

# Synthesis, chemical characterization and antifungal activity of thin layers prepared by sol–gel method

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Sol–gel method was used to prepare SiO<sub>2</sub>–TiO<sub>2</sub> thin layers on the microscope slide glasses with additions of Cu, Ag, Au compounds. The films were calcined at 150 °C for 1 hour. We studied the morphology of the following samples by scanning electron microscopy (SEM with EDS analysis), and the X-ray photoelectron spectroscopy (XPS). Antifungal properties of the layers were tested with the use of fungi *Penicillium*. The results have shown that the best antifungal effect among the examined layers has got the sample with Au ions addition.

Keywords: antifungal thin layer, sol–gel method, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS).

## 1. Introduction

For the last several years, the increasing awareness of diseases and infections transmitted from microorganisms have caused that the number of antimicrobial products, such as protective clothing for medical and chemical works, packing materials and tissue papers, has recently increased [1]. The materials with antimicrobial activity have been widely used in medicine, dentistry and furthermore in non-medical applications such as carpets [2, 3], hand soap [4], wallpapers, paints, gloves, pavement-marking materials and also self-cleaning windows [5–7]. Some experts estimate that there are about 600 to 700 different products which can contain some form of antimicrobial materials [5]. The food industry is particularly interested in the surface that can reduce microbial loads. Another non-medical industry with great concern in antimicrobial material is the construction industry [8–12]. Builders and users of residential and commercial properties are looking for the new ways to prevent the growth of mold in building materials and ventilation systems [6].

A very interesting and probably the most common antimicrobial agent is silver. Silver ions are thought to inhibit bacterial enzymes, interfere with the electron transport

and damage DNA. It is also worth to mention that silver in the form of silver sulfadiazine was also one of the primary antimicrobial agents used in the treatments of burned patients [5].

Recently, the nanomaterials have been investigated intensively on their potentially antimicrobial properties [2, 13, 14]. Silver nanoparticles (AgNPs) are well-known for their board spectrum of antimicrobial activity and high toxicity to different types of microorganisms [3, 4]. AgNPs are inert in their metallic state, but become ionized upon contact and reaction with moisture of skin and wound. The strong reactivity of ionized Ag causes cell destruction and microorganism death, as the bacteria cell wall undergoes structural changes once AgNPs binds to tissue proteins [2]. The antimicrobial properties of AgNPs are believed to be size-dependent, where smaller AgNPs with larger surface area accessible for interaction provide more antimicrobial effect than larger AgNPs [3].

The aim of this study was to compare antifungal properties of Ag, Au and Cu in the form of nanoparticle and ions (Cu) in sol–gel prepared films.

## 2. Experimental procedure

### 2.1. Sol preparation

The sol solutions were prepared using tetraethyl orthosilicate (TEOS), tetraethyl orthotitanate (TEOT), and methyltrimethoxysilane (MTMS) Sigma-Aldrich. Ethanol 95% and 2-propanol (Polish Chemicals) were used as solvents. Hydrolysis reaction was catalyzed by 1 M HCl (Polish Chemicals).  $\text{AgNO}_3$ ,  $\text{AuCl}_3$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$  (Polish Chemicals) and  $\text{CuC}_2\text{H}_6\text{O}_2$  (copper methoxide) – Sigma-Aldrich, were used as a source of silver, gold and copper.

T a b l e 1. Chemical compositions of the sols.

	Symbol				
	ST12	ST12_CuM	ST12_CuA	ST12_Au	ST12_Ag
TEOS [mol]	1	0.5	0.5	0.5	0.5
$\text{C}_2\text{H}_5\text{OH}$ [mol]	6	6	6	6	6
TEOT [mol]	2	2	2	2	2
$\text{H}_2\text{O}$ [mol]	2.6	2.6	2.6	2.6	2.6
HCl [mol]	0.05	0.05	0.05	0.05	0.05
$\text{C}_3\text{H}_8\text{O}$ [mol]	50.2	50.2	50.2	50.2	50.2
MTMS [mol]	1.0	1.0	1.0	1.0	1.0
$\text{Cu}(\text{CH}_3\text{COO})_2$ [mol]	–	–	0.2	–	–
$\text{CuC}_2\text{H}_6\text{O}_2$ [mol]	–	0.3	–	–	–
$\text{AgNO}_3$ [mol]	–	–	–	–	0.1
$\text{AuCl}_3$ [mol]	–	–	–	0.07	–

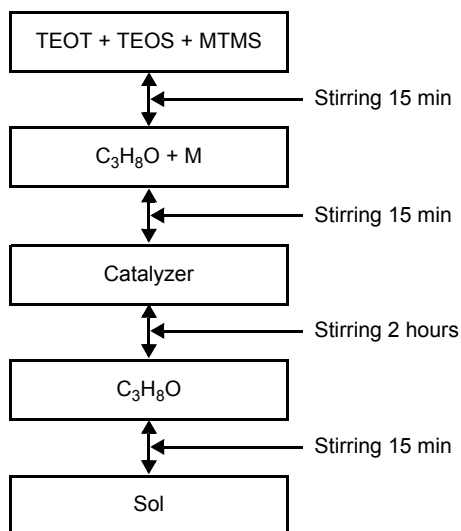


Fig. 1. Sol preparation procedure (M – AuCl<sub>3</sub>, AgNO<sub>3</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub>, CuC<sub>2</sub>H<sub>6</sub>O<sub>2</sub>).

Chemical composition of the sols is shown in Table 1, while the preparation procedure in Fig. 1.

## 2.2. Preparation of the thin films

Microscope slide glasses were used as a support. First we washed glasses in distilled water, then dried them and washed in ethanol. The procedures were carried out in ultrasonic bath. A thin film was prepared by the dip-coating technique using different speeds of withdrawing. The samples were dried at room temperature and calcinated at 150 °C for 30 min.

## 2.3. Characterisation of the films

A Jasco V 630 UV–VIS spectrophotometer was applied to study the optical absorption characteristic of the films, while an ellipsometer – PHE 102 from Angstrom Advance was used to measure the refractive index. Surface compositions of the samples were estimated from XPS measurements using a VSW spectrometer. Al K $\alpha$  200 W was used as an X-ray source. All spectra were calibrated with the binding energy of the apparatus carbon C1s peak  $E_b = 284.6$  eV [15-17]. The curve fitting procedure was carried out using a XPSPEAK 4.1 program (Raymunda W.M. Kwok, The Chinese University of Hong Kong).

The core levels of different elements were deconvoluted by using Gaussian–Lorentz components, after Shirley background subtraction. The size of nanoparticles and their distribution on the film surface were determined using the Scanning Electron Microscope Nova Nano SEM 200, FDI.

## 2.4. Antifungal test

The antifungal activity of the thin layers against the *Penicillium Fungi* was investigated using the so-called antifungal drop-test. The antifungal properties of thin layers doped with silver, gold and copper were tested optically using an optical microscope with 70 $\times$  magnification. Before the microbiological experiment all samples (microscope slide glasses with thin layers) were cleaned using ethanol. Saburo substratum infected by fungi spores was dropped on the glass samples surface and covered by a thin microscope glass. All samples were prepared in the same way and put into the aseptic watery drain in the Petri bowl and kept in moisture conditions. Fungi growth process was observed and registered by the optical microscope.

## 3. Results

### 3.1. Optical properties

Optical properties of prepared layers are very good with transparency higher than 90% – Fig. 2. In case of silver and gold containing layers the maxima due to plasmons generation are observed – inset in Fig. 2. Silver plasmon wavelength is 497 nm, while gold shows two plasmons with the wavelength 489 and 699 nm.

The refractive indexes of the layers are higher than the refractive index of the glass substrate due to titania content in the sol – Fig. 3. The refractive index depends also on the chemical composition of the sol and the highest value was measured for Ag and Au containing layers. It is connected with the microstructure of the layer, which is less porous than in case of Cu containing films.

### 3.2. XPS results

The photoelectron spectroscopy technique was used to confirm the presence of silver, gold and copper in the tested samples and determine their nuclear states. Figure 4 shows high resolution spectra of these elements with the given binding energy.

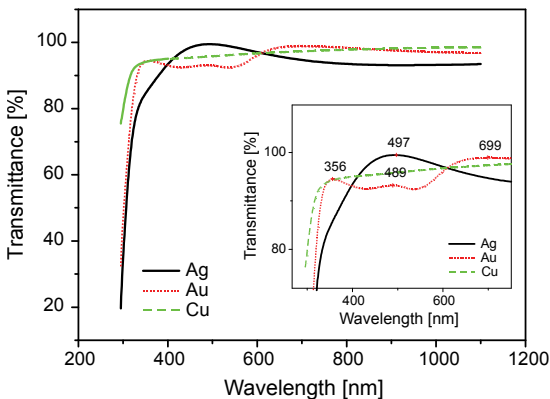


Fig. 2. Transmittance of silica titania films containing silver, gold and copper. Maxima due to plasmon generation are shown as an inset.

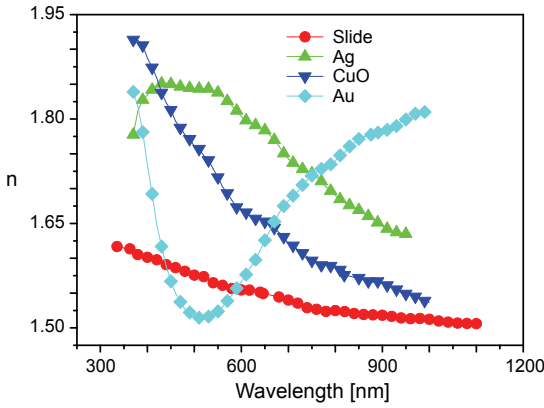


Fig. 3. Refractive index of studied films as a function of wavelength. Observed changes in the refractive index in case of Au film are due to multipy reflection on the thickness of the film.

The determined binding energy of gold Au  $4f_{7/2}$  is 83.8 eV, so the gold is in a metallic form. Also, silver is on a zero oxidation state and binding energy Ag  $3d_{5/2}$  is equal to 367.9 eV. Analyzing a sample with copper, it was found that the copper Cu  $2p$  is present as  $\text{Cu}^{1+}$  and the binding energy is 933.2 eV.

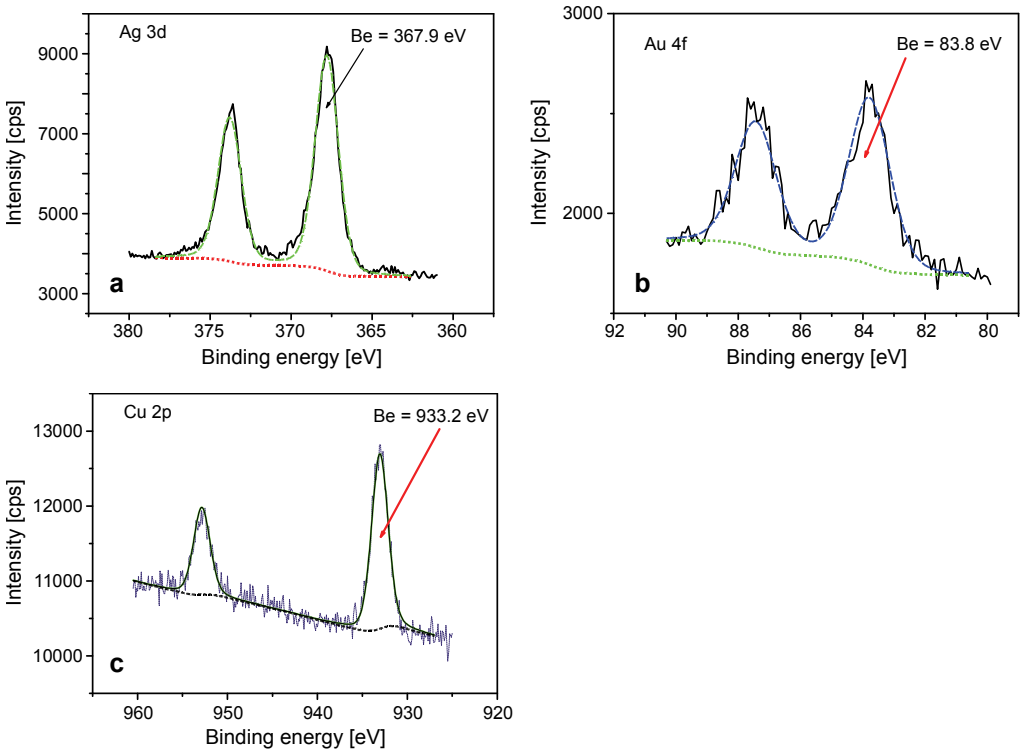


Fig. 4. XPS high resolution spectra of Ag (a), Au (b) and Cu (c).

### 3.3. SEM (EDS) analysis

The results of SEM observation of selected layers are shown in Fig. 5. Silver nanoparticles are clearly visible with the diameter ranging from 50 to 90 nm – Fig. 4a. Silver has a high tendency for coagulation so sol with smaller nanoparticles is difficult to obtain. The particles of Au are much smaller than Ag and they are not seen in Fig. 5b,

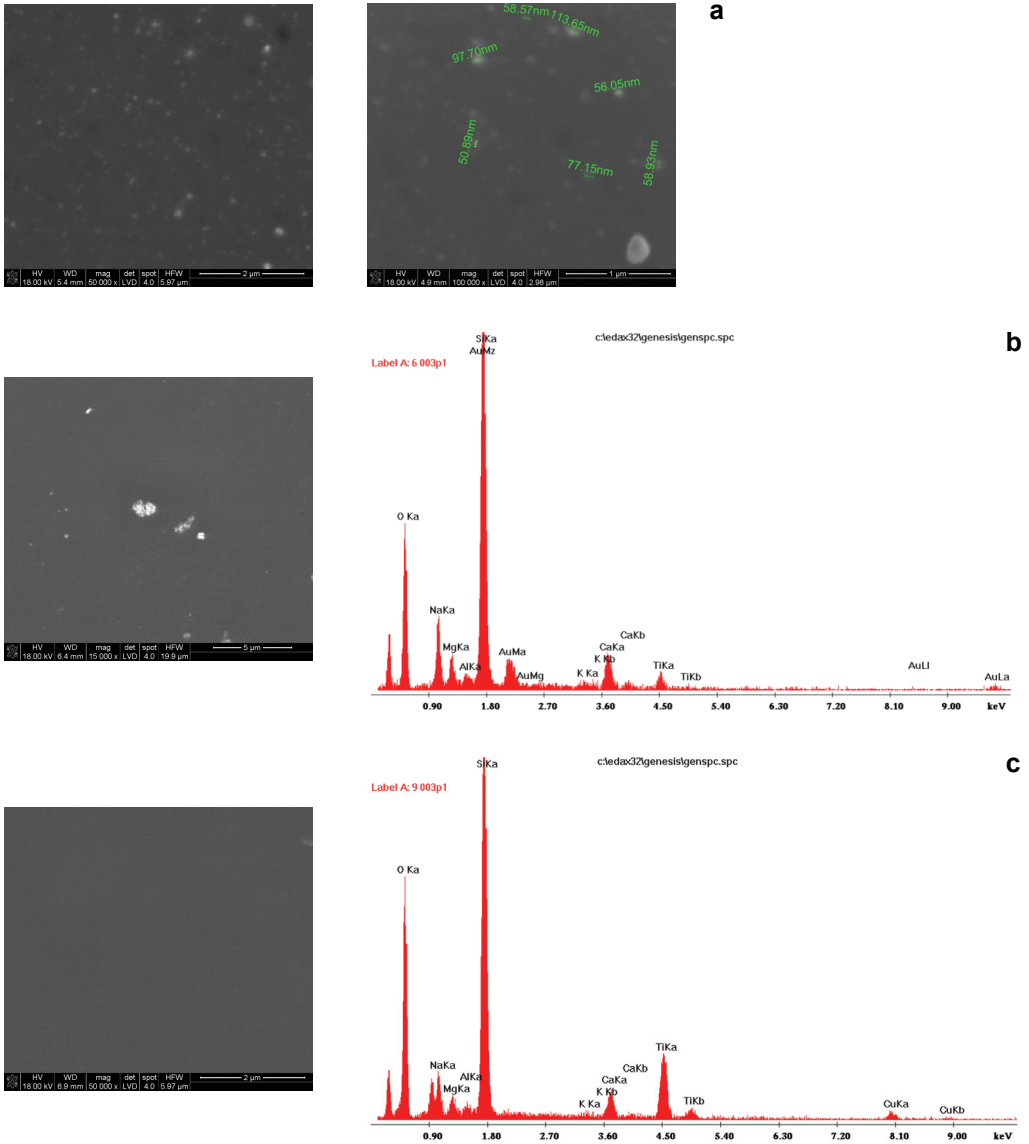


Fig. 5. SEM/EDS analysis of the samples with Ag (a), Au (b) and Cu (c) additions.

however the presence of gold was confirmed by EDS analysis. The presence of copper was also confirmed by EDS analysis – Fig. 5c.

### 3.4. Antifungi properties

The results of an antifungi test are shown in Fig. 6. After 48 hours no fungi were observed on the sample having Ag and Au. Some fungi grew on the sample with Cu prepared from methoxide, but on the sample prepared from acetate, the number of fungi was very high. After 168 hours of incubation (7 days) fungi were observed on

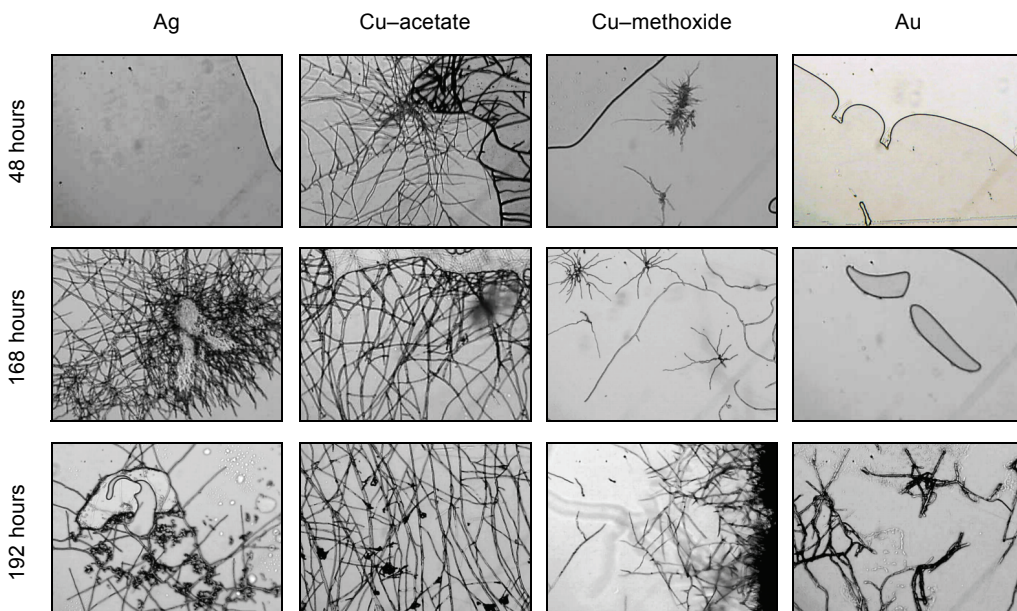


Fig. 6. Fungicide properties.

the Ag and Cu–acetate sample, some on Cu–methoxide but not on the Au sample. 192 hours of incubation led to some fungi on the Au sample and more on the Cu–methoxide sample. A large colony of fungi was observed on the Cu–acetate and Ag sample.

## 4. Conclusions

Thin layers of silica–titania doped with silver, gold and copper were successfully prepared and their fungicidal properties were tested. It was found that the most antifungal properties possess the samples with gold  $\text{Au}^0$  in the form of nanoparticles. Antifungal properties of  $\text{Ag}^0$  containing samples have not been stated, most probably

because of a relatively large size of silver nanoparticles. The activity of Cu towards fungi depends mainly on the chemical form of Cu compound and Cu–methoxide was much more active than Cu–acetate.

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