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Optical Transmittance Method for In-situ Analysis of Adsorption Phenomena from Residual Gases

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In this paper, the feasibility of optical control of adsorption processes during thin film deposition, based on developed optical technique as well as experimental results are discussed. The kinetics of the optical absorbance of the growing film was registered in-situ measuring optical transmission of the film-substrate structure. These measurements were done in parallel to the ex-situ absorption (UV-VIS) and reflection spectra analysis. The main results were compared with the optical constants defined by the in-situ technique. Two different groups of samples that were prepared by thermal evaporation method on glass substrates were investigated. The first group included silver films (as a model material) and the second one – barium getter films. Such complex measurements enabled to follow adsorption process from the residual gases during the thermal evaporation as well to control adsorption process after the evaporation. It was shown that the presented method is very sensitive in small thickness region of deposited films (5 nm – 50 nm) and can be employed for evaluation of Ba getter efficiency.
Keywords: optical transmission, spectra analysis, thermal evaporation, adsorption process.

1. INTRODUCTION

The last few decades has seen an explosive growth in research on the physics and chemistry of metal surfaces. With the advent of modern spectroscopic methods several aspects of metallic surfaces and their interactions with gases could be explained. Solid surfaces show strong affinity towards gas molecules that it comes in contact with and some of them are trapped on the surface. The process of trapping or binding of molecules to the surface is called adsorption. So the adsorption of atoms and molecules on solid surfaces is such a condition is connected with changes of all surface properties. An adsorption event is frequently observed in nature and found to be of technical importance in many industrial processes: production of vacuum devices [1, 2], formation of ultra thin metallic layers (silver, gold) for plasmonic applications [3, 4] and others. For this reason, surface science is interdisciplinary by its very nature and thus an important intermediary between fundamental and applied research. In solving many fundamental and technological problems, developing of new methods or improving existing ones that enable to monitor the processes of adsorption and desorption in-situ is a challenging task.

The aim of this work was to develop and calibrate an optical instrument (with a wireless data transfer) suitable for measurement and control the kinetics of growth of the films and adsorption phenomena from residual gases. Such developed technique allows to follow process of the deposition, as well as to define the efficiency of active materials.

2. EXPERIMENTAL DETAILS

2.1. Experimental set-up

The samples of thin metallic silver films and films of barium getter (mixture of the $BaAl_4$ alloy and nickel powder) were prepared by thermal evaporation method. Glass of the Menzel-glaser (Germany) with thickness of 1 mm and area of 13 mm ×13 mm was used as a substrate.

The principle scheme of a vacuum device is shown in Fig. 1. The vacuum chamber has a volume of 0.2 m^3 and it is equipped with pump combination, consisting of a rotary vane pump (RP) and turbomolecular pump (TMP).

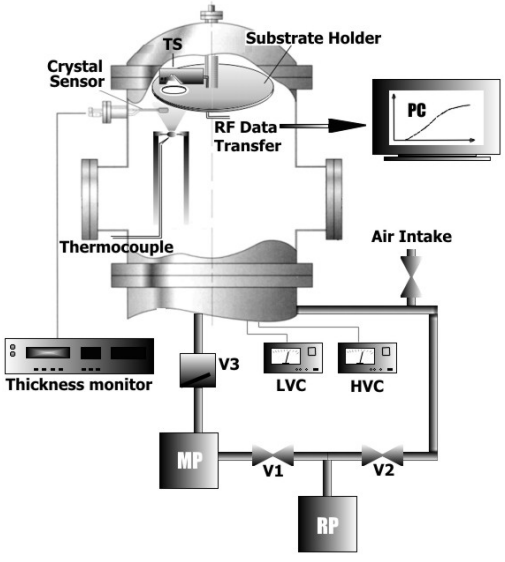

Fig. 1. Experimental set-up of the vacuum coater: PC – personal computer, V1, V2, V3 – valves, TS – transmittance sensor, LVC and HVC – low and hight vacuum controller

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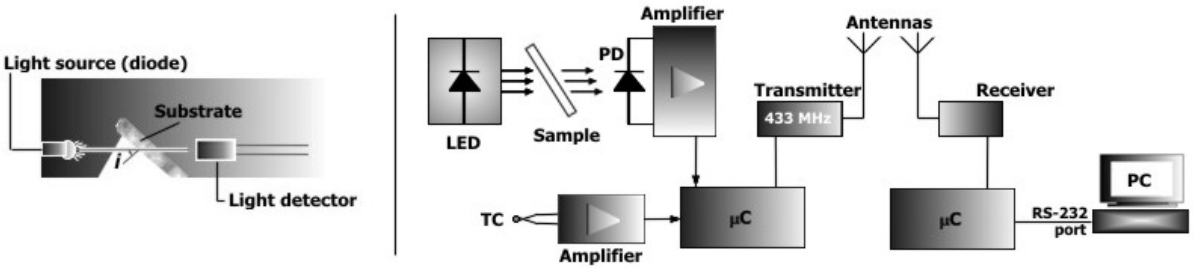

a b

Fig. 2. Principal (a) and electrical (b) scheme of optical transmittance sensor, for the in-situ measurements: LED – light-emitting diode, PD – photodiode, TC – thermocouple, μC – microcontroller

The base pressure of 2.5×10^{-3} Pa after a pumping time of 1 h was achieved. Pressure variation was controlled by Ar gas with a purity of 99.999 %. Deposition rate varied between 0.5 nm/min – 50 nm/min.

Optical transmission measurements in the chamber during the film growing process were performed to follow the process of deposition and residual gas adsorption. Evaluation of the optical transmittance in time scale was performed by using the transmittance sensor (TS), equipped with the wireless RF data transfer. The results of optical transmission were displayed in real time by the program based on Visual Basic software package. The principal scheme of the transmittance sensor is shown in Fig. 2, a. One can see that the sensor consists of a light source (diode), film-substrate system and light detector (photodiode). An angle i of light incidence was 45°.

An electrical scheme of the transmission sensor is shown in Fig. 2, b. Analogical transmittance signals are converted to the digital signals by precision of 10 data bits. The system comprises a wireless 433 MHz transmitter, which is operative to transmit coded signals by Manchester code format. A receiver is then used for recognition of the transmitted "information" signal. The received RF signal then is processed by a microprocessor, which inputs data to the computer through RS-232 port. The program based on Visual Basic software package enables monitoring of the results of measurement graphically and saving data.

The additional use of the quartz crystal thickness monitor (Quartz Microbalance-331) during the film growth in the chamber allowed thickness control of the metallic films.

Dependence of the photometric data of the film-substrate structure on the wavelength was performed by an ex-situ optical set-up. Reflection and transmittance spectra for the obtained thin Ag films were measured by a spectrometer FO-1 (EUROLAB, Russia, operating range 364 nm – 750 nm) and photo spectrometer Avantes (AvanSoft, Netherlands, operating range 200 nm – 1100 nm) respectively.

2.2. Experimental procedure

When a beam of radiation of specific wavelength impinges on a substance, the energy of the incident beam may be changed by the following three processes: reflectance, transmission and absorption. These processes are connected with each other:

$$R + T + A = 1, \tag{1}$$

where R is the reflectance coefficient, T is the transmission coefficient, A is the absorbance coefficient.

When light radiation is incident on a layer of thickness d with single surface reflectance coefficient R and absorption coefficient α in the substance or film, the relationship between R, α and the transmission T is given by [5]:

$$T = (1 - R)^2 e^{-\alpha d}. \tag{2}$$

In order to calibrate the optical transmittance system for the in-situ measurements, series of the ex-situ experiments were performed with Ag films.

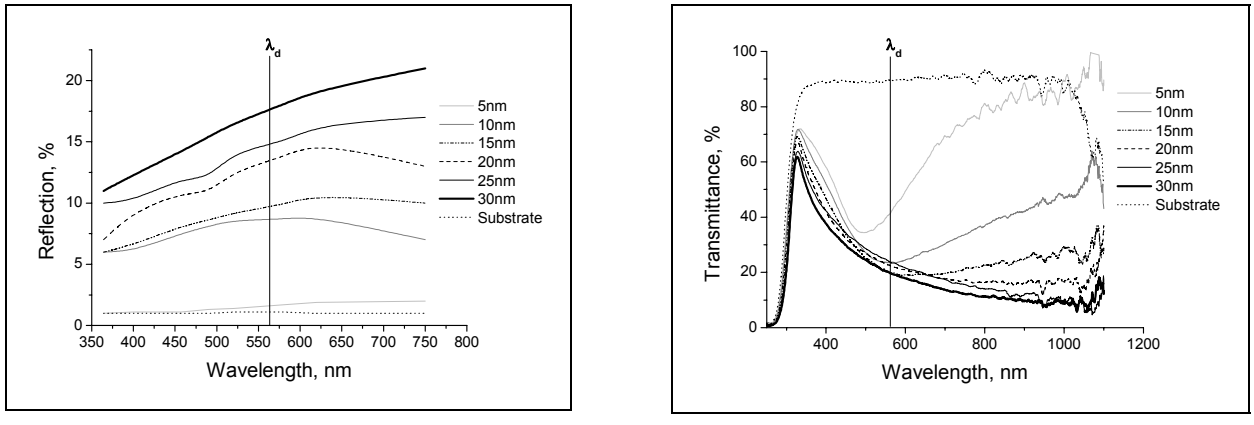

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Fig. 3. Reflection (a) and transmission (b) spectra for the Ag films on glass substrate in dependence on the wavelength (small thickness range 5 nm – 30 nm). λ_d indicates the wavelength of the in-situ transmittance detector

The main idea was to calculate the light absorption coefficient for the films of different thicknesses from the transmittance and reflectance spectra. The calculations were done for the particular wavelength of light source of transmission sensor ($\lambda_d = 565$ nm) and the absorption coefficient was found from equation (2):

$$\alpha(\lambda_d) = 1/d \ln[(1 - R(\lambda_d))^2 / T(\lambda_d)]. \quad (3)$$

The main results of optical constants defined by ex-situ measurements and calculations were compared with the results of the in-situ measurements and the calibration curves for Ag films were obtained, as it will be shown in the next sections.

3. RESULTS AND DISCUSSIONS

3.1. Ex-situ measurements of thin Ag films

Ag films with thickness between 5 nm and 130 nm were deposited on glass substrates in order to analyze the optical properties in dependence on the film thickness. Dependence of the photometric data (reflection and transmission) on wavelength is shown for obtained "thin" 5 nm – 30 nm Ag films in Fig. 3. The uncoated substrate shows an absorption edge in UV spectral region at a wavelength of 320 nm (Fig. 3, b).

3.2. Calibration of optical transmittance (in-situ) sensor

The spectral distribution of the light source of the optical sensor was determined by Avantes spectrometer software and it is shown in Fig. 4. The peak in spectra shows the wavelength of light diode and it's equal to $\lambda_d = 565$ nm.

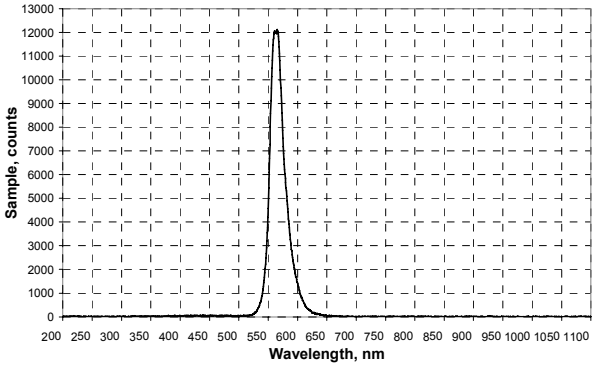

Fig. 4. The spectral distribution of the light source of the optical sensor

The vertical line (in Fig. 3) noted as λ_d indicates the typical wavelength of the light source employed in the in-situ measurement system. One can see, the resultant transmittance of the Ag film-substrate varies significantly in the region of small thicknesses (5 nm – 30 nm) and the chosen wavelength ($\lambda_d = 565$ nm) can be used for these measurements enabling high sensitivity of the system.

So, all the successive calculations will be given for the particular wavelength ($\lambda_d = 565$ nm) of the transmittance sensor light source. The absorbance A for Ag films of different thicknesses was calculated from the transmittance T and reflectance R spectra by the equation (1). The results are shown in Fig. 5.

It should noted that absorbance increases with increase of the film thickness as well with the coverage of the substrate surface, like it was detected experimentally in [6].

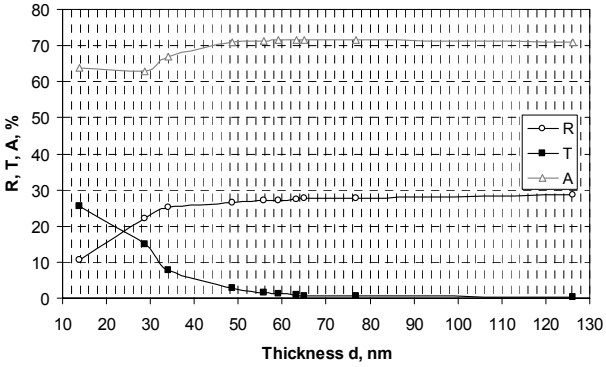

Fig. 5. Optical reflectance, transmittance and absorbance dependence on Ag film thickness ($\lambda_d = 565$ nm)

The relationship between the in-situ and ex-situ measurements is shown in Fig. 6 by calibration curves defined for the Ag films. The calibration results show that the transmittance sensor ($\lambda_d = 565$ nm) equipped with RF data transfer is most sensitive in a region of small thickness of deposited films (5 nm – 50 nm).

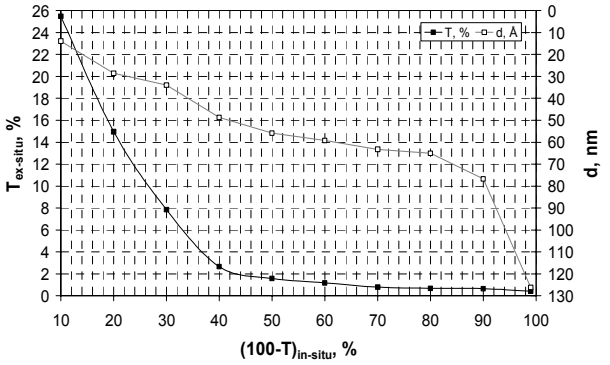

Fig. 6. Calibration curves for Ag films (thickness d = 5 nm – 130 nm) of transmittance sensor ($\lambda_d = 565$ nm)

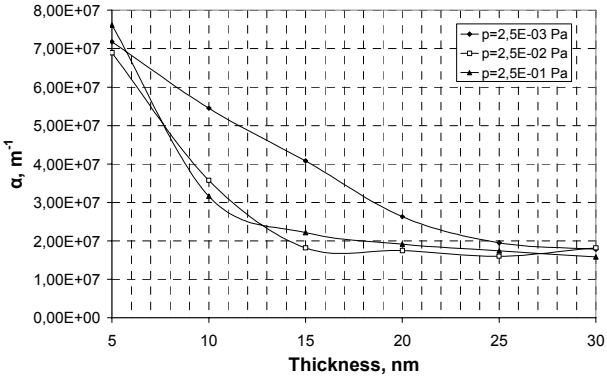

Fig. 7. Dependence of the absorption coefficient on thickness for Ag films ($\lambda_d = 565$ nm)

Fig. 7 illustrates variation of the calculated optical absorption coefficient α versus thickness d measured at the different pressure during Ag thermal evaporation (deposition rate is 0.5 nm/min). One can see that changes in optical properties can be followed by the designed in-situ measurement system.

3.3. Analysis of adsorption processes during thermal evaporation of barium getter

The developed optical sensor was applied to follow kinetics of the gas adsorption from the ambient during (or after) Ba getter film deposition (Fig. 8). The analysis of transmittance relaxation due to adsorption of residual gases was done for the same thickness of barium films (d = 100 nm) in different pressure ranges (2.5×10^{-1} Pa – 2.5×10^{-3} Pa).

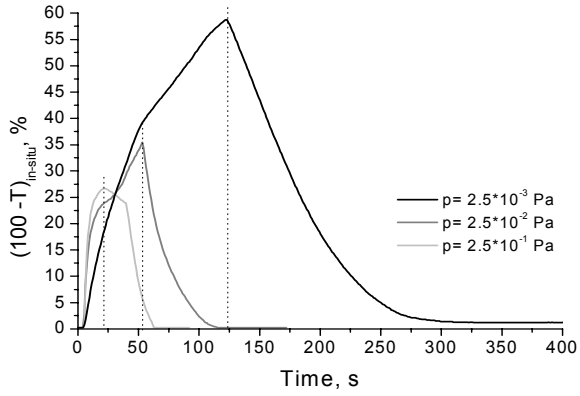

Fig. 7. Optical transmittance of the Ba getter-glass system during evaporation of getter material and adsorption of residual gases

It was found that the typical time for the detected transient process (getter pumping) was 50 s – 150 s and it was strongly dependent on the residual gas pressure. It is known [2], that once the barium getter has been released, the sorption (pumping) process starts and the total pressure of residual gases decreases. The variation of pressure in time is given by equation:

$$p(t) = (p_i - Q/S) \times \exp[-(S/V)t] + Q/S\,, \qquad (4)$$

where: p_i is the initial pressure, V is the volume, S is the pumping speed of the barium film, Q is the outgassing rate. The exponential term of the equation was estimated from the optical measurements and the indicator of the exponents, describing efficiency of the getter (S/V) was found to be 0.0164 1/s, 0.0522 1/s and 0.09872 1/s and dependent on the corresponding pressure during evaporation (2.5×10^{-3}, 2.5×10^{-2}, and 2.5×10^{-1} Pa).

4. CONCLUSIONS

1. The optical in-situ method with a wireless data transfer was developed to control kinetics of growth of the films (Ag, Ba getters) and adsorption phenomena from the residual gas.

2. The calibration results show that the transmittance sensor (λ_d = 565 nm) equipped with a RF data transfer is most sensitive in a region of small thicknesses of the deposited films (5 nm – 50 nm).

3. The developed technique operating at 433 MHz enables to control influence of the process parameters: residual gas pressure (10^{-1} Pa – 10^{-3} Pa), deposition rate (0.5 nm/min – 50 nm/min) and others.

4. The optical transmission kinetics allowing to follow growth of the getter films, enables one to follow process of the deposition, kinetics of adsorption of residual gases, as well as to define numerical values of the efficiency of getters.

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