In situ analysis of adsorption process from residual gases during thin film deposition

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Abstract. In this work we present the developed experimental technique as well as results of optical control of adsorption processes during thin film deposition. Different metallic films: (silver) as a model material and barium getter films were studied. Thermal evaporation method has been used to deposit thin metallic films and films of barium getter on glass substrates. Kinetics of the optical absorbance of the growing film was registered in situ measuring transmission of the film-substrate structure. These measurements were done in parallel to the ex-situ absorption (UV-VIS) and reflection spectra as well as XRD analysis. Such complex measurements enabled us to follow adsorption process from the residual gases during thermal evaporation as well to control adsorption process after the evaporation.

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. 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.

Development of optical method to control kinetics of growth of the films and adsorption phenomena from residual gases is the aim of this study.

2. Experimental set-up
Thin metallic Ag films and films of pure barium (actual gettering material) were deposited on glass substrates using thermal evaporation method. In the case of barium evaporation, the mixture of the BaAl₄ alloy and Ni powder was used that was placed in to a crucible. In order to release pure barium a necessary reaction between Ni and Al must occur at 800 °C. The equation of such reaction is given by: BaAl₄ + 4Ni → Ba↑ + 4NiAl. The principle scheme of a vacuum device is shown in figure 1. The vacuum chamber has a volume of 0.2 m³ and is equipped with a pump combination, consisting of a
rotary vane pump (RP) and turbomolecular pump (TMP). The base pressure of $2.5 \times 10^{-3}$ Pa after a pumping time of 1h was achieved. Pressure variation during evaporation was controlled by Ar gas with a purity of 99.999%.

Glass of the Menzel-glaser (Germany) with a thickness of 1 mm and area of 13×13 mm was used as a substrate. Preparation of the substrates included: boiling in dimethylformamide (DMF) solvent (about 30 min.); soaking in clean DMF; boiling in acetone solvent (about 10 min.); dehumidifying by air or nitrogen.

In-situ control of the deposited metallic layers was possible employing optical transmission measurements in the chamber. The transmittance sensor (TS) (equipped with wireless RF data transfer) allowed evaluation of the optical transmittance of the film-substrate system during the film growing process. The principal scheme of the transmittance sensor, which consists of a light source (diode) and light detector, is shown in figure 2.

The additional use of the Quartz Microbalance–331 device in the chamber allowed thickness control of the metallic films. Typical thicknesses of the Ag films were 5 – 130 nm, and barium getters – 100 nm. Deposition rate varied between 0.5 – 50 nm/min.

3. Results and discussion

To calibrate optical transmittance system for the in-situ measurements, series of the ex-situ experiments were performed with Ag films and the main results were compared with the optical constants defined by the in-situ technique.

3.1. Dependence of the Ag photometric data on wavelength (ex-situ measurements)

Ag films with thickness between 5nm and 130nm were deposited on glass substrates in order to analyze the optical properties in dependence on the film thickness. Base constant pressure of $2.5 \times 10^{-3}$ Pa was achieved after a pumping 1h. Dependence of the photometric data on wavelength and film thickness was performed by 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 – 750 nm) and photo spectrometer Avantes (AvanSoft, Netherlands, operating range 200 – 1100 nm) respectively. These spectra are shown for “thin” 5-30 nm Ag films in figure 3. (The vertical line noted as $\lambda_d$ indicates the wavelength of the light source employed in the in-situ measurement system).

The uncoated substrate shows an absorption edge in the UV spectral region at a wavelength of 320 nm (figure 3b). One can see, the resultant transmittance of the Ag film-substrate system varies significantly in the region of small thicknesses (5-30 nm) and the chosen wavelength ($\lambda_d = 565$ nm) for in-situ measurements can be used enabling high sensitivity of the system.
3.2. Calibration of the optical transmittance (in-situ) sensor
The spectral distribution of the light source of the optical sensor was determined by Avantes spectrometer software. The relationship between the in-situ \((100-T)_{in-situ} = f(d)\) and ex-situ \((T_{ex-situ} = f(d))\) measurements is shown in figure 4 where calibration curves were measured for the Ag films by two methods. The calibration results show that the transmittance sensor \((\lambda_d = 565 \text{ nm})\) equipped with RF data transfer is most sensitive in a region of small thickness of deposited films \((5 – 50 \text{ nm})\). The calculations of optical absorption coefficient was performed from the reflection – R and transmittance – T spectra using an equation:

\[
\alpha = \frac{1}{d} \ln\left(\frac{(100-R)^2}{T}\right)
\]

Figure 5 illustrates variation of the optical absorption coefficient versus thickness \(d\) measured in-situ during Ag thermal evaporation (deposition rate is 0.5 nm/min) at the different residual pressure. The absorption increases with the increase of the film thickness as well with the coverage of the substrate surface, like it was detected experimentally in [5]. One can see that changes in optical properties of the film-substrate system can be followed by the designed in-situ measurement technique.

3.3. Phase composition of bulk getter and analysis of adsorption process during Ba film evaporation
Phase composition of the bulk Ba getter (before evaporation) has been investigated using X-ray diffractometer DRON-3 (Russia). X-ray tube with Cu-K\(_\alpha\) anode was used as X-ray source, operating at 30 kV voltage and 30 mA current. Anode radiation wavelength was \(\lambda = 0.154178 \text{ nm}\). The phase identification results are shown in figure 6. According to the X-ray analysis the evaporable Ba getter consists of compounds including tetragonal BaAl\(_4\) phase, cubic Ni phase and tetragonal AlNi phase.

The pure Ba films (evaporated) were produced of the same thickness \((d = 100 \text{ nm})\) at 3 different, Ar controlled residual pressures inside the chamber. The developed optical sensor was applied to
follow kinetics of the gas adsorption from the ambient during (or after) Ba getter film deposition (figure 7). (The vertical lines indicate the end of evaporation process). The analysis of transmittance relaxation due to adsorption from residual gases was done and it was found that typical time for the detected transient process (getter pumping) was 50 – 150 s and it was strongly dependent on the residual gas pressure (figure 7). 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: $p(t) = (p_i - Q/S) \times \exp[-(S/V)t] + Q/S$, where $p_i$ – initial pressure, $V$ – volume, $S$ – pumping speed of the barium film, $Q$ – 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 ($2.5\times10^{-3}$, $2.5\times10^{-2}$, and $2.5\times10^{-1}$ Pa).

![Figure 6. X-ray diffraction pattern of the Ba getter (bulk material).](image1)

![Figure 7. Kinetics of the optical transmittance of the Ba film-glass system during evaporation of the bulk getter material and adsorption from residual gases.](image2)

4. Conclusions
The optical in-situ method was developed to control kinetics of growth of the films and adsorption phenomena from the residual gas. The calibration results show that the transmittance sensor ($\lambda_d = 565$ nm) equipped with a RF data transfer is most sensitive in a region of small thicknesses of the deposited films (5 – 50 nm). These measurements enable to control influence of the process parameters: residual gas pressure ($10^{-1}$ – $10^{-3}$ Pa), deposition rate ($0.5$ – $50$ nm/min.) and others. The optical transmission kinetics allowing to follow growth of the Ba 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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