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# Determination of chemical composition of implanted nanolayers by analysis of their optical properties

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The method for determining the composition of nanolayer from the experimental spectra of optical transmission and reflection was developed. Modeling of the optical properties of the composite was carried out on the basis of Bruggeman's effective medium theory. This method was applied to samples of silica glass implanted with $Cu^-$ ion beam of 60 keV energy and at various current densities. The structure and thickness of nanolayer are determined using transmission electron microscopy method. On the basis of the optical spectra analysis the range of photons energy (3.5 ÷ 4.5 eV) was selected. Composition of the implanted layers in the form of volume concentrations of it's components (copper, cuprous oxide ($Cu_2O$) and substrate material) were obtained.

Разработана методика определения состава нанослоя с использованием экспериментальных спектров оптического пропускания и отражения. Моделирование оптических свойств композитного материала слоя проводилось на основании теории эффективной среды Бруггемана. Данный метод был опробован на образцах из кварцевого стекла, имплантированных пучком ионов $Cu^-$ с энергией 60 кэВ и различными плотностями тока. Структура и толщина (60 нм) нанослоя определены методом просвечивающей электронной микроскопии. На основе анализа оптических спектров был выбран диапазон энергий фотонов (3.5 ÷ 4.5 эВ). Получены составы имплантированных слоев в виде объемных концентраций их составляющих (меди, гемиоксида меди ($Cu_2O$) и материала подложки).

## 1. Introduction

Ion implantation is widely used to produce metal-composite materials with the nonlinear optical properties [1]. Implantation of the metal species into insulators leads to formation of the composites with optical properties and composition which depend on the nature of species and parameters of implantation. Implantation of the metal ions into insulator causes changing the optical properties such as luminescence and absorption. Both phenomena can be used to control the formation of complex defect aggregates, the production of new crystalline phases or the destruction of crystallinity. As an example, the implantation of Cu ions into different substrates leads to a drastic change in the luminescence properties of the materials [2–4].

Composition defines the main functional properties of the implanted layer. Layer-by-layer mass spectrometry analysis [5] or X-ray photoelectron spectroscopy [6] can be used for determining the composition of the implanted layer. But both methods are destructive and they require very lengthy studies and high vacuum for their implementation.

In this paper we studied properties of the samples with implanted layer and their dependence on the current density of ion beam. We also determined a composition of the implanted layer using measured optical characteristics of the samples.

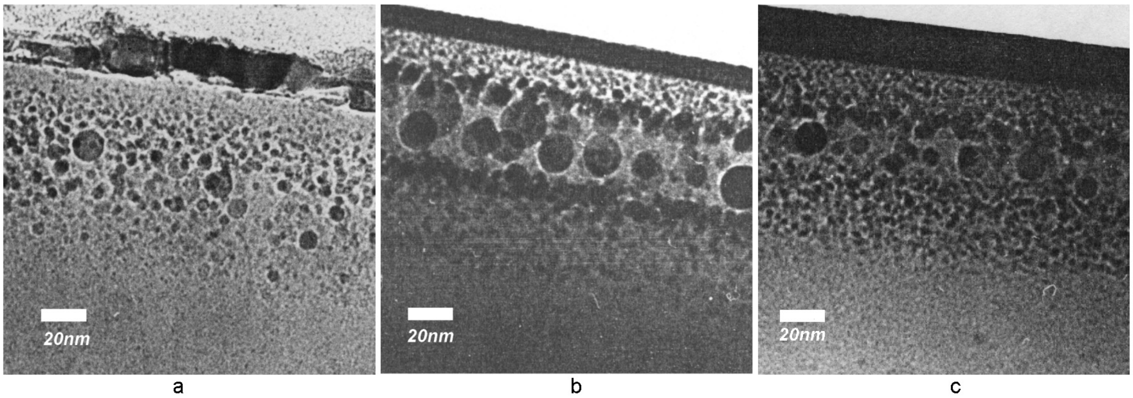


Fig. 1. Cross-section TEM images of silica glass implanted with $Cu^-$ ions of 60 keV to the total dose of $3{\cdot}10^{16}$ ions/cm$^2$ at different current densities: a) 1, b) 3 and c) 10 μA/cm$^2$. A black layer on the top of implanted area is a Cr layer used for the marker.

## *2. Experimental*

Negative Cu ions of 60 keV energy were produced by a plasma-sputter-type ion source. The implantation techniques have already been described elsewhere [7]. In our experiment we used four current densities of 1, 3, 10 and 30 μA/cm$^2$, total dose irradiation achieved the value of $3.0 \cdot 10^{16}$ ions/cm$^2$. As substrates the optical grade silica glasses of 15 mm in diameter and 0.5 mm thick were utilized. Optical transmittance and reflectance were measured in wavelength range from 190 to 2500 nm using a dual beam spectrophotometer. Transmission electron microscopy (TEM) was carried out to evaluate the structure of copper implanted region.

TEM images of the implanted layers in three samples fabricated at different current densities of 1, 3 and 10 μA/cm$^2$ are shown in Fig. 1. Samples obtained at different current densities of the ion beam have significant differences in the structure and concentration of nanoparticles. From these TEM images we can estimate volume occupied by copper nanoparticles in the glass matrix and thickness of the modified layer. The overall thickness of implanted layer is about 60 nm.

In Fig. 2 the transmittance spectra of implanted layer obtained at different current density are presented. These spectra were measured with pristine glass in reference beam and represent the net effect of the ion implantation. The spectra demonstrate the minimum of transmittance at photon energy of 2.2 eV, which corresponds to absorption band related to surface plasmon resonance (SPR) of Cu-metal nanoparticles. Difference in optical transmittance values of the implanted layer obtained at current densities of 1, 3, 10 and 30 μA/cm$^2$

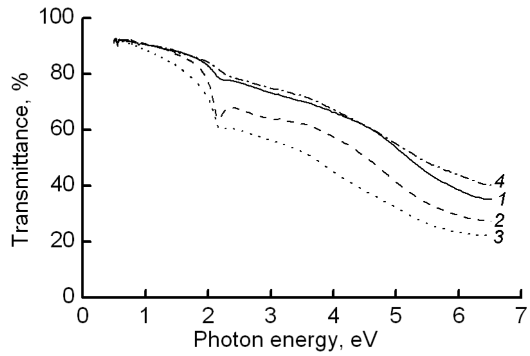


Fig. 2. Transmission spectra of $Cu^-$-ion implanted layer in silica glass obtained at different current densities: *1* — 1, *2* — 3, *3* — 10 and *4* — 30 μA/cm$^2$.

is due to the dynamics of nanoparticle formation. Temperature of the samples under the implantation rises with increasing current density. This leads to more intensive copper atoms nucleation and the formation of nanoparticles. We determined that at current density of 3 μA/cm$^2$ the temperature of the sample reaches 320 K and of 10 μA/cm$^2$ — 420 K. As a result the diffusion and rate of defects production grow up.

Optical specular reflectance spectra of the implanted samples relative to aluminum mirror are shown in Fig. 3. These spectra demonstrate the effect of surface plasmon resonance from copper nanoparticles and essential differences for the different ion current densities.

## *3. Theoretical model*

The method of determination of the implanted layer composition is based on comparison of the experimental and theoretical spectra of optical transmission and reflection.

Theoretical spectra were calculated taking into account the possible composition of the composite, and the optical properties of its components. Among all the theoretically possible compositions that composition for which the theoretical spectrum has the smallest average deviation from the experimental one is considered to be true.

The structure of the sample was determined from the TEM images. The samples consist of three layers. The first one is thin layer of glass with thickness of about 10 nm. The second one is the modified layer $d_l$ of 60 nm thick, and the third is the substrate of silica glass. Transmission and reflection of the top layer was estimated by Fresnel formulas for a thin transparent film. Reflection coefficient of the top layer at wavelength of $\lambda = 400$ nm is less than 0.1 %. Therefore, this layer was not taken into account in calculating the theoretical spectrum. The sample was considered as the homogeneous thin ($d_l < \lambda$) modified layer with refractive index $n_l$ and extinction coefficient $k_l$, on the thick ($d_g >> \lambda$) substrate of glass.

To calculate the transmission and reflection spectra Fresnel formulas for the transmittance $T_{Fr}$ ($n_l$, $k_l$, $n_g$, $d_l$, $\varepsilon$) and reflectance $R_{Fr}$ ($n_l$, $k_l$, $n_g$, $d_l$, $\varepsilon$) of thin absorbing layer between two semi-infinite transparent media [8] were used. We also took into account the coefficient of reflectance $R_{g-a}(n_g)$ from the plane boundary of air and transparent medium. In these expressions $n_g$ is the refractive index of glass and $\varepsilon$ is the photon energy.

Optical constants of the implanted layer were determined on the basis of Bruggeman effective medium theory [9]. Bruggeman theory allows calculating the optical constants of the composite material using volume fractions and optical constants of the constituent substances. We supposed material of the composite layer to consist of metallic copper, cuprous oxide ($Cu_2O$) and substrate material ($SiO_2$). The algorithm of the method for determining composition of the implanted layer from the experimental spectra is presented below.

*Step 1.* Optical constants of the composite material for all possible compositions of the implanted layer are calculated. Composition of the material is defined by the volume fractions of copper ($x_1$), cuprous oxide ($x_2$) and the substrate material ($x_3 = 1 - x_1 - x_2$). To find the functions of $n_l(x_i)$ and $k_l(x_i)$ an equation of the effective medium theory is solved for each set of $x_i$:

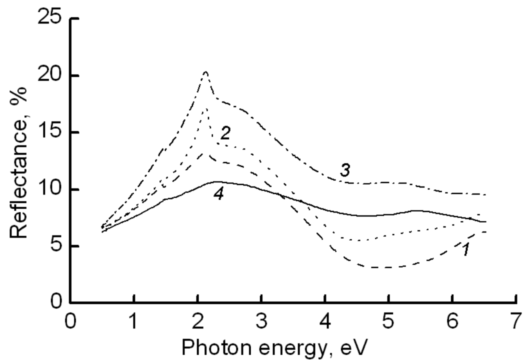


Fig. 3. Reflectance spectra of $Cu^-$-ion implanted layer in silica glass obtained at different current densities: *1* — 1, *2* — 3, *3* — 10 and *4* — 30 μA/cm$^2$.

$$\sum_i x_i \frac{\tilde{n}_i - \tilde{n}_{eff}}{\tilde{n}_i - 2\tilde{n}_{eff}} = 0, \qquad (1)$$

here $\tilde{n}_i$ is the complex refractive index of $i$-th substance: $\tilde{n}_i = n_i + ik_i$, $n_i$ is the real part of refractive index, $k_i$ is the extinction coefficient; $\tilde{n}_{eff}$ is effective refractive index of the composite layer.

The characteristic equation is solved in two stages. The first step is finding the global minimum of (1). For this purpose we use the method of linear search with a large mesh size ($30 \times 40$ points). Second stage is clarification of the optical constants $\tilde{n}_{eff}$ values by using Newton's method. Such approach allows us to obtain values of the optical constants of the composite with sufficient precision, but with low cost of computing. This aspect is important, because the procedure must be repeated $10^3 \div 10^5$ times depending on the number of parameters taken into account and the chosen precision.

*Step 2.* Optical constants $n_l(x_i)$ and $k_l(x_i)$ obtained at the first step are substituted into expressions for the optical transmittance $T_{calc}$ ($x_i$,$d_l$,$\varepsilon_j$) and reflectance $R_{calc}$ ($x_i$,$d_l$,$\varepsilon_j$):

$$T_{calc}(x_i,d_l,\varepsilon_j) = \qquad (2)$$
$$= T_{Fr}\left(n_l(x_i),k_l(x_i),n_g,d_l,\varepsilon_j\right) \times \left(1 - R_{g-a}(n_g)\right),$$

$$R_{calc}(x_i,d_l,\varepsilon_j) = T_{Fr}\,(n_l(x_i),k_l(x_i),n_g,d_l,\varepsilon_j) + \qquad (3)$$
$$+ R_{g-a}(n_g) \times T_{Fr}\,(n_l(x_i),k_l(x_i),n_g,d_l,\varepsilon_j).$$

At the calculation of theoretical reflection and transmission spectra the densification of silica glass due to ion beam irradiation was taken into account.

Spectral range for the analyzing experimental data was selected according to the following several demands:

1. The range should not contain any specific features. Minimum in the transmission spectra and maximum in the reflection spectra are associated with the surface plasmon resonance on nanoparticles of copper. But the theoretical model ignores this phenomenon and we can not use the data.

2. In the low-energy photon range, $h\nu < 2.6$ eV, the cuprous oxide has a very low extinction coefficient. This leads to large errors in the calculations, that is why the low-energy photons are also excluded from the chosen spectral range.

3. In our theoretical model we utilize two assumptions. First, we consider that substrate is transparent. Second, we ignore scattering of light on the sample surface. Both assumptions are not valid at high photon energies, when the absorption of radiation induced defects and the scattering by surface irregularities become significant.

Basing on these criteria, the range of the spectrum $2.75 \div 3.75$ eV ($330 \div 450$ nm) was selected. Within this range, 5 points were chosen for processing.

*Step 3*. For each composition, the standard deviation of the theoretical spectra from the experimental ones are calculated. The characteristic function can be written as follows:

$$f(x_1,x_2) = \sum_j \left(\left(T_{meash}(\varepsilon_j) - T_{calc}(x_1,x_2,d_l,\varepsilon_j)\right)^2 + \left(R_{meash}(\varepsilon_j) - R_{calc}(x_1,x_2,d_l,\varepsilon_j)^2\right)\right). \quad (4)$$

Composition, for which the function (4) takes the minimum value, is considered to be true.

## 4. Results and discussion

The method was applied to the samples shown in Fig. 1. The volume fractions of the substances, which were contained in the modified layer, were found. In the Table we show the composition of the implanted layers obtained for different ion current densities. In the considered range of wavelengths the isolated atoms influence weakly on the absorption spectra of the samples. So, the proposed method for determining the chemical composition of the nanolayers is not sensitive to them, and this method allows registering the presence of nanoclusters or large particles of Cu and its compounds.

At the current density of 1 μA/cm$^2$ the small values of $\rho$ and $\gamma$ are obtained because of low rate of nanoparticles creation and high probability of the small nanoclusters oxidation.

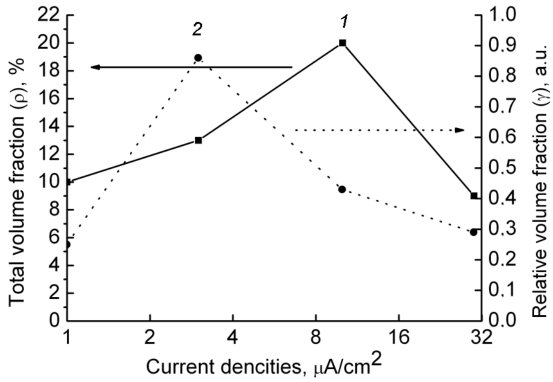


Fig. 4. The plots of total volume fraction of copper and cuprous oxide ($\rho = x_1 + x_2$) and the ratio of their volumes ($\gamma = x_1/x_2$) as a function of the current density of ion beam.

For the sample irradiated at current density of 3 μA/cm$^2$ the $\gamma$ reaches the maximum value. Formation of larger nanoparticles leads to decreasing the oxidation rate due to enhancement of ratio of the nanoparticles surface to their volume. The more intensive diffusion results in increase of $\rho$.

Under irradiation by ion beam with current density of 10 μA/cm$^2$ almost all copper atoms gather in nanoclusters. The maximum of $\rho$ and considerable sputtering of the top glass layer is observed. The trend of $\gamma$ decreasing remains. In current range of $10 \div 30$ μA/cm$^2$ an effect of sputtering becomes important. And at the current den-

Table. Composition of the ion implanted nanolayers derived from the optical characteristics as a function of the set of the spectra measurements and the beam current density

| Current density, μA/cm$^2$ | Used spectra | Composition | |
|---|---|---|---|
| | | $x_1$ (Cu), vol.% | $x_2$ ($Cu_2O$), vol.% |
| 1 | *T* and *R* | 2 | 8 |
| | *T* | 2 | 9 |
| 3 | *T* and *R* | 6 | 7 |
| | *T* | 6 | 7 |
| 10 | *T* and *R* | 6 | 14 |
| | *T* | 6 | 14 |
| 30 | *T* and *R* | 2 | 7 |
| | *T* | 2 | 7 |

sity of 30 μA/cm$^2$ considerable sputtering of the sample surface leads to decrease of ρ.

Thus, by varying the beam current density during the ion implantation, one can control the chemical composition and optical properties of the implanted layer.

Spectra of optical transmission and reflection were measured from both the irradiation side and the substrate side. The results of "front" and "back" spectra analysis differ only slightly. This confirms the validity of the model approximation of the homogeneous modified layer.

The results of processing the both spectra $T_{meas}(\varepsilon)$ and $R_{meas}(\varepsilon)$, and $T_{meas}(\varepsilon)$ are compared in Table. As one can see the results are almost identical.

Thus, this technique allows using the transmission spectra end only $T_{meas}(\varepsilon)$. In this case, the sufficiently high accuracy is maintained, and calculations are simplified. Furthermore, this advantage is important, because the most commercial spectrophotometers can measure the transmission spectra only.

In this case, the characteristic function (4) takes the following form:

$$f(x_1,x_2,x_3) = \sum_j \left(T_{meas}(\varepsilon_j) - T_{calc}(x_1,x_2,x_3,d,\varepsilon_j)\right)^2. \quad (5)$$

The composition, for which the function (5) takes the minimum value, is determined in the way described above.

## 5. Conclusions

Thus, the method for determining the composition of the implanted layer based on comparison of the experimental and the theoretically calculated spectra is developed. This method is successfully applied to analysing the copper implanted layer in a glass substrate. The structure of the implanted layers obtained at varying ion current density was studied. Thickness of the layers, that is required in theoretical calculations, was determined from TEM images. Based on chemical composition and structure of the modified layer an interpretation of the role of various processes taking place in the implanted layer at the different current densities of the ion beam is given.

## References


1. Y.Takeda, J.P.Zhao, C.G.Lee et al., *Nucl. Instr. and Meth. Phys. Res. B*, **166**, 877 (2000).
2. P.D.Townsed, R.Brooks, D.E.Hole et al., *Appl. Phys. B*, **73**, 345 (2001).
3. T.Karali, N.Can, L.Valberg et al., *Physica B*, **363**, 88 (2005).
4. A.Ishizumi, C.W.White, Y.Kanemitsu, *Appl. Phys. Lett.*, **84**, 2397 (2004).
5. C.J.Vriezema, K.T.F.Janssen, P.R.Boudewijn et al., *Appl. Phys. Lett.*, **54**, 1981 (2009).
6. V.G.Kesler, S.G.Yanovskaya, G.A.Kachurin et al., *Surf. Interface Anal.*, **33**, 914 (2002).
7. N.Kishimoto, V.T.Gritsyna, K.Kono et al., *Nucl. Instr. and Meth. Phys. Res. B*, **127,128**, 579 (1997).
8. M.Born, E.Wolf, Principles of Optics, Cambridge University Press, Cambridge (2002).
9. D.Striud, *Superlattice Microst.*, **23**, 567 (1998).


# Визначення елементного складу імплантованих наношарів на основі їх оптичних властивостей

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Розроблено методику визначення складу наношарів з використанням експериментальних спектрів оптичного пропускання і відбиття. Моделювання оптичних властивостей композитного матеріалу шару проводилося виходячи з теорії ефективного середовища Бруггемана. Даний метод випробувано на зразках з кварцового скла, імплантованих пучками іонів $Cu^-$ з енергією 60 кеВ та різними густинами струму. Структуру та товщину наношару (60 нм) визначено методом просвічуючої електронної мікроскопії. На основі аналізу оптичних спектрів обрано діапазон енергій фотонів (3.5÷4.5 еВ). Отримано склад імплантованих шарів у вигляді об'ємних концентрацій їх складових (міді, геміоксиду міді ($Cu_2O$) і матеріалу підкладки).