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# Microstructure and optical properties of thermally evaporated very thin silver films

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The present paper shows results for the optical properties of nanocrystalline silver thin films in attempt to understand the effects of the particle size. Ag-films with thickness from 10 nm to 20 nm were deposited on optical glass by thermal evaporation. Depending on the deposition rate, due to different sizes of the grains building the layers, it was observed variation in the color of the coatings from red to blue. The grain size was determined by X-ray diffraction from the formula of Debye-Scherrer. A strong absorption band due to surface plasmons was observed in the transmittance spectra of the films. The absorbance maximum is positioned in the spectral range 400–550 nm in dependence of the film's grains size. The evolution of the thin silver films during vacuum annealing was investigated. It was established that the heating of 25 nm films at 250°C leads to aggregation of the grains.

**Key words:** silver nanoparticles, very thin films, Debye-Scherrer formula, X-ray diffraction, grain size, optical properties

## INTRODUCTION

Thin silver films have found many applications in different optical devices such as solar cells, light emitting diodes, to improve the properties of organic semiconductor materials and to launch new metamaterials [1–3].

It is well-known that the deposition conditions (deposition rate, vacuum pressure and substrate type and temperature) control the aggregation of the grains during the deposition of the thin metal films [4,5]. On its part, the size of the crystalline grains building the metal coatings affects the electrical and optical properties of the metals layers [6]. The thickness dependence of very thin silver films (with thickness up to 2.8) was investigated in [7]. The authors found that the refractive index of the thin films was significantly increased and the extinction coefficient is slightly increased compared with the bulk at visible and infrared wavelengths. They observed that with the increasing of the thin film thickness, the refractive index decreased, while the extinction coefficient and absorption increased. The influence of the deposition rate on the structure was investigated in [8]. The authors found that the deposition rate influences strongly the microstructure of thin silver films.

In our previous work we investigated thin silver films obtained by cathode sputtering [9]. We found that the deposition rate influences significantly the microstructure of the thin films and respectively – their optical properties. The object of investigation of the present work is the influence of the deposition rate and film's thickness on the optical properties of thin silver coatings obtained by thermal evaporation.

## EXPERIMENTAL DETAILS

The films with thickness ranging in 10-25 nm were deposited by thermal evaporation in vacuum $\sim 1 \times 10^{-3}$ Pa on an optical glass and Si wafer. The thickness of the thin films was controlled after film deposition by profilemeter "Talystep". The annealing of the thin films at 200°C was performed in vacuum of $10^{-3}$ Pa for 1 hour.

The transmittance ($T$) and reflectance ($R$) were measured by a UV-VIS-NIR spectrophotometer Cary 5E (Australia) in the range 350-2000 nm to an accuracy of $\Delta T = \pm 0.1\%$ and $\Delta R = \pm 0.5\%$.

X-ray diffraction patterns were collected by X-ray diffractometer "Philips 1710" – with monochromatic Cu-K$\alpha$ emission ($\lambda = 1.54056$)Å and Bragg-Brentano focusing geometry.

## RESULTS AND DISCUSSION

The phase structure of the thin films deposited by thermal evaporation at deposition rates 0.03 and 0.1 nm/s was probed by X - ray diffraction (XRD). The XRD patterns of the thin silver films are shown in Fig. 1. For comparison the XRD pattern of a thin silver film deposited by radio-frequency (*rf*) sputtering is given. Peaks due to diffraction from the crystallographic planes (111) and (200) at $2\theta = 38^{\circ}$ and $44^{\circ}$, respectively are seen in the pattern. The diffraction pattern of the thin film deposited at 0.1 nm/s demonstrates the sharpest and most intensive diffraction peaks.

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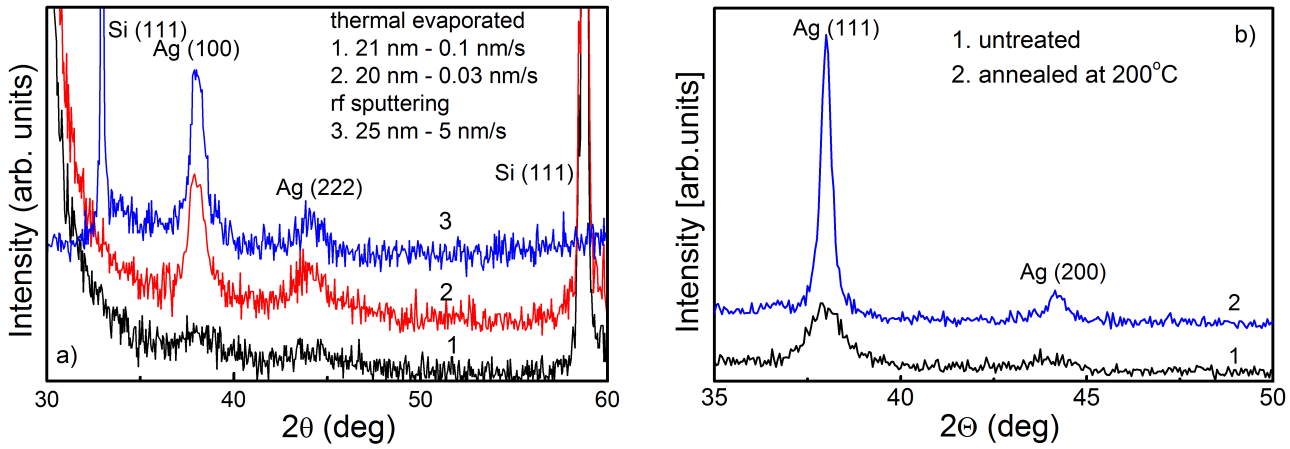


Fig. 1. X-ray diffraction patterns of thin silver films deposited by thermal evaporation on Si-wafer at deposition rates 0.03 and 0.1 nm/s and rf sputtering with thickness, $d \sim 0.02$ $\mu$m (a); X-ray diffraction patterns of a thin silver film deposited by thermal evaporation before and after annealing in vacuum ($\sim 10^{-3}$ Pa) at 200°C (b).

The microstructure of the thin silver films deposited by thermal evaporation at different rates in the range 0.04-0.44 nm/s is investigated in [8]. The authors found that silver shows a preferred orientation in (111) crystallographic plane. It was found that the average grain size and the intensity of X - ray diffraction peak, its width at half maximum (FWHM) depend on the deposition rate.

It is seen that the diffraction pattern of the thin film deposited by cathode sputtering demonstrates narrow peaks. It was determined that the temperature of the substrate during the sputtering process was arisen to 200°C. According to [10] the annealing temperature of very thin silver films is a key factor for the transformation of the size of the grains building the layer. Depending on the temperature, collision or separation can be observed. Therefore we annealed the thin silver film in vacuum ($\sim 10^{-3}$ Pa) at 200°C. In Fig. 1b the X-ray diffraction patterns before and after annealing are shown. It is seen that after annealing the diffraction peaks become narrower and possess higher intensity.

The Debye-Scherrer formula was applied for the calculation of the average crystallite size:

$$d_p = \frac{0.94\lambda}{\beta cos\Theta}, \qquad (1)$$

where $\beta$ is the peak width, $\lambda$ is wavelength of the X-rays (in the present study Cu$\alpha$ line was used and $\lambda = 1.54056$ Å).

The data from the XRD pattern and the results from the calculation of the grain size are summarized in Table 1. It is seen that the increase of the deposition rate in the thermal evaporation decreases the grain size of the thin films. The deposition of the thin films on the warm substrate, i.e. by sputtering leads to an increase of the size of the grains.

Table 1. The half-width (FWHM) of diffraction peak for Ag (111) and the grain size, $d_g$

| Deposition rate, V [nm/s] | Peak half-width (FWHM) [rad] | Particle size, $d_g$ [nm] |
|---|---|---|
| 0.03 | 0.027 | 8.18 |
| 0.10 | 0.015 | 10.5 |
| 5 *(rf sputtering)* | 10 | 11 |

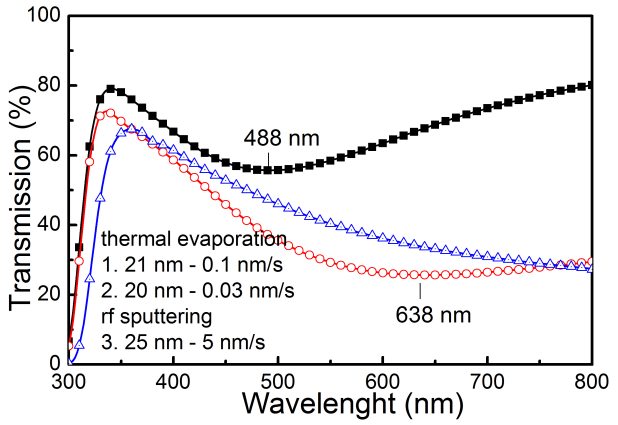


Fig. 2. Transmittance spectra of thin silver films deposited by thermal evaporation (deposition rates 0.03 and 0.1 nm/s) and *rf* sputtering.

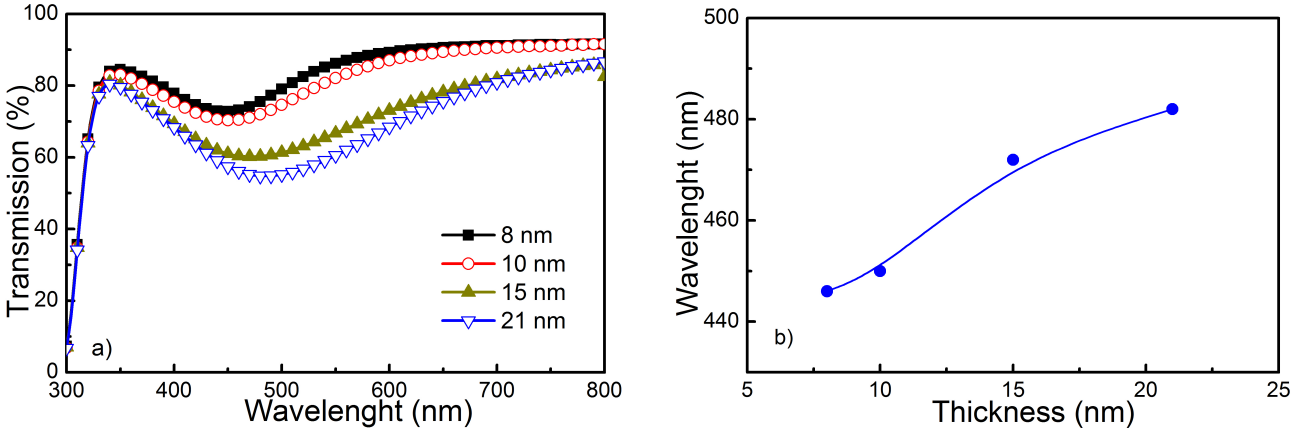


Fig. 3. Transmittance spectra of thin silver films deposited by thermal evaporation at 0.03 nm/s (a) and position of maximum absorption in dependence of the film's thickness (b).

The transmittance spectra of the same thin films in the spectral range 300-800 nm are shown in Fig. 2. A presence of absorption bands is seen in the spectra of the thin films deposited at the deposition rates 0.03 and 0.1 nm/s. It is seen that the increase of the size of the grains leads to a shift of the absorption band to longer wavelengths.

The transmittance spectra of thin silver films in the thickness range 8–21 nm and deposited with deposition rate 0.1 nm/s are given in Fig. 3a. It is seen that the position the absorbance band is varied from 448 to 488 nm. In the thickness range of 10–20 nm we can expect that the film is structured with discrete islands similar to nanoparticles [10]. According to [11] the small metal particles (with diameter $< 40$ nm) absorb energy through the following mechanisms: (i) Collective excitations of the "free" electrons, which give rise to surface modes or surface plasmon resonances that are determined by the particle shape and variations of the dielectric function; (ii) Electron transitions of bound electrons from occupied to empty bands of different index, also called interband transitions; (iii) Surface dispersion or scattering of the "free" electrons, when their mean free path is comparable with the size of nanoparticles. The resonance wavelength depends on the orientation of the electric field relative to the particle and the size and form of the nanoparticles. According to different literature sources [11,12], the maximum absorption of the silver nanoparticles is placed in the spectral range of 420-650 nm. The dependence of the position of maximum absorption on the film's thickness is shown in Fig. 3b. According to [10] with the increasing of the thin films the average size of grains which built the thin films increases

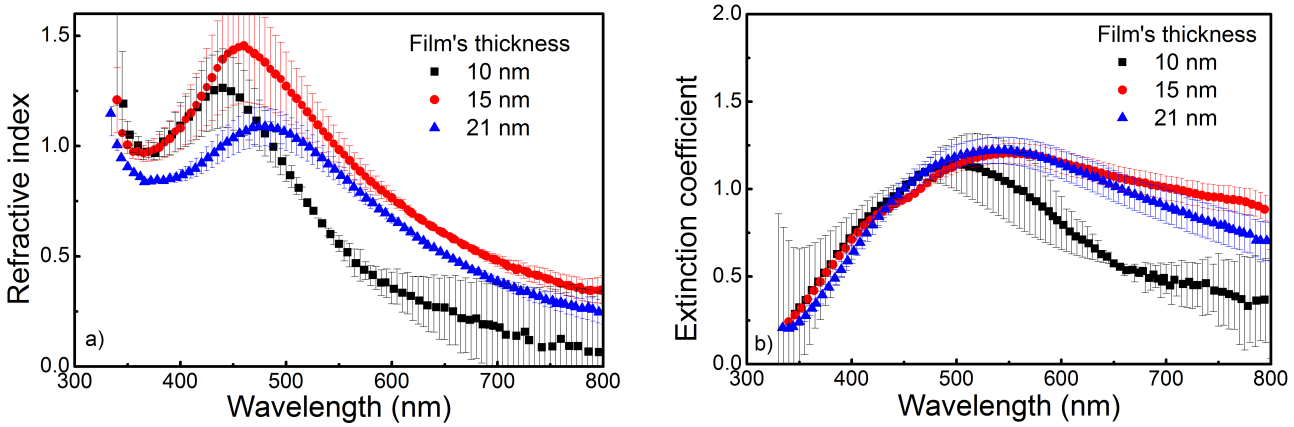


Fig. 4. Refractive index, $n$ and extinction coefficient, $k$ of thin silver films in the thickness range 10–21 nm.

and maximum scattering is expected to shift to longer wavelengths.

The optical constants (refractive index, $n$ and extinction coefficient, $k$) of the thin films are given in Fig. 4. The calculation method is detailed in our previous work [9]. The maximal error is determined assuming $\pm 5$ nm accuracy in the thickness determination. As expected, the experimental error for the refractive index is higher in the range of resonance wavelengths and it decreases for wavelengths longer than 550 nm for thin films with thicknesses 15 and 21 nm. It is seen that the thin film with thickness 10 nm possess smaller values for the refractive index and extinction coefficient in the spectral range 500–800 nm while the thin films with thicknesses 15 and 21 nm have nearly similar optical constants. The increase of the extinction coefficient with increase film's thickness can be explained with increasing of the number free electrons. Similar trend in thickness dependence of the extinction coefficient has been observed in [13]. It is seen that trough the variation of the thickness of the thin films we can varied the position of the absorption band in the visible spectral range.

## CONCLUSIONS

The present paper is focused on the investigation of the optical properties of nanocrystalline silver thin films and attempts to understanding the effects related to the particle size. Ag-films were deposited by thermal evaporation on optical glass with thickness from 10 nm to 20 nm. The grain size, determined from the X-ray diffraction patterns applying the Debye-Scherrer's formula, was in the range of 2–10 nm.

It was found that the size of the grains building the thin films depends on the deposition condition and that the dimension of the particles governs the optical properties of the thin films. The present results can be used for modeling of metal-dielectric composite coatings for application as sun absorbers for photovoltaic elements.

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# МИКРОСТРУКТУРА И ОПТИЧНИ СВОЙСТВА НА МНОГО ТЪНКИ СРЕБЪРНИ СЛОЕВЕ ОТЛОЖЕНИ ЧРЕЗ ТЕРМИЧНО ИЗПАРЕНИЕ

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(Резюме)

Настоящата работа показва резултати за изследване на оптичните свойства на тънки нанокристални сребърни филми с цел да се установи тяхната зависимост от размера на частиците (зърната) изграждащи слоевете. Тънки сребърни филми бяха отложени чрез термично изпарение върху подложки оптично стъкло и силиций с дебелина от 10 до 20 nm. В зависимост от скоростта на отлагане, поради различния размер на зърната изграждащи слоевете се наблюдаваше вариране на цвета на покритията от червен до син. Размера на зърната беше определен чрез рентгенова дифракция чрез формулата на Дебай-Шерер. В спектрите на коефициента на пропускане се наблюдаваше абсорбционна ивица дължаща се на повърхностните плазмони. В зависимост от размера на зърната максимума на поглъщането е в обхвата от 400 до 550 nm. Изследвано е влиянието на термично третиране във вакуум ($10^{-3}$ Pa) върху размера на зърната. Установено е, че нагряването на филмите с дебелина 25 nm при температура 250°C води до агрегация на зърната.