F)/\hbar^2)^{1/2}$. P is spin polarization of electrons. Here, $N_F{}^{\uparrow(\downarrow)}$ is the state density at the Fermi energy E_F for electrons with spin up and down, and $s \sim 2$ nm, $m^* \sim 0.3m_e$, and $V \sim 1.5$ eV are the barrier thickness, the effective electron mass, and the barrier height, respectively, for $Fe_{0.35}(SiO_2)_{0.65}$ [2, 6]. For saturation case ($m = M/M_S = 1$), the relative polarisation of the magnetic materials will lead to relationship (3). The Fermi energy value for conduction electrons, according to [2], approximates $E_F \approx 1$ eV. Using the estimated values for $2qs$ and the experimental values of $\Delta\rho/\rho \approx 0.04$, we have calculated the relative polarization of the magnetic grains (Fe), $P \approx 0.37$. This magnitude for P is reasonable for ferromagnetic Fe when compared with experiments of the polarization of conduction electrons [10]. Note that the maximum magnetoresistance value is observed just below the percolation threshold at $x \sim 0.35$.

Fig. 2 shows the relative change of IR reflection for $Fe_x(SiO_2)_{1-x}$ granular films as a function of wavelength for non-polarized incident light in a magnetic field of 12 kOe. The magnetorefractive effect in ferromagnetic metal-insulator granular nanostructures $Fe_x(SiO_2)_{1-x}$ was investigated in IR spectral region in the wavelength range from 5 to 20 μm. The effect magnitude varies from 0.1 to 0.35 % for different nanocomposites and depends strongly on the

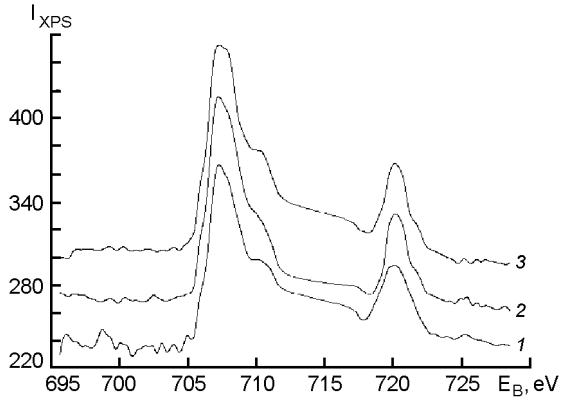

Fig. 3. XPS spectra of Fe $2p$ in $Fe_x(SiO_2)_{1-x}$ granular films: (*1*) — $x = 0.29$; (*2*) — 0.35; (*3*)— 0.41.

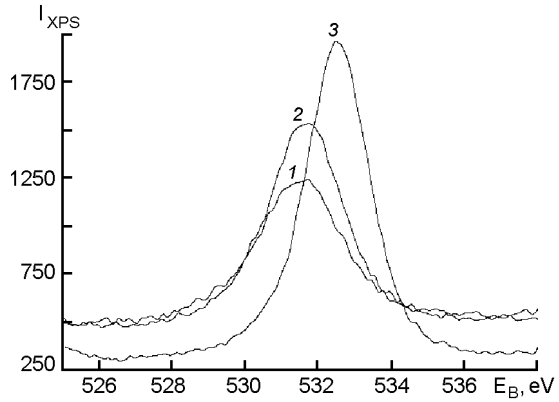

Fig. 4. XPS spectra of O $1s$ in $Fe_x(SiO_2)_{1-x}$ granular films: (*1*) — $x = 0.29$; (*2*) — 0.35; (*3*) — 0.41.

light frequency and magnetoresistance (Fig. 2). MRE spectra exhibit a similar shape with one local maximum around λ ~10.5 μm and the height of the MRE peaks increases with the applied field strength.

The IR reflection spectra of $Fe_x(SiO_2)_{1-x}$ granular films show a complex character of vibration modes. The spectra show a pronounced peak at λ ~10.5 μm which can be associated with the longitudinal optical (LO) vibration mode of SiO_2 [11]. Furthermore, the position of the prominent features of MRE spectra is shifted towards larger wavelength λ as the volume content of Fe in granular films rises (Fig. 2). The MRE spectra for $Fe_x(SiO_2)_{1-x}$ granular films in the 2.5–7.5 μm region show a similar shape to those observed in CoAg granular GMR films [4], with a broad positive peak in the MRE located between 2.5–5.0 μm, consistent with magnetically induced modification of the scattering of Drude-like free electrons in Fe metal.

Experimental results show that the MRE effect in $Fe_x(SiO_2)_{1-x}$ granular films takes place only for films possessing a large TMR effect. According to the Hagen-Rubens relation, the TMR and MRE effects are related to each other [12]. In this case, the reflectivity, R, is a function of the dc resistivity ρ_0, $R = 1 - [2\varepsilon_0\omega\rho_0]^{1/2}$, where ε_0 is the permittivity of free space. The change in reflectivity, $\Delta R/R$, is then given to first order by differentiating R with respect to ρ_0 giving

$$\frac{\Delta R}{R} = -\frac{1-R}{R} \times \frac{\Delta\rho}{\rho_0}, \qquad (4)$$

where $\Delta\rho/\rho_0$ is the TMR for granular films. It is evident from Eq.(4) that $\Delta R/R$ depends directly on tunnel magnetoresistance TMR. Including in a Hagen-Rubens relation the dependences of $R(\lambda)$ and TMR, one can describe accurately the MRE effect in metal granular films and show the correlation between the magnetorefractive and magnetoresistive effects. Our calculations reproduce successfully the variation of magnitude and shape of the MRE curves as a function of the Fe volume concentration, x, and TMR behavior.

It should be noted that the wavelength at which the main feature in $\Delta R/R$ spectra occurs rises with increasing volume content of Fe. Based on the experimental and theoretical investigation of MRE effect, we can suppose that the strong TMR reduction even down to zero can be governed by the scattering of electrons on the phonons at the interface between all nearest particles. The physical mechanism of this effect is related with the excitation of LO phonons in the system (electron-phonon interaction). Due to these processes, the new channels of electron scattering appear.

Figs. 3 through 5 show typical XPS core-level spectra of Fe, Si, and O in $Fe_x(SiO_2)_{1-x}$ granular films. The Fe spectrum exhibits two peaks at 707 and 720 eV, corresponding to the Fe $2p_{3/2}$ and $2p_{1/2}$ doublets (Fig. 3). According to reference XPS data [13, 14], the binding energy (BE) position of the doublets corresponds exactly to that of metallic Fe. The BE difference between the doublet peaks is in the range of 13.0–13.5 eV for metallic Fe and 12–12.5 eV for Fe_2O_3 [13, 14]. The BE difference for our samples is 13 eV, implying that metallic Fe has been formed. In these spectra, a clear small peak is detected at 710.5 eV (see Fig. 3). It is suggested to be due mainly to Fe_2O_3 having

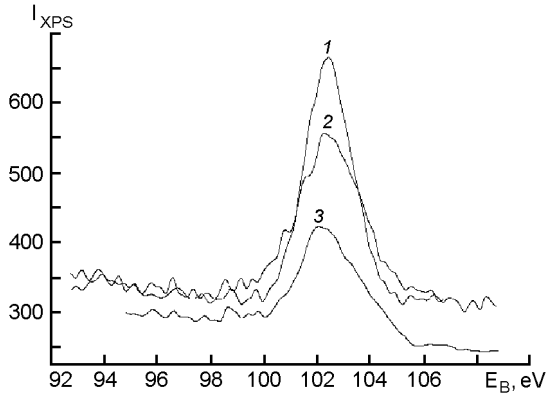

Fig. 5. XPS spectra of Si 2*p* in $Fe_x(SiO_2)_{1-x}$ granular films: (*1*) — $x = 0.29$; (*2*)— 0.35; (*3*) — 0.41.

the peak at 710.9 eV [13]. These data suggest that Fe reacts with oxygen released from SiO_2. The intensity at 710.5 eV is smaller than that at 707 eV, indicating that the oxidation extent of Fe is not large. The Fe oxidation rate becomes larger with increasing SiO_2 concentration. In contrast to the samples with lower TMR values, the 710.5 eV peak of the $Fe_{0.35}(SiO_2)_{0.65}$ granular film is much weaker, although these samples have been deposited in the same conditions and exposed to atmospheric O_2 for the same period of time. This leads to conclusion that the Fe grains in film with maximum magnetoresistance are more resistant against oxidation and have more metallic behavior than those in other samples. This conclusion is confirmed by XPS spectra measurements for the O 1*s* and Si 2*p* peaks. In the O 1*s* spectrum (Fig. 4), the main component at 531.5–532.7 eV is due to SiO_2 and a very small shoulder at 530.5 eV results from Fe_2O_3 [13], in agreement with the results of the Fe 2*p* spectra (Fig. 3). The O 1*s* peak of $Fe_{0.35}(SiO_2)_{0.65}$ sample is more intense and shifted by 1.2 eV to higher binding energy. The native oxide shows a large O 1*s* peak at 532.9 eV [13, 14]. The Si $2p_{3/2,1/2}$ spectrum exhibits a main peak at 102.5 eV and a shoulder around ~103.5 eV (Fig. 5). The main peak is due to Si in SiO_2, in agreement with the accepted values [13]. No evidences for silicides are observed. For Si in silicides, the Si 2*p* BE should be about 1.0 eV lower than that for metallic Si (99.8) due to the more negative electron environment of the silicides as compared to elemental Si, i.e., ~98.8 eV [13, 14]. This peak is more likely due to metallic Si. We can see (Figs. 4, 5) that the peak position of both Si 2*p* and O 1*s* shifts toward higher energy when the Fe concentration in $Fe_x(SiO_2)_{1-x}$ granular films decreases.

Thus, the $Fe_x(SiO_2)_{1-x}$ granular films possess a large magnetoresistance attaining about 3.7 % maximum for $x = 0.35$. The tunnelling TMR effect appears at $x < 0.45$. The x dependence of TMR ratio could be explained phenomenologically by the distance between the nearest-neighbor grain surfaces. A direct relationship has been found between the behavior of the magneto-optical properties and the magnetoresistance effect in granular magnetic films at various content of the ferromagnetic phase. The energy shift of Si 2*p* and O 1*s* core-level determined by XPS shows that the Fe grains react with O released from SiO_2. The oxidation rate of Fe grains is higher in films with smaller TMR values.

References

1. S.Mitani, S.Takahashi, K.Takanashi et al., *Phys. Rev. Lett.*, **81**, 2799 (1998).
2. J.Inoue, S.Maekawa, *Phys. Rev. B*, **53**, R11927 (1996).
3. J.C.Jacquet, T.Valet, in: Magnetic Ultrathin Films, Multilayers and Surfaces, ed. by E.Marinero, Materials Research Society, Pittsburg (1995).
4. V.G.Kravets, D.Bozec, J.A.D.Matthew et al., *Phys. Rev. B*, **65**, 054415 (2002).
5. J.van Driel, F.R.de Boer, R.Coehoorn, G.H.Rietjens, *Phys. Rev. B*, **60**, 6949 (1999).
6. B.A.Aronzon, A.A.Likalter, V.V.Rylkov et al., *Phys. Stat. Sol. (b)*, **205**, 151 (1998).
7. M.Julliere, *Phys. Lett. A*, **54**, 225 (1975).
8. C.J.Adking, in: Metal-Insulator Transitions Revisited, by ed. P.P.Edwards and C.N.R.Rao, Taylor&Francis, London (1996).
9. J.S.Moodera, L.R.Kinder, *J. Appl. Phys.*, **79**, 4724 (1996).
10. J.C.Slonczewski, *Phys. Rev. B*, **39**, 6995 (1989).
11. Handbook of Optical Constants of Solids, ed. by E.D.Palik, Academic, New York (1985).
12. A.V.Sokolov, Optical Properties of Metals, Blackie, Glasgow (1967).
13. J.F.Moulder, W.F.Stickle, P.E.Sobol, K.D.Bomben, Handbook of X-Ray Photoelectron Spectroscopy, Physical Electronics, New York (1995).
14. C.D.Wagner, W.M.Riggs, L.E.Davis et al., Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Praire (1978).

ТМО, МРЕ та рентгенівська фотоелектронна спектроскопія гранулярних плівок $Fe_x(SiO_2)_{1-x}$

В.Г.Кравець, Л.В.Поперенко, К.Л.Вінніченко

Магнітні гранулярні плівки $Fe_x(SiO_2)_{1-x}$ із змістом металу, нижчим за перколяційний поріг, досліджувались за допомогою тунельного магнітоопору, магніторефрактивного ефекту та рентгенівської фотоелектронної спектроскопії. Максимальне значення магнітоопору 3,7 % при кімнатній температурі було знайдено для плівок $Fe_{0,35}(SiO_2)_{0,65}$. Експериментальні результати та теоретичний аналіз показують кореляцію між тунельним магнітоопором (ТМО) та магніторефрактивним ефектом (МРЕ). Це дозволяє використовувати МРЕ для безконтактного вимірювання ТМО. Хімічний склад поверхні плівок $Fe_x(SiO_2)_{1-x}$ аналізувався за допомогою рентгенівської фотоелектронної спектроскопії (РФС) та порівнювався з даними для поверхонь SiO_2 і Fe. РФС-спектри гранульованих плівок $Fe_x(SiO_2)_{1-x}$ характеризуються двома смугами при енергіях 707 та 720 еВ, які відповідають енергетичним рівням Fe $2p_{3/2}$ та Fe $2p_{1/2}$. Також спостерігався незначний максимум при 710,5 еВ завдяки внеску Fe_2O_3.