ULTRA-THIN ORGANIC LAYER STACKS – A NEW VACUUM DEPOSITION SOLUTION

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A precise system for a discreet, successive deposition of ultra-thin layers by individual polyimide (PI) precursors was worked out. The discontinuation of the different molecular flows by a controllable closure of their sources allows for the build – up of a multi-layer (stack) system with precursor layers of programmed thickness. The method renders a possibility for creating laminar molecular fluxes which is a guarantee for the production of films devoid of defects.

By means of controlling the evaporation time of the individual sources varying from microseconds to seconds a control of the chemical composition of the organic layer (thickness < 100 nm) is made possible and hence its micromechanical, electrical and optical parameters.

Keywords: polyimide, thin organic layer, vacuum deposition

1. INTRODUCTION

Obtaining ultra-thin organic layers (thickness < 100 nm) raises a special interest with regard to modern optoelectronics, molecular optics, microsensorics [1-3]. PIs are known to have low dielectric, excellent anti-corrosion and wear - resistant properties [4]. The role of PI as an interlayer in polymer electroluminescence devices [5, 6] is also well-known: firstly, as a diffusion barrier, the PI layer prevents the inward diffusion of impurities originating from ITO. Secondarily, the PI layer acts as a blocker of hole injection and causes a balanced recombination of holes and electrons.
Also, the formation of such a type of layer is in itself a technological challenge due to the significant problems stemming from the discrepancies between the organic nature of the molecules and the principles of physical vapour deposition. Organic materials of the PI class which by polycondensation of their precursors on the substrate can form such films belong to this group of thin – layer materials.
PI films are conventionally prepared from polyamic acid solution (the precursor of PI) by coating on a substrate and transformation to the PI through thermal or chemical dehydration. PI thin layers can be obtained by ionized cluster beam deposition (ICB) [7], sputtering [4,8] and vapor deposition [9,10]. The ICB technique is employed to fabricate crystalline PI layers. Sputtering is not successful in producing well identified PI materials. The PI layers obtained through a process utilizing the co-evaporation of the dianhydride and diamine precursors are amorphous and randomly chain oriented. But there are some difficulties in securing the correct stoichiometry to avoid incorporating excess precursor. There is also some

competition from the unwanted, iso-imide reaction. It is proposed that controlled, alternating exposure to the dianhydride and diamine with imidisation, after each deposition will provide optimal oligimide layers [11]. These would have strong film/substrate bonds based on carboxylate links.

We have developed such a new method for precise evaporation of both precursors of the PI - 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) and for formation of a stack from both precursors. The aim of the paper is to present the block diagram of the developed experimental device and to discuss the possibilities for creating ultra thin organic layers.

2. EXPERIMENTAL SET – UP

2.1. Design, possible variations of the constructive realization and advantages of the solution of choice

The developed system for simultaneous controllable evaporation from two sources represent an open loop system for automatic control designed to successively block either the first or the second source. There are two feasibly conceived ways for function to be effected:

a/ via a rotary motor and a disk with slots along the circle length fixed to its axis;

b/ by an electromagnet and a leverage system with a shaft with two shutters fixed to it and consecutively closing in a non-activated state of the electromagnet the first source and with the electromagnet turned on the other source.

The transition of the system from activated to normal condition is performed by means of a recurrent spring. Depending on the leverage system type it can be one with a step-by-step movement or with a rotation around an axis. The second variation of the lever system is of preference since it allows for a maximally light construction with very insignificant friction forces only limited to the area of the rotation point with preservation of its stability. These factors are very important for the reduction of the dispersed power of the electromagnet.

In the system developed the second approach was applied and especially its second variation because of the great advantages that it renders expressed as follows:

a/ a possibility for individual regulation of the times during which the corresponding sources are open depending on the requirements of the given experiment;

b/ a simple mechanical construction characterized with a low weight and small friction forces;

c/ small dispersed power which is basically released for a short time only at switching. During the other time there is no electric current through the electromagnet or the current is very small and only serving for maintenance and counteraction to the recurrent spring;

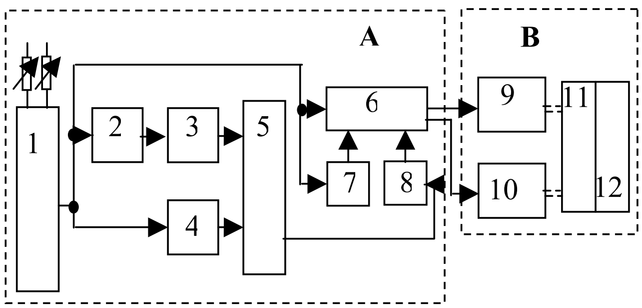
d/ there are no problems in the cooling of the electromagnet due to the low dispersed power which otherwise in the conditions of vacuum constitutes a problem. The fact that the open coil of the electromagnet is used also contributes to that;

e/ no problems are to be solved related to the vacuum realization in the case of a rotary motor in use which for reasons of better cooling is placed out of the recipient and only the disk with the slots is found inside it.

3. RESULTS

3.1. The block diagram of the developed experimental device and design of the individual blocks of the scheme

The developed experimental system for simultaneous controllable evaporation from two sources is basically composed of two parts: excutive electromechanics and control electronics. The block scheme of the system is presented in Fig. 1.



1. Base Generator
2. Invertor
3, 4. Differentiating stage
5. Pulse Generator
6. Differential Driver
7. Continvous Current Generator
8. Pulse Current Generator
9, 10. Electromagnet
11. Shaft
12. Shutter

Fig. 1 Block diagram of the experimental device: **A -** control electronics, **B -** excutive electro mechanics.

A. Control electronics:

- Basic Generator: it works as relaxation oscillator and starts to generate upon turning on the power of the system. It creates a signal of a rectangular shape with an option for regulation of the times separately both at a high and low level of its duty cycle voltage. In this way, the period of the generated signal and its duty cycle can be controlled in rather broad limits. These rich possibilities for regulation broaden the range of application of the system. This generator is effectuated on the basis of an integrated circuit of a 555 type timer.
- Invertor: produces a signal of a rectangular shape representing an inverted image of the output voltage from the basic generator. It is realized as a transistor stage.
- Differentiating stage 3: it produces short negative pulses from the output voltage of the invertor in each signal edge front from the basic generator. It is realized on the basis of an RC circuit.
- Differentiating stage 4: it produces short negative pulses in each back edge of the signal from the basic generator. It is realized also like differentiated stage 3 on the basis of an RC circuit.

- Pulse Generator: it works in monostable regime and produces a short pulse of a duration of about 35 ms any time there is an entry of differentiated pulses from the differentiating stages i.e. upon each switch of the basic generator from one state into the other. It is realized on the basis of an integrated circuit of the 555 type.
- Differential Driver: it represents a differential amplifier realized with powerfil transistors and is designed for direct control of the electromagnets constituting the executive electromechanics. At a high level of the signal from the basic generator the upper output of the driver is activated and at a low level of the input signal its lower output is activated.
- Continuous Current Generator (Generator of constant current): it determines the amount of the current flowing through the electromagnet for switching of the shutters at a high level from the outlet of the basic generator so that it could counteract to the spring aiming incessantly to draw back the shaft supporting the shutters to the initial state. The current in this case is about 0,12 A and the generator it self is based on a transistor.
- Pulse Current Generator: it is only turned on at the time of the switch of the signal from the basic generator from one state into the other for about 35 ms determined by the duration of the pulses formed by the pulse generator, the generated pulses being transmitted to the differential driver with an amplitude of about 0,6 A. At a high level of the output voltage from the basic generator the current pulses from the upper output of the driver are transmitted to electromagnet 9 and at a low level of the signal from the basic generator to electromagnet 10. The generator of pulse current is realized on the basis a powerful transistor.

B. Excutive electromechanics:

- Electro-magnet 9: it is used for the shifting the shaft with the shutters from the initial state to an activated state upon the current flow through its coil.
- Electro-magnet 10: it is used for damping the transient process being aimed at its quicker fading upon shifting the shaft with the shutters under the action of the recurrent spring from an activated state to the initial state of the mechanical lever system. This element is a supplementary one and is not functionally obligatory thus only improving the functioning of the device.
- Shaft with Shutters: it represents the mobile part of the electromechanics which is put into action in one direction by electromagnet 9 and into the other by the recurrent spring and as an element it is a lever of the first order with the axis of rotation placed at its one end and the two shutters at the other.

3.2. Basic characteristics of the developed system

The developed system for simultaneous controllable evaporation from two sources displays the following features:

- range of the shutters moving **l** =12 mm. There is a possibility for control of the times of stay in all positions of the shutters (separatly);
- range of control of the times of staying in the corresponding position of the shutters - **Δt** =200 ms – 2 min;

- power: U = 9 V ± 10%, I_{max} ≤ 0.75 A, in the given case Average value of current (I_{av}) ≤0.1 A.

3.3. Capacities of the developed device

The developed experimental device is installed in the vacuum setting. Production of thin PI layers has been experimented using this new technique for controllable layer-by-layer evaporation from two sources. Vacuum deposited films of a thickness ranging from 80 nm to 30 nm have been obtained. The layers are homogeneous and devoid of defects prior to the thermal treatment.

The layers were subjected to a thermal treatment for different periods and at different temperatures: 6h 170^o C, 1h 170^o C+1h 250^{o}C and 1h 170^o C+1h 300^{o}C. After the thermal treatment (ensuring accomplishment of the imidization processes) even at the highest temperature the obtained thin organic layers are homogeneous devoid of microcracks and defectless. Most probably the layer-by layer build – up of the films via an alternating controllable deposition of the initial PI precursors ODA and PMDA and a possibility for imidization after each deposition will provide for obtaining optimum oligimide layers (Fig. 2). An amelioration of the adhesion to the substrate is secured due to the strong film/substrate bonds based on carboxylate links. This method of formation of the PI layer in combination with a more reactive precursor of the p-phenylene diamine (p-PDA) type ensuring an improvement of the stoichiometry and respectively a decrease of the number of the chemical defects opens the possibility for an outward growth of an oligimide by alternate exposure to PMDA and p-PDA, in a two-step reaction scheme analogous to the PI formation (Fig. 3). The developed experimental device allows for the build – up of a stack system with PI layers of programmed and controllable thickness.

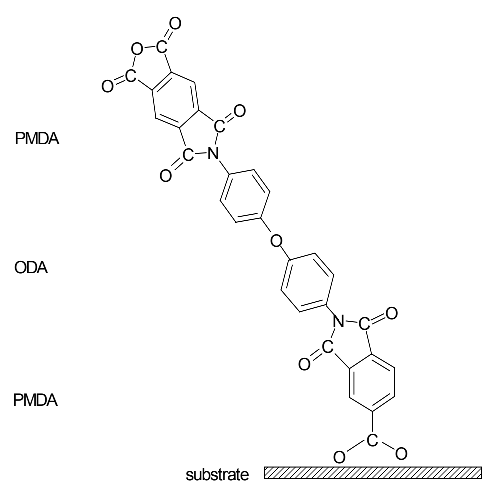


Fig. 2 Model of the outward growth of an oligimide film by deposition and reaction of alternating layers of ODA and PMDA molecules

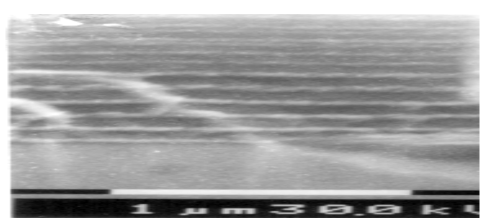


Fig. 3 Cross-sectons of PI multy layer stack system

4. Conclusion

A precise system for a discreet, successive deposition of layers by individual precursors of nanomicron thickness was worked out. Both molecular fluxes of both PI precursors - 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) are formed by low-temperature sources (under 130^o C). The discontinuation of the different molecular flows by a controllable closure of their sources allows for the build – up of a multi-layer (stack) system with precursor layers of programmed thickness. The method renders a possibility for creating laminar molecular fluxes which is a guarantee for the production of films devoid of defects. By means of controlling the evaporation time of the individual sources varying from microseconds to seconds a control of the chemical composition of the organic ultra thin layer is made possible and hence its micromechanical, electrical and optical parameters.

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