HOW THE SOL AFFECTS QUALITY OF OPTICAL LAYERS CONTAINING Cu^+ IONS

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The aim of the presented research is to design and experimentally verify preparation of multiple optical layers (covers) containing copper 1+ (I) ions for utilization in active photonic structures (devices). The layers were deposited on the surfaces of common silicate glasses by sol-gel method using dip-coating technique. The sols were CuCl, TEOS and three types of surfactants as Triton, Ludox or PEG. The deposited layers were tested with regard to their quality and optical properties. The resulting Cu^+ containing layers were then covered with silicate thin film in order to preserve the oxidation state of Cu^+. The best quality of the examined layers were found with three-layers (2 containing Cu^+ plus one cover layer) ones prepared using PEG-400. We have proved that by modification of experimental conditions of the deposition it is possible to significantly affect not only quality but also blue-green luminescence of the samples.

INTRODUCTION

Planar optical waveguides in glass substrates have become to be a common component of a whole range of special optical and photonics structures. Among them the waveguides containing ions of copper create a very interesting topic as they can be utilized in both passive (Cu^{2+}) as well as active (Cu^+) photonics devices.

Exclusive properties of Cu^+ is its photoluminescence in the visible blue-green part of the spectra, which is a consequence of $3d^{10} \rightarrow 3d^9 4s^1 (p^1)$ transition [1-4]. However, Cu^+-based devices is difficult to make, because of a poor stability of Cu^+ (I), which readily oxidizes to Cu^{2+}(II). Nevertheless, we have proved in our previous research [5,6] that it is possible with a sophistically done ion exchange to prepare the waveguides, which contained exclusively Cu^+. Unfortunately, this way of producing the Cu^+ containing thin optical layers is a time-consuming and demanding technique, which is rather restricted for a common use.

Here we are going to report on our new approach to deposit Cu^+ containing layers onto commercially available silicate glasses. This sol-gel approach is based on dip-coating [7,8], which is a technique suitable for covering large surfaces. In our case it enables to create copper-doped silicate thin films having high chemical purity and thought specific properties [9], such as, e.g., antibacterial [10] or optical [11-13]. Copper is added to the sol in a form of copper (II) acetate [14], copper (II) nitrate [15-17], copper (I) or copper (II) chlorides [18], or, eventually copper (II) sulphate [19]. Thickness and properties of the sol-gel films can be modified with adding of other additives like non-polar surfactant Triton X-100 [20-22], PEG 200-400-600 (polyethylene glycol) [23,24] or amorphous silica Ludox [25].

EXPERIMENTAL

The substrates were common microscope glasses. The first thing to do with them was to test presence and content of the ions that might affect the oxidation state of copper. The testing was done using XRF- spectrometer ARL 9400 XP. We found that chemical compositions of the both side surfaces are different. On "upper" side it was found higher amount of tin and iron traces (see Table 1) so that for deposition of optical layers was used the "bottom" side. Prior the experiments the glass slides were thoroughly washed with detergents, de-mineralized water and ethanol, and let dry 15 min at 60 °C.

Table 1. Composition of microscopic glass slide (wt.%).

Elements	Upper side	Bottom side
Na_2O	14.09	14.20
MgO	4.17	4.27
Al_2O_3	0.664	0.678
SiO_2	71.17	71.64
P_2O_5	0.0041	< 2e
SO_3	–	0.169
S	0.074	–
Cl	0.0110	0.0067
K_2O	0.338	0.325
CaO	8.82	8.67
TiO_2	0.0194	0.0198
Fe_2O_3	0.0229	0.0178
SrO	0.0032	0.0028
ZrO_2	< 2e	0.0048
SnO_2	0.609	< 2e

Silicate sols containing copper (I) ions were prepared by successive adding of reagents as listed in Table 2. The basic component of the sols was tetraethyl orthosilicate (TEOS) with surfactants as TRITON X-100 (sol SCT), Ludox (sol SCL) and PEG-400 (SCP). As the reference sol was used pure SCR sol without surfactants addition. All the chemicals came from Sigma-Aldrich. Copper in the form of CuCl was dissolved in concentrated hydrochloric acid (HCl, 36 %). The sols were prepared by continual stirring at room temperature. According to our previous experiments the ageing of the sols occurred 7 days at room temperature in darkness.

Table 2. Composition of the silica-cupper sols.

Reagents	SCR	SCT	SCL	SCP
CuCl	0.5 g	0.5 g	0.5 g	0.5 g
HCl (36%)	20 drops	20 drops	20 drops	20 drops
Triton X-100	–	15 ml	–	–
Ludox	–	–	15 ml	–
PEG-400	–	–	–	15 ml
Ethanol	30 ml	15 ml	15 ml	15 ml
TEOS	10 ml	10 ml	10 ml	10 ml
H_2O	1 ml	1 ml	1 ml	1 ml

In order to preserve oxidation state of copper (I) within the deposited films we prepared Cu-free silicate sols (Table 3) as coating layer. These coating copper-free silicate sols (ST, SL, SP) contained the same kind and same amount of surfactants as the functional copper-silicate sols. Reference silicate sol was surfactants-free sol (SR).

Pre-cleaned glass slides were dipped (rate 20 cm min^{-1}) with help of dip-coater into particular copper-silicate sols and then pulled out (rate 6 cm min^{-1}), so that the idle periods in the sols were 30 s. This way, by repeating the dipping procedure, we prepared 1,2 or 3-layers copper-silicate surfaces. Last coating layer (silicate) was deposited using the way as the copper-doped layers (Fig. 1). The samples were let to dry and then they were annealed 120 min at 400 °C; the rate of the heating-up was 2 °C min^{-1}. The last step of the procedure was cooling of the samples, which proceeded in the same oven till the next day.

The annealed samples were characterized with scanning electron microscope HITACHI S4700 with the SDD detector at accelerating potential 15 kV. Later the samples were for 80 s let to coat with metal Au-Pd layer.

Photoluminescence spectra of the samples were taken in the region 300-700 nm by Hitachi F-4500 (Hitachi Ltd., Tokyo, Japan) spectrophotometer.

Table 3. Composition of the silicate sols.

Reagents	SR	ST	SL	SP
HCl	20 drops	20 drops	20 drops	20 drops
Triton X-100	–	15 ml	–	–
Ludox	–	–	15 ml	–
PEG-400	–	–	–	15 ml
Ethanol	30 ml	15 ml	15 ml	15 ml
TEOS	10 ml	10 ml	10 ml	10 ml
H_2O	1 ml	1 ml	1 ml	1 ml

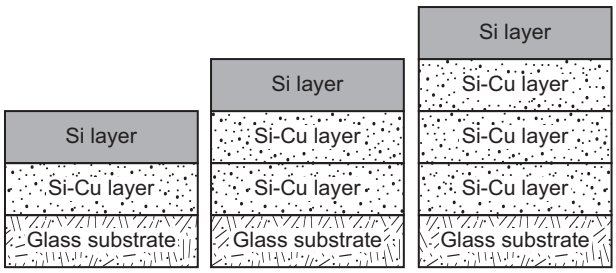


Figure 1. Multi-layer silica-cupper coating on the glass substrate.

RESULTS AND DISCUSSION

In Figs. 2a-d are given the SEM/EDS analyses of the two-layer (one function copper-containing layer plus one coating layer) surfaces. The figures clearly show significant impact of the used surfactants on the quality, i.e., homogeneity of the deposited layers.

The SCR surface without surfactant (Fig. 2a) is not homogeneous, it contains larger amount of grouped particles and in the detailed figure there are clearly visible pores in otherwise smooth surface. SCT surface (Fig. 2b) under smaller magnification seems to be homogeneous, without cracks; however larger magnification reveals that it consists of the ball-shaped particles. Fig. 2c displaces SCL thin film containing Ludox, which is

markedly crackled and shows two clearly visible layers of the coating. More detailed picture reveals also here the ball-shapes consistence of the surface. Last figure (Fig. 2d) concerns PEG-400 containing SCP-covered sample; this surface is very similar to the SCT one, however here the thickness of the SCP film is approximately 500-600 nm, which is a substantial difference comparing with the thickness of the SCT film.

Direct EDS analysis to confirm presence of Cu^{+} in the deposited layers could not work, as the pertinent layers were always coated with silicate, copper-free films.

Based on the checking of quality of the deposited layers we prepared the samples having multilayered thin films with PEG and Triton. In this part of the experiments very careful control of conditions of drying and annealing was inevitable to ensure homogenization of the deposited films. (One example of poor ligature of the layers is given in Fig. 3).

The best results we obtained with 3-layered structure consisting of 2 functional Cu^{+}-containing layers plus one coating layer, when using PEG-400 surfactant. The prepared optical thin film was smooth, cracks-free and homogeneous.

Photoluminescence characterization of the prepared samples is one the most significant features of merit of the deposited films. The spectra were taken in the region 300-700 nm and one of that measurement is shown in Fig. 4, where is given the luminescence spectrum of the optical (SCP) layer with three important luminescence

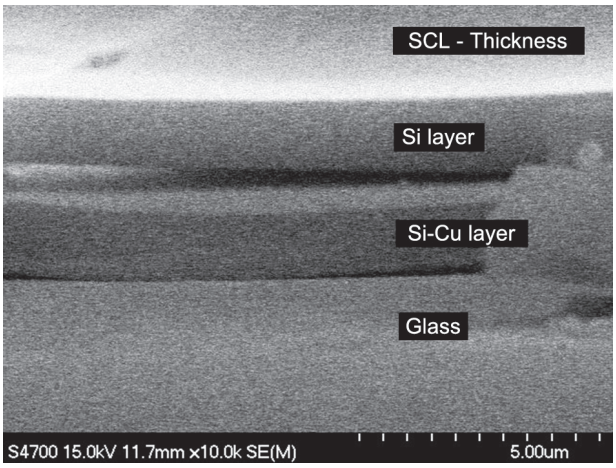
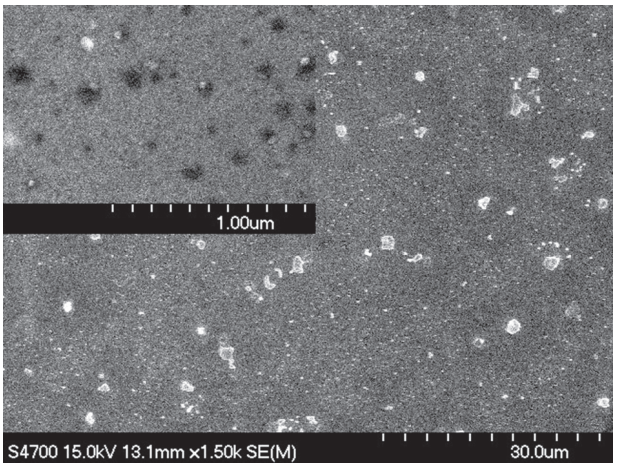
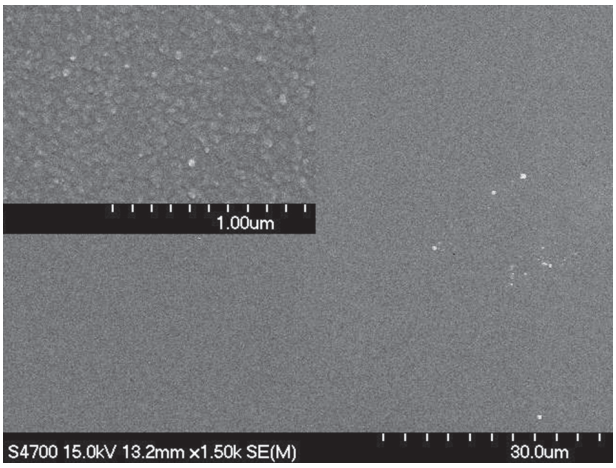


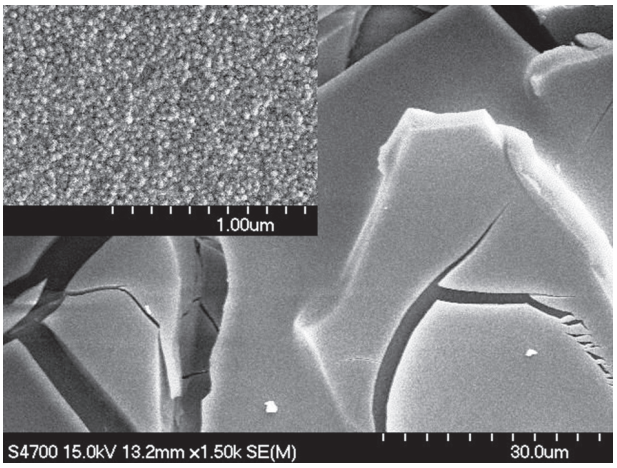
Figure 3. SEM/EDS cross-section of SCL coating.



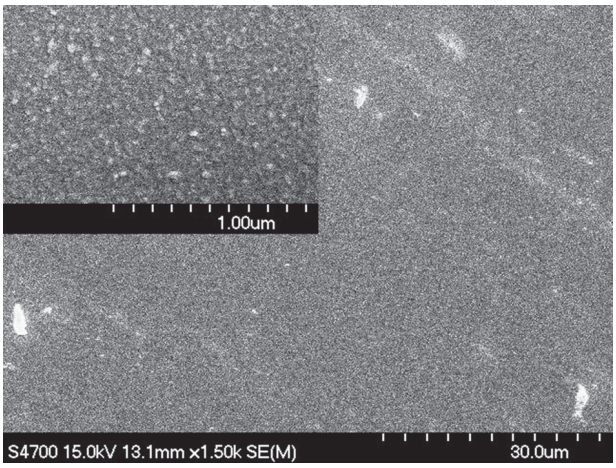
a) SCR



b) SCT



c) SCL



d) SCP

Figure 2. SEM/EDS Surface of coatings: a) SCR, b) SCT, c) SCL and d) SCP.

maxima. Position of the Cu^+ luminescence peaks is strongly affected by its surrounding, which can have tetragonal or octahedral symmetry. We found that in our samples both possibilities of the Cu^+ coordination really occurred, as the emission band around 390 nm is attributed to Cu^+ in cubic (octahedral) sites and that around 490 nm to the Cu^+ in tetragonal sites.

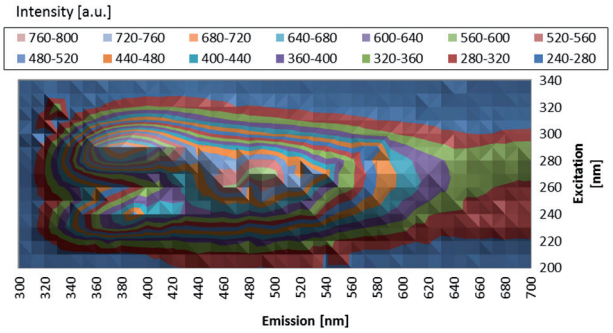


Figure 4. Example of luminescence spectrum of optical layer containing Cu^+ ions with 3 important maxims (SCP coating).

CONCLUSION

We have succeeded in designing and preparation of four types of the silicate sols containing Cu^+ ions and four types of coating copper-free silicate sols. Using the prepared sols we were able to deposit many types of functional copper-containing optical layers on the surfaces of common soda-lime silica glasses by the sol-gel and dip-coating technique.

Best quality provided SCP and SCT films. The prepared optical thin films were smooth, cracks-free and homogeneous.

The best results we obtained with 3-layered structure consisting of 2 functional Cu^+-containing layers plus one coating layer, when using PEG-400 surfactant (SCP film). The thickness of the layers thus prepared was 2.9-3.4 μm.

Photoluminescence spectra proved that the deposited films contained Cu^+ ions and that they were in the sites having both tetragonal as well as cubic symmetry. The intensity of the blue-green luminescence and the positions of the luminescence bands were strongly depended on used sols and on thickness of fabricated layer.

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