

Studying of kinetic growth of organic thin films

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Materials

ABSTRACT

Purpose: of this paper: Studying of growth kinetic of organic thin film prepared by vacuum thermal evaporation technology.

Design/methodology/approach: Applying of quartz crystal microbalance to thickness control of organic thin films deposition process.

Findings: Results of this issue suggesting that the kinetics of organic thin films is depending of current flowing through the crucible (crucible temperature).

Research limitations/implications: Kinetics of vacuum evaporation of thin film is different from that of inorganic thin films during the growth process.

Practical implications: The means of connect the quartz crystal microbalance MSV 1843/AB with vacuum chamber, function and means of thickness and deposition rate measuring has been described. This scientific paper include also description of researching results of kinetics of organic and metallic thin film evaporation process by MSV 1843/AB quartz crystal microbalance and verification these results by comparing them with results from other measuring techniques.

Originality/value: Controlling thickness of thermally evaporated organic thin film during the film growth process.

Keywords: Engineering polymers; Thin films; Deposition rate

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1. Introduction

Thin films of organic low weight materials have been of great importance for their optoelectronic properties making them suitable for photovoltaic and optoelectronic applications since many years [6,7,15]. There are many deposition methods

of organic thin film, among them the vacuum thermal deposition sometimes called physical vapour deposition has been widely used. Structure, morphology and properties of thin films are found to be dependent on deposition conditions and on the substrate used [14]. Thin films are deposited mainly on transparent substrates made of glass or quartz, especially while optoelectronic or photovoltaic devices are concerned. Thickness

of the thin film is of great importance because the thinner film is the stronger influence of transition interface between the substrate and a film. In case of optoelectronic or photovoltaic applications too thick film can influence optical or electrical parameters of a structure [4,6,11].

Then, monitoring of the film thickness during its growth process is very important and the deposition can be interrupted when the film thickness required for a film role in optoelectronic structure is achieved. This technique is widely used in technological processes when thin film layered structures of inorganic semiconductors are prepared. The aim of this paper is to present mounting quartz crystal monitor inside the deposition chamber, which is placed at the same distance from the source as the substrate, near to it and verify how efficient such film thickness monitoring is while organic thin films are prepared [2,3,4,9,12].

2. Experimental

Thin films of organic compounds, were deposited by vacuum thermal evaporation under vacuum 10^{-5} hPa on glass substrate at room temperature.

The experimental setup for vacuum evaporation consists of vacuum chamber, system vacuum pumps and control panel. The scheme of evaporation setup is presented in Fig. 1.

Vacuum chamber is closed by glass shade standing on the background by rubber gasket.

There are substrate holder, wolfram crucible with supply connections, and shutter inside of the chamber. The shutter is located between source and substrate and is used to cut off vapour stream from impinging onto the substrate [2,8].

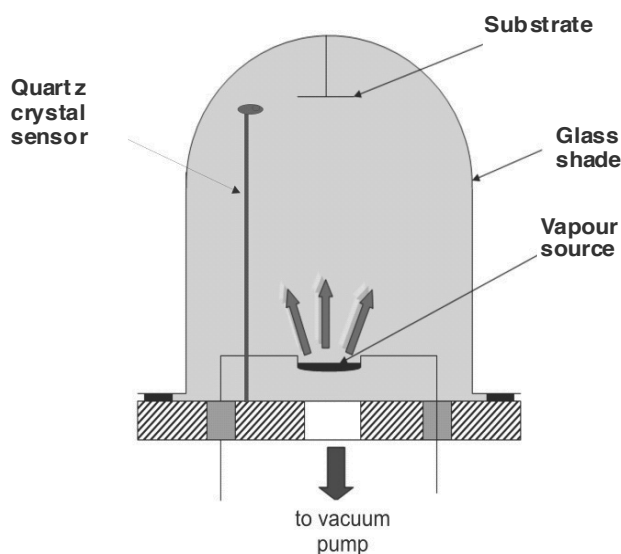


Fig. 1. Vacuum chamber with crystal sensor

The evaporation process starts after relevant vacuum in the chamber has been attained. This process can be divided into three steps [1,2,3]:

- sublimation of source generated by high temperature
- transport of vapour towards the substrate
- vapour condensation and thin film growth on the substrate (substrate may be heating to 200-300°C for better adhesion).

The sublimation is a process of solid – to – vapour transformation of the source material, and sublimation for unit of surface area is associated with temperature, pressure, and atomic mass of the material by Equation 1 [2,6].

$$S = 6 \cdot 10^{-28} p \cdot M / T [\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}] \quad (1)$$

Where:

p – pressure [hPa]

M- atomic mass [kg]

T- temperature in absolute scale

The vapours of source material are transported towards the substrate. Molecules of transported material impinge onto the substrate and are absorbed on it. They move within the adsorption layer to incorporate to growing film. If their energy is too high they can come back to the vapour to be removed from the chamber by means of the pumps. This technology is used to prepare thin films with controlled chemical composition [2,3,13].

Thickness of a growth thin film can be determined by interferometric method after its deposition process [5,10].

However in our work quartz crystal microbalance MSV1843/AB (Fig.2b) was used to monitor the thickness of a film during its growth process. The idea of film thickness monitoring takes advantage of parallel a film deposition onto the sensor plate with film growth on the substrate. The crystal sensor is located into vacuum chamber near the substrate so that distance from the source to the sensor and substrate is the same (Figure 2) [10].

The films growing on the sensor surface change the oscillation frequency of the sensor plate (Fig.2a). Equation 2 relates mass on the sensor surface (Δm) with sensor frequency (f) [5,10]:

$$\Delta m = C \Delta(1/f) = C \Delta t \quad (2)$$

Where:

$\Delta(1/f) = \Delta t$ is time period.

Mass increase Δm can be expressed by film area (F), thickness of film of material deposited on sensor surface (Δd) on density of deposition material (ρ) (Equation3) [5,10].

$$\Delta m = F \cdot \rho \cdot \Delta d \quad (3)$$

Then the increase of thin film thickness shows Equation 4 [10].

$$\Delta d = \Delta m / (F \rho) = C \Delta t / (F \rho) \quad (4)$$

By replace $K= C/F$, Equation 5 show increase of thin film thickness [10]

$$\Delta d = (K/\rho) \cdot \lambda t \quad (5)$$

Constant K characterizes sensor come (Equation 6):

$$K \approx 4,42 \cdot 10^6 \text{ g/cm}^2 \text{ 2sec} \quad (6)$$

To avoid any temperature influence on sensor, it must to have a minimal value of coefficient of thermal expansion (resonance frequency of sensor is proportional to temperature).

Therefore in this case quartz sensor has a indent $35^\circ 10'$. This shape is assuring constancy of frequency in temperature spectrum of $20\text{-}60^\circ\text{C}$ [5].

Using quartz crystal microbalance MSV 1843/AB (Fig. 3) growth kinetics of thin films of organic compounds: Perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA), Titanyl - phthalocyanine (TiO-Pc), Nickel - phthalocyanine (Ni-Pc) were studied.

During the evaporation process the values of thickness growth and deposition rate were measured and shown by graphs.

These figures were demonstrated deposition rate changes and thickness growth of layers versus time for selected current flowing through the crucible. The recorded thickness and deposition rate values versus time are shown in Figs. 3-8.

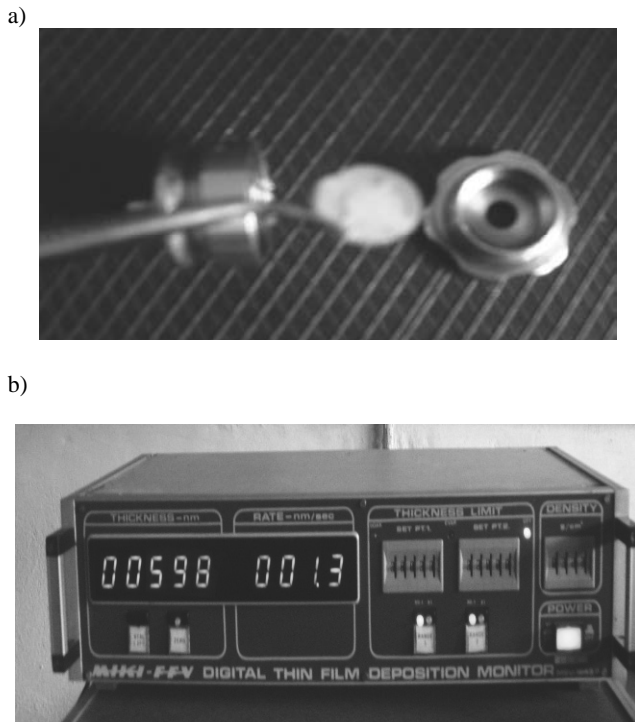


Fig. 2. Quartz crystal microbalance MSV 1843/AB, a) front panel, b) quartz sensor

3. Results

Thickness changes versus deposition time for PTCDA film evaporated with currents 40A, 45A and 50A are shown in Fig. 3.

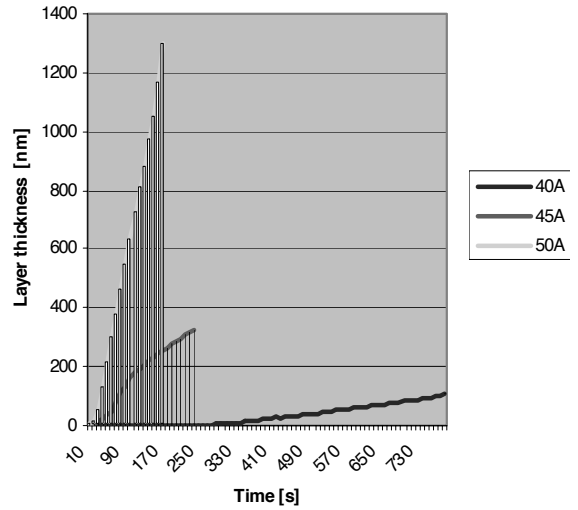


Fig. 3. Thickness changes of PTCDA thin films in time

As can be seen in this figure that the film thickness increases linearly for $I=40\text{A}$, while for 45A and 50A being non linear.

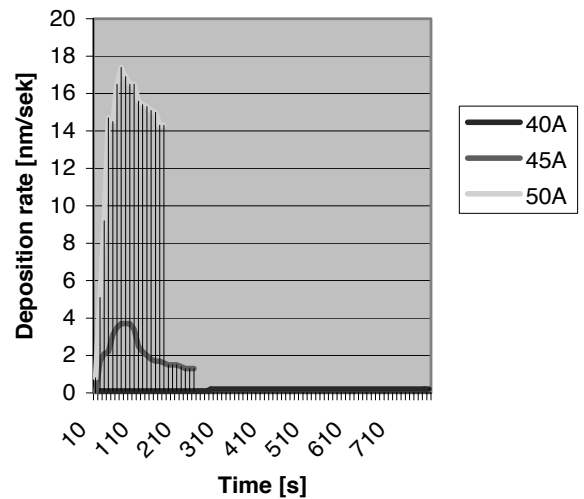


Fig. 4. Deposition variations changes of PTCDA thin films in time

Changes of deposition rate during the deposition process are shown in Fig. 4.

For PTDCDA graphs line demonstrates deposition rate variation of 40A which indicate nearly constant deposition rate.

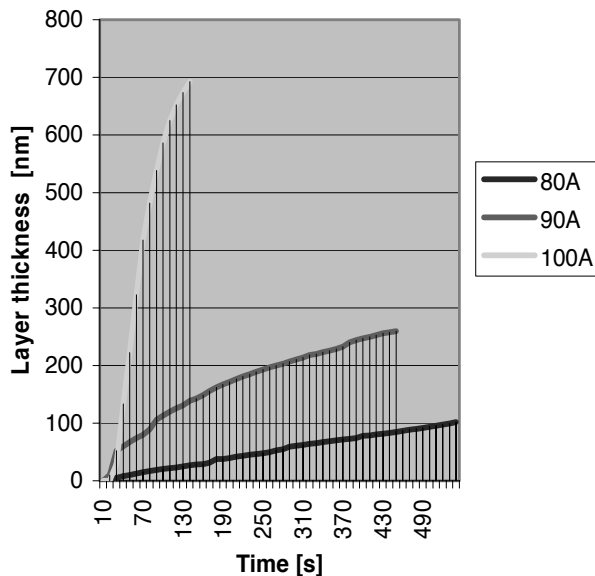


Fig. 5. Thickness changes of TiO-Pc thin films in time

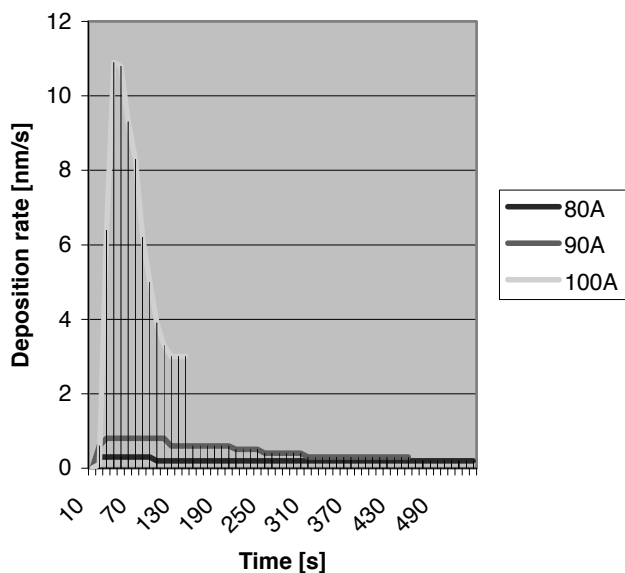


Fig. 6. Deposition rate variations of TiO-Pc thin films in time

With increasing current the deposition rate becomes non linear function of time.

It is seen in Fig. 4 that for currents of 45A, and 50A that deposition initial stage of evaporation process deposition rate undergoes abrupt increase followed by abrupt decrease down to nearly constant value after of 200s

Graphs in Figure 5 demonstrate thickness changes of TiO-Pc thin films versus time for selected current intensity flowing through a crucible.

Thin films of TiO-Pc were prepared at higher currents than PTDCDA ones. The measurements were taken for current intensities equal to 80A, 90A, 100A.

For 80A TiO-Pc thin films thickness increase has low constant value and the layer growth is nearly linear function.

Increase of current flowing through the crucible effects that the graph lines which representing thickness increasing aren't linear and the gradient of these lines becomes higher.

Thickness increasing for 90A reveals sharp increase of thickness in first period of process. After that increasing thin film thickness down to steady growth.

The rapid increase in first period of process is more abrupt for 100A than for 90A.

Graph in Fig. 6 shows deposition rate variations of thin films versus time for selected current intensities of crucible power supply for TiO-Pc.

In the case of 80A current deposition rate is low and rather linear. It is charactering of deposition rate behavior for 90 and 100A that its strong increase is observed in the initial stage with steep decline with time to constant value.

Similarly like for TiO-Pc the measurements were taken for current intensities equal to 80A, 90A and 100A.

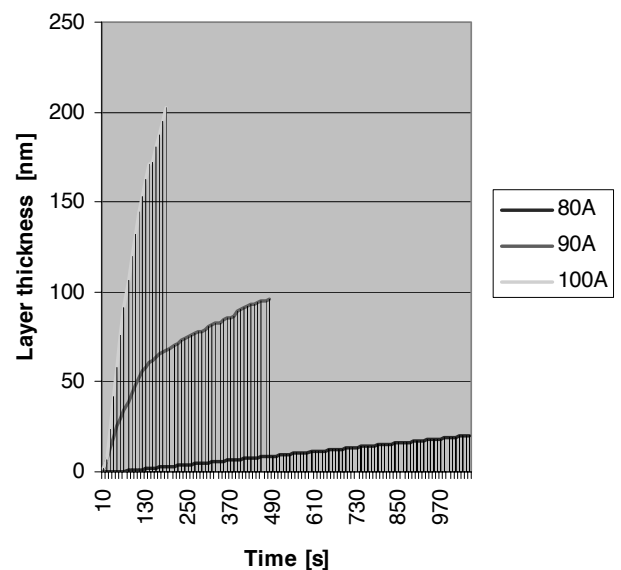


Fig. 7. Thickness changes of Ni-Pc thin films in time

The thickness variations during the Ni-Pc thin film deposition process are shown in Figure 7.

Ni-Pc thin film growth is steady for current flowing through the crucible equal to 80A what is demonstrated by straight line.

When current intensity is 90A thickness increase of Ni-Pc thin film is nonlinear with strong gradient and their values were equal to 100 nm.

For the 90A growth is faster and isn't linear function. Thin film thickness growth of Ni-Pc for 100A is non linear with strong gradient.

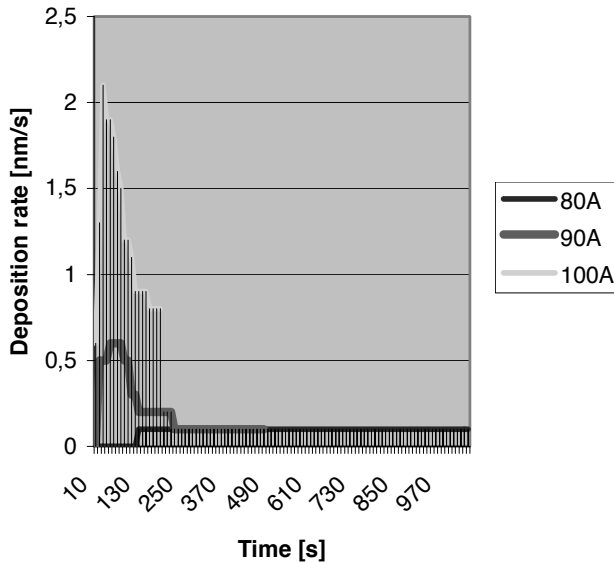


Fig. 8. Deposition rate variations of Ni-Pc thin films in time

Deposition rate of Ni-Pc (Fig. 8) is slow and constant for 80A.

When 90A current was used the deposition rate reveals rapid increase during the initial period of deposition process. Then the deposition rate goes down to constant value. For 100A current these variations are more pronounced.

Surface morphology of researched as-deposited films was examined with atomic force power (AFM).

The growth of all as-deposition thin films have appeared to be columnar, but the grain size is seen to diminish as the current intensity decreased.

As an example AFM pictures taken on PTCDA thin films are illustrated in Fig. 10 a,b,c for current of 40A, 45A, 50A, respectively.

For comparison studies of thin film growth were made on silver thin films. It is seen in Fig. 11

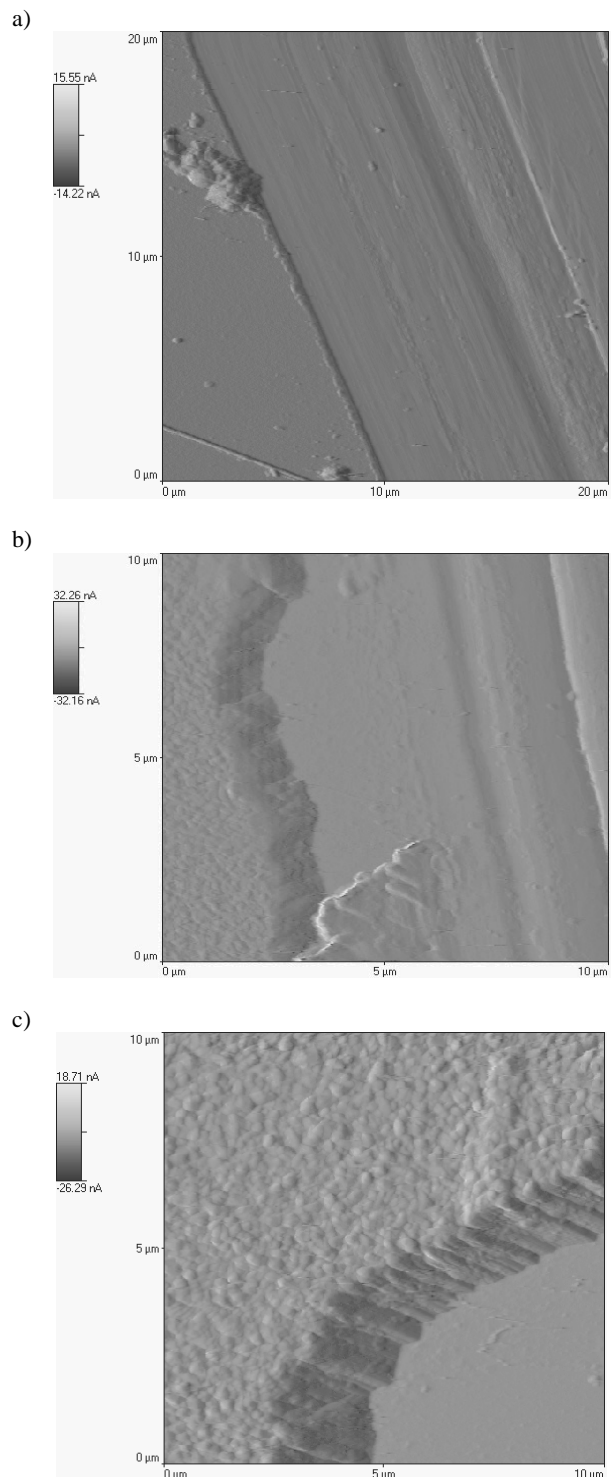


Fig. 10. AFM images of PTCDA layers surfaces for current of power supply: a) 40A, b) 45A, c) 50A

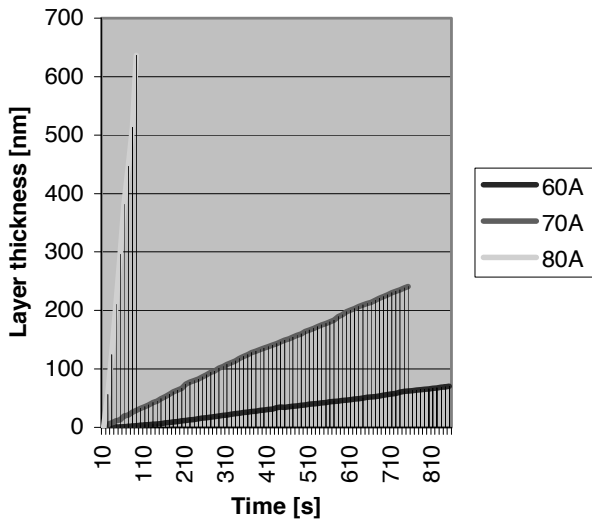


Fig. 11. Silver layer thickness changes in time for different current flow through the crucible

In case of silver thin films for current intensity of crucible power supply 60A thickness increase is low and constant.

For higher values of current of 70A, 80A lines performing thin film growth is linear.

As for the organic thin films for the silver thin films the course of deposition rate was examined. Changes of deposition rate during the deposition process are shown in Fig.12.

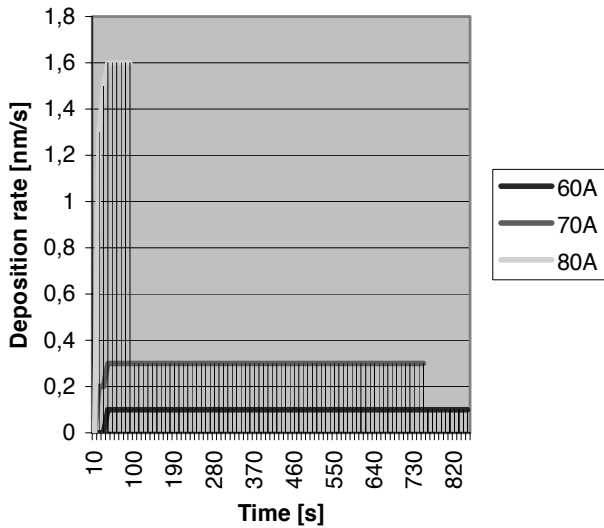


Fig. 12. Deposition rate variations of silver thin films in time

Deposition rate of silver thin films after heating crucible process due to current flowing through the crucible appears to be linear for 60A, 70A and 80A currents.

AFM pictures taken on silver thin films grown with different currents are given in Fig. 13.

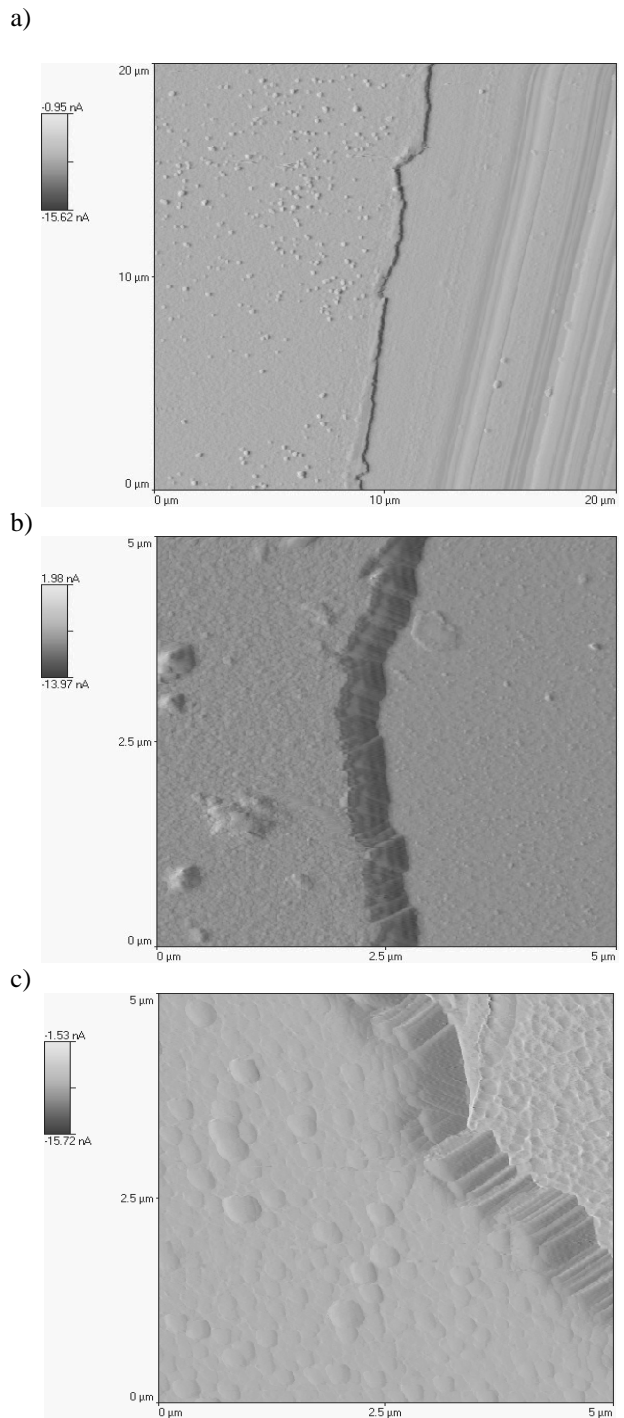


Fig. 13. AFM images of silver layers surfaces for current of power supply: a) 70A, b) 80A, c) 90A

Like in case of organic materials for silver thin films visible is columnar growth of thin films and the size of grain diminishes with current intensity decreased. (Figs.10 b,c).

4. Discussion

Analyzing reordered results can divide the organic thin film deposition process into three steps. The first initial one is characterised by abrupt film thickness increase during same 100s. After that there is decline in deposition rate resulting in steady constant value. Essentially, the three stages are more or less comparable but gradients associated with them appear to be the higher for higher intensity was.

Though for the lowest currents for each organic film one can see constant deposition rate confirmed by linear film thickness increase with time. For higher currents the initial increase is more abrupt for higher currents. Similarly the steady deposition rate attained in each process has appeared to be the higher for higher current intensity was.

While comparing kinetics of organic thin film growth with silver thin film one, it is seen that initial stage of metal film deposition is connected with crucible heating process, with attains after short time constant steady level. There is no saturation effect of film deposition growth in case of silver, and the film deposition rate is proportional to the current.

While comparing deposition rates recorded with MSV-1843/AB with results obtained by interferometric or AFM method, one can see rather good their coincidence in case of silver thin films within 10% (Table 1).

Table 1. Performance of layers thickness measurement results obtained by different techniques for silver

Current	Value of MSV 1843/AB research result [nm]	Value of interferometer research result [nm]	Value of AFM research result [nm]
Silver			
40A	70.5	64.5	-
45A	240.9	248.2	260.8
50A	570.5	542.7	563.1

For organic thin films the discrepancy of results is observed which is attributed to organic thin films density estimates. They are thought to be too low and further examinations are needed (Table 2).

AFM pictures of organic and metallic thin films reveal rather similar morphology and columnar film growth model.

Table 2. Performance of layers thickness measurement results obtained by different techniques for organic compounds

Current	Value of MSV 1843/AB research result [nm]	Value of interferometer research result [nm]	Value of AFM research result [nm]
PTCDA			
40A	104.5	224.1	216.5
45A	328.4	467.3	451.9
50A	1299	1597.3	1522.5
TiO-Pc			
80A	101.6	228	-
90A	260	285.2	-
100A	692.7	824.8	-
Ni-Pc			
80A	20.1	75.0	-
90A	95.8	148.2	210.9
100A	202.6	422.6	446.2

5. Conclusions

Mounting inside the evaporation chamber quartz crystal microbalance monitor MSV 1843/AB makes possible controlling and monitoring deposition process of organic thin films.

The results obtained are rather qualitative in character. Additional studies on organic thin film are needed for qualitative character of measuring process.

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