

VACUUM DEPOSITED POLYIMIDE – A PERFECT MATRIX FOR NANOCOMPOSITE MATERIALS

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Polyimides represent a class of aromatic hydrocarbons of excellent dielectric, thermal and optical capacities. The possibilities for their synthesis as thin layers by the vacuum evaporation from precursors render them especially attractive for the modern optic and optoelectronic technologies. The application of vacuum deposition allows for a controllable embedding in them of inorganic and organic components (dielectrics, semiconductors or metals) as “guests”. The exceedingly high chemical stability and low-dielectric-constant of the polyimide makes these layers a medium of good prospects for embedding meso- and nano- clusters. The process of vacuum deposition of polyimide layers (precursors: oxidianiline and pyromellitic dianhydride) in the range of 500 – 1000 nm has been investigated. The influence of thermal treatment and the ratio between both precursors on the properties of the formed layers have been studied and a technological window for PI film creation has been established. The composite system dielectric/semiconductor – where PI is used as a 3D and 2D matrix and the organic semiconductor (phthalocyanine) a “guest” has been subjected to investigation. The obtained PI and nanocomposite thin layers are especially attractive for the thin-layer technologies on organic basis for microelectronics as insulating layers with a flexible dielectric constant, in LCD as color filters and orientated layers, in OLED as protective, insulating and barrier layers, in sensorics as membranes or active layers.

(Received May 5, 2005; accepted May 26, 2005)

Keywords: Polyimide, Thin films, Nanocomposites

1. Introduction

In 2000, the Nobel Prize Committee granted the Award in Chemistry to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for their fundamental studies, started already in 1974, which lead to the discovery of the organic semiconductors and synthetic metals. In this way, the materials’ “triad” **Dielectrics – Semiconductors – Conductors**, which in 1947 created the basis for the development of microelectronics, was entirely completed for organic materials as well. A real “boom” was expected both in the arising special chemistry and in microelectronics, optoelectronics, and information technologies, where these materials should find application. In fact, this was observed to some extent, but very soon it became clear that both the theory and the technologies in the field of inorganic materials can very hardly, with some approximations, be adapted to the “organic” materials and in some cases this was just impossible. For this reason, extensive fundamental research combined with technological studies are required in the search of new routes and the finding of new solutions. It is known that organic materials are used in microelectronics and optoelectronics, as photoresists (since 1960), passivating and insulating layers (1960), planar light wave guides (1980), organic light emitting devices (OLED) (1990). What is the reason for the keen interest in these materials? First of all, it is the diverse properties of organic polymer materials, which determine their technological applications.

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1.1 Technologically important properties of organic polymer materials:

- Practically unlimited variety;
- Easy or relatively easy preparation, on the micro- to macro tonnage production scale, at reasonable economic parameters;
- Combine numerous physical, optical and micromechanical properties that are extremely important for their technological application;
- In many cases, by the use of relatively simple procedures, they can be deposited onto large areas;
- Under the action of external factors, such as photons, plasma or thermal treatment, they can be synthesized (poly-condensation and polymerization) or destructed to materials with other properties, or they can pass into another phase;
- They can easily undergo surface modification and structuring, also in the nano-size range;
- They are compatible with a substantial number of inorganic materials and can be adapted to the inorganic technologies including microelectronic productions;
- Many of them are biocompatible;
- At the same time, numerous problems and drawbacks exist, which impose important restrictions in the technological usage of organic materials;
- The conductive polymers have a low current mobility. They are hard or impossible to be doped;
- Thermal stability to relatively low temperatures (max. 350-400 °C);
- Restricted use of physical methods of deposition, primarily in the field of thin layer technologies due to the substantial size of their molecules. The difference in molecular weight is very large – 60-70 for inorganic molecules, and from 100 to many-thousand for organic molecules;
- Low mechanical stability;
- During storage and under the action of external factors (moisture, oxygen, solvents) their properties deteriorate;
- They are sensitive to radiation, including the short-wave spectrum;

Due to their exceptional electrical, physical and chemical properties, many organic materials are now key-materials in most sophisticated devices, such as OLED, liquid crystal displays (LCD), and other optoelectronic devices. It is obvious that, in conformity with the new and ever growing requirements in numerous production fields, the necessity of thin and ultra-thin layers and the development of methods for their controlled formation is also constantly growing. The physical methods for the preparation of thin organic layers are particularly attractive in various technological applications.

1.2 Some peculiarities of organic materials

Upon application of thin layers in the respective technical fields, attention should be focused on some peculiarities of organic materials.

Let us consider, for instance, the electrical conductivity of organic materials. It is mainly of the p-type, i.e., they possess hole conductivity which is more stable and with a higher mobility as compared to the electron (n-type) conductivity. However, the electrical conductivity of organic materials is lower than that measured in inorganic semiconductors. For instance, in the conductive polymer *Pentacen* the hole mobility is about 2 cm²/V.s (compare with 500 cm²/V.s of Si). It is also established that here the π -electrons have a much higher mobility than the σ -electrons.

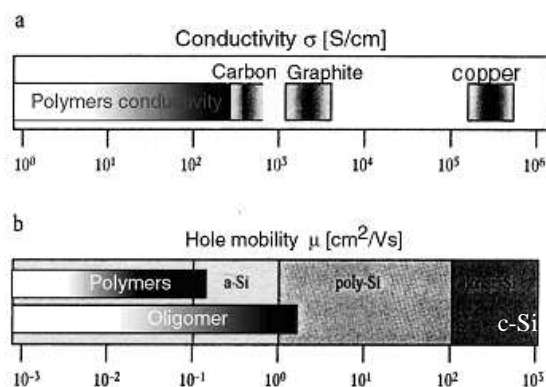


Fig. 1. a) Comparison of organics electroconductivity with copper; b) Comparison of hole mobility of polymer semiconductors with a-Si, poly-Si, c-Si.

In the inorganic semiconductors, the movement of the current carriers is practically free, while in the organic semiconductors, the “holes” are moving along the polymer chain and, via a tunnel effect, they pass from one to another polymer molecule. For this reason, the conjugation of molecules in polymer materials plays an important role. However, there exists also other factors which can worsen the situation; these are the so-called “chemical” defects, i.e., molecules with other bond types which are formed both due to deviations from stoichiometry and as a result of the external energetic action. The primary chemical defects can possibly cause secondary reactions and in this way to increase their total number [1].

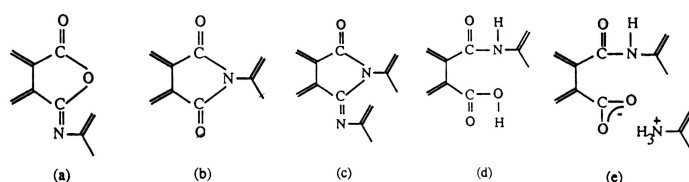


Fig. 2. Carbon-nitrogen bonding configuration that may occur polyimide: (a) isoimide, (b) imide, (c) imine, (d) amide and (e) ammonium salt.

Another peculiarity - many inorganic thin films are anisotropic within the substrate plane, due to the formation of columnar microstructures inclined towards the vapor source during the deposition. It is necessary to obtain angles larger than 60° . By organic thin films, the deposition angle is larger than 25° . The inorganic molecules have strong ionic or covalent bonds between their atoms and show mostly a spheroidal shape (diameter of 2-4 Å). For instance, the polyimide precursors are in the shape of rigid rods with a length of 12-14 Å.

The hydrogen bonding is due to the interaction of the carboxylic H atom and the non-bonding electron pairs of the O and N atoms, i.e., several bonding possibilities exist. In these organic molecules, the strongest hydrogen bonds are between carboxylic and pyridyl groups (head-to-tail) $N\cdots H-O-$ and between carboxylic groups (tail-to-tail) $=O\cdots H-O-$ (Fig. 2; Fig. 3).

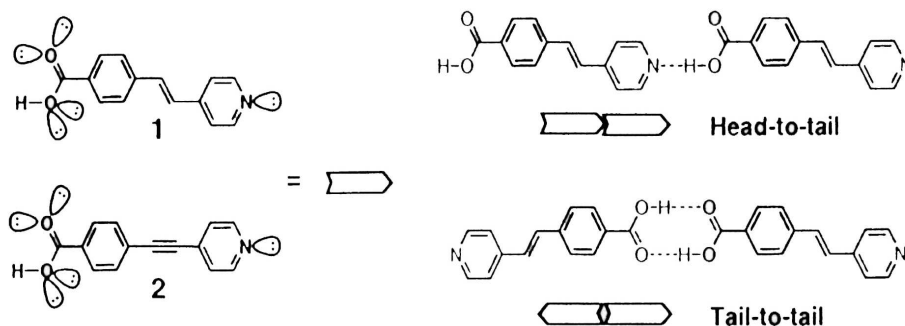


Fig. 3. Molecular structures and non-bonding electron pairs of 1 and 2, and the strongest hydrogen-bonded dimmers of 1.

2. Experiment and results

This report is a presentation of our investigations related to the obtaining of micron and submicron layers of polyimide by physical vacuum deposition (PVD). By this method, both organic and inorganic layers can be prepared in the same vacuum system. The technological schemes are shown below (Fig. 4). One can strongly influence the electronic and optical layer properties by the precise control of the deposition conditions.

Aromatic polyimides were developed for practical use in the early 1960s as heat resistant polymers. [2-4] This class of polymers exhibits a unique combination of thermal and chemical stability, excellent electrical properties (dielectric constant $\epsilon - 2.91-3.5$, permeability-dissipation factor $\tan \delta - 0.008$), important optical properties (80-85% transparency in the range of 550-800 nm). For about 40 years, polyimides are used as interlayer dielectrics in microelectronics, insulating layers and foils in electronics (Kapton™) [5,6]. Simultaneously, the majority of polyimides are hardly soluble in organic solvents (highly polar solvents, such as N-methylpyrrolidone), they are susceptible to rapid gel formation (short shelf-life), their solutions are highly viscous and, therefore, it is very difficult to obtain submicron thin films. The applied solvents pose environmental and health problems.

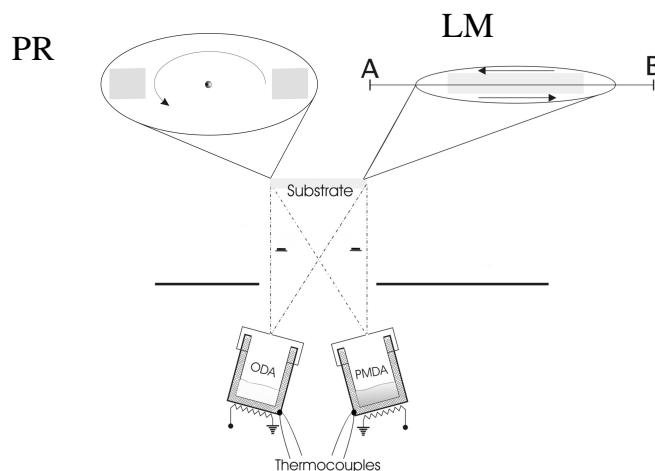


Fig. 4. Technology scheme of PVD. PR – planetary rotating substrates (60 rpm) ; LM – linear moving substrates (5 mm/sec).

During the last decade, the interest in thin polyimide films has grown due to their new applications related to the miniaturization – for ultra-large-scale-integration (ULSI) – as insulating-, barrier-, or stop-layers; as alignment films for LCD; as color micro-filters; as optical wave guides in

optoelectronics; in sensorics as membrane protectors; as matrices for dyes and chromophores; for electrophotographic laser printers; for membranes as promising medical materials, e.g., for intravascular oxygenators with high CO₂/O₂ gas exchange and excellent blood compatibility, etc.

A possible alternative route to the preparation of polyimide thin films is the polycondensation of two vacuum deposited precursor oligomers – diamine (ODA) and dianhydride (PMDA) – Fig. 5.

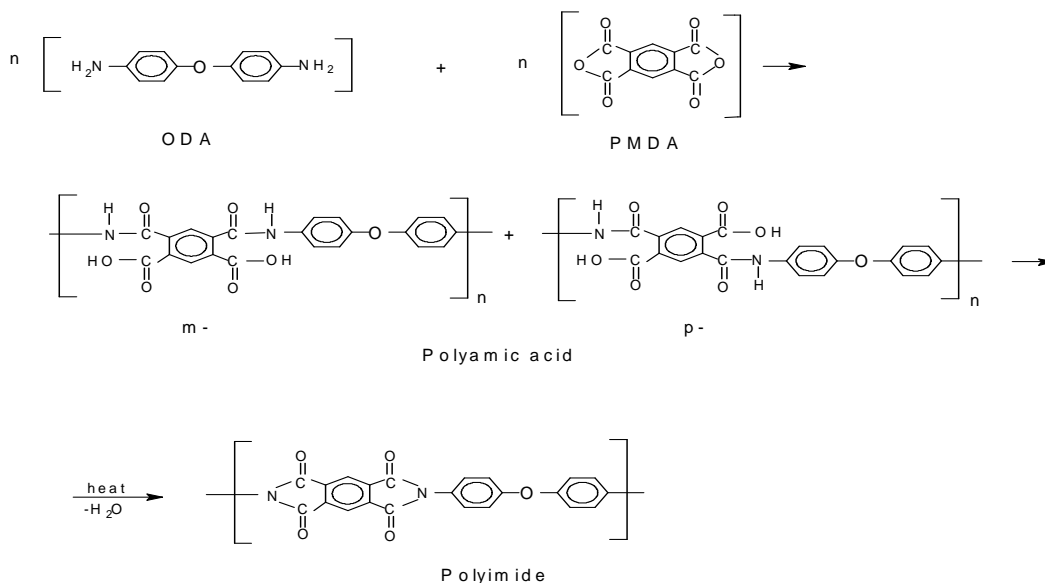


Fig. 5. Schematic diagram for the reaction of PMDA with ODA to form polyimide via the intermediate polyamic acid.

After the reaction [7], leading to the synthesis of a polyamic acid, by thermal treatment at 250-300 °C, in air, neutral atmosphere or vacuum, imidization takes place. The first experimental studies by American and Japanese authors of the preparation of vacuum deposited polyimide layers date back to 1986 [8,9].

The interest in these studies has gradually grown with the scientific and technological progress in organic electronics and optoelectronics. For the preparation of thin polyimide layers, many authors have applied thermal evaporation as well as the well-known R.F. magnetron sputtering and laser ablation. [10,11]. It is established that by resistive thermal evaporation only, it is possible to create defect-free, optically clean and uniform layers. There are several reasons for this – the preparation is related to the process of polycondensation requiring an intimate, stoichiometric mixing of the two monomers. The energetically rich sputtering provokes uncontrolled breaking of some chemical bonds, creates numerous chemical defects, incorporates, as a result of destruction, carbon impurities in the layer. In addition to these problems, the laser ablation is related by itself to eruption of matter.

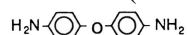
The necessity of obtaining of thin and ultrathin layers (from $\leq 1 \mu\text{m}$ to 10 nm) with improved optical and electrophysical characteristics, as well as their deposition on substrates of various shapes and types require knowledge of the structure of the precursors and the resulting polyimide molecule, control and management of the polymer layer deposition process, and possibilities for the energetic enhancement of the layer formation. These are the prerequisites for the creation of oriented “conjugated” molecules in the polymer layer, or in the unorientated, chaotic layer.

In the search of new improvements in the polyimide layer properties, various precursors are continuously synthesized. [7]:

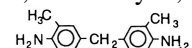
Diamines:

4,4'-oxydianiline (ODA) -Weights of ODA molecule $3,06 \times 10^{-25}$ kg.

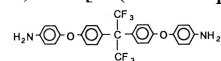
O-tolidine (OTD),



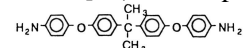
3,3'-dimethyl 4,4' - diaminodiphenyl methane (MeMDA),



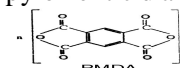
2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDFA)



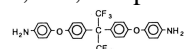
2,2-bis[4-(4 amino phenoxy)phenyl]propane (BAPP)

**Dianhydrides:**

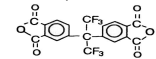
pyromelitic dianhydride (PMDA) -Weights of PMDA molecule $3,62 \times 10^{-25}$ kg.



3,3'-4,4' biphenyl tetracarboxylic dianhydride (BRDA)

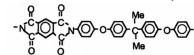


4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) (6FDA)

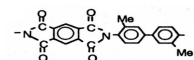


The combination diamine/dianhydride formed:

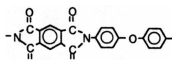
PMDA/BAPP; PMDA/ MeMDA .



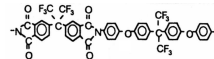
PMDA/OTD and BPDA/OTD - rod-like polyimides



PMDA/ODA - semi-rod-like polyimides



6FDA/BDAF - fluorinated polyimide



We investigated the evaporation of the two basic polyimide precursors (ODA and PMDA). Since the synthesis of the two oligomers takes place in the solid state, the polycondensation was studied by thermogravimetric (TGA) and differential thermal analysis (DTA) of the separate oligomers and their stoichiometric (1:1) mixture. Thermal stability up to 227 °C was established in all cases. The TGA curves (Fig. 6a) show two reverse peaks at 177 °C and 297 °C, related to a weight loss of 3 and 9%, respectively, which correspond to 1 and 3 moles of water. The DTA (Fig. 6b) curves exhibit one exothermal and two endothermal peaks at 177 °C, 277 °C and 347 °C, respectively. This can be assumed as an indication of the start of the solid-state reaction between the monomers (polycondensation). As a result of the reaction, a water molecule is released (the first weight loss peak in TGA). With the rise of temperature, the imidization process is enhanced.

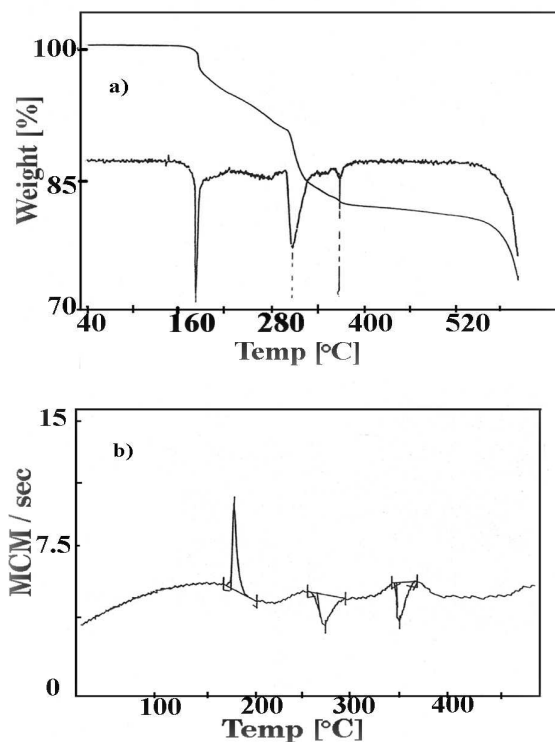


Fig. 6. a) TGA and b) DTA of PMDA and ODA in stoichiometry (1:1).

In the FTIR spectra (Fig. 7) of the initial PMDA, frequencies are found that prove the presence of -COOH groups as admixtures, most probably arising from admixed pyromellitic acid. Following thermal processing, signals for the aromatic nucleus (3100 cm^{-1}) are registered while signals for OH (1305 ; 1118 cm^{-1}) and for -COOH (1680 cm^{-1}) groups (only traces of the peak are found) are not registered. Consequently, the analyzed product contains admixtures in the form of water or pyromellitic acid, which requires either a preliminary purification or appropriate thermal treatment prior to the beginning of the vacuum deposition on the substrate.

The FTIR spectra of the films formed by ODA: PMDA = 52:48 (spectrum A), 40:60 (spectrum B, excess of PMDA) and 60:40 (spectrum C, excess of ODA) are presented in Fig. 8. Except for the shoulders (Fig. 8) around 1780 and 1720 cm^{-1} and the partly resolved band around 1400 cm^{-1} , the spectra are typical of bulk PI. Normally, the imidization ratio is followed by the disappearance of the anhydride peaks (at 1860 , 1806 and 1770 cm^{-1} for PMDA). As seen, the spectra in Fig. 7 are quite similar and do not reveal anhydride peaks. The absence of bands near 1660 and 1550 cm^{-1} indicates that the polyamic acid has disappeared after thermal treatment. Ring closure is responsible for the bands at ≈ 1720 and $\approx 1380\text{ cm}^{-1}$ (due to the C=O and C-N stretch, respectively).

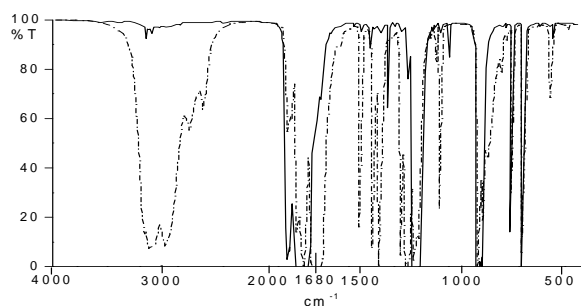


Fig. 7. Changes of FTIR spectra of PMDA in the transmission mode: (—) after thermal treatment 1h 314° C, 1.10^{-4} torr; (—•—) thermally untreated.

Spectra A and C show pronounced shoulders around 1780, 1720 and 1380 cm^{-1} (after deconvolution, the positions of these shoulders were estimated to be at 1793, 1709 and 1399 cm^{-1} , respectively) characteristic of *iso*-imide groups [1,12]. The presence of imine bonds can be ruled out because they give a strong band at 1660-1640 cm^{-1} . Our data (the presence of the 1793 and 1709 cm^{-1} bands and the broadening of the C-N stretching band at 1380 cm^{-1} caused by the appearance of a shoulder around 1399 cm^{-1}) indicate that an excess of ODA causes formation of *iso*-imide groups. The results from the curve fitting procedure indicate that the *iso*-imide content of film A is about 2.5% and that of film C is 5.4%. The excess of ODA leads to films with *iso*-imide content, probably because not only the nucleophilic acyl substitution, but also the nucleophilic addition on the carbonyl carbon is possible.

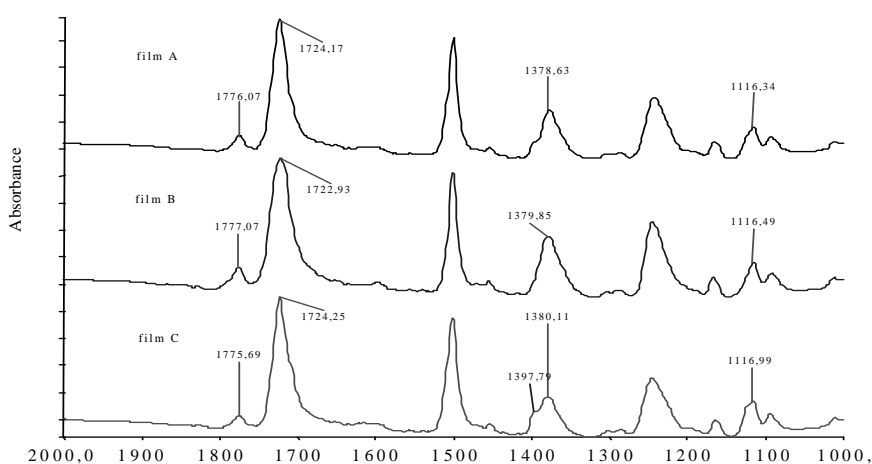


Fig. 8. FTIR spectra of polyimide films: A (ODA: PMDA = 52:48), B (ODA: PMDA = 40: 60), C (ODA: PMDA= 60:40).

Physical deposition of polyimide layers, methods:

The preparation of PI layers by PVD offers some very promising advantages:

- This is an all "dry" process (no solvents);
- Does not exhibit the rheological effects and solvent retention of solution-cast films;
- The method is appropriate for controlling the film thickness.

- The method is attractive for the production of thin nanocomposite films as matrices by co-deposition of metals, their salts, organic or metallo-organic (e.g., phthalocyanines) compounds. This makes the PI a very important material for organic light emitting-devices, integrating organic and inorganic materials (Fig. 9).

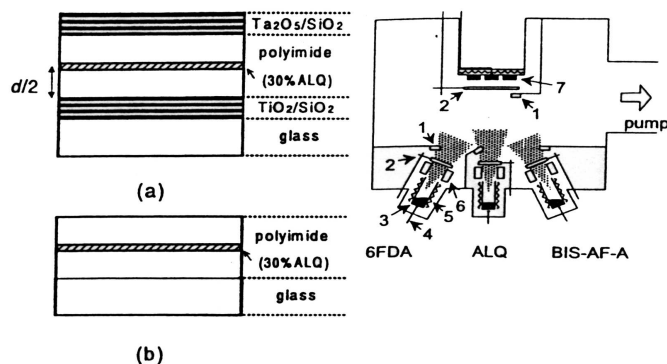


Fig. 9. A VD apparatus to prepare the polyimide layer doped with Alq₃: (1) quartz thickness monitor; (2) shutter; (3) source cell; (4) thermocouple; (5) heater; (6) cold trap; and (7) substrate. Base pressure is 3×10^{-5} Pa. Illustration of (a) a microcavity structure and (b) a reference sample. The black layers indicate TiO₂ or Ta₂O₅ layers [13].

From the very beginning of our long experimental practice, these problems were taken into account in the present approach. In the vacuum chamber, the low-energetic flux of “heavy” (molecular weight over 200) precursor molecules are strongly influenced by local temperature changes, as well as by the transitions from laminar to turbulent flows. Taking into account the presence of such a complex situation in the vacuum chamber and in the zone of the substrates, two types of samples were prepared depending on the dynamic state of the substrates [Fig. 4]. The samples of the first type were prepared on the linearly moving (LM) substrates (with fixed rate of 5 mm/s) situated at 10 cm above the two sources for the monomers evaporation. As for the other type, the monomer vapors were deposited on planetar-rotating (PR) substrates (30 rpm). By deposition on LM substrates, the films were built up via layer-by-layer formation, while the films on the PR substrates were grown continuously. In all cases, the substrates (soda-lime glass plates) were kept at room temperature. The vacuum chamber was evacuated to a base pressure of $\leq 5 \times 10^{-4}$ Pa. The monomers ODA and PMDA were evaporated from two independent thermally heated Knudsen type vessel sources. Typical temperatures for evaporation were 120-145 °C for PMDA and 100-110 °C for ODA to achieve deposition rates from 0.2 to 2 Å/s controlled by quartz oscillators. Thus, the optimal desired ratio in the vapor molecular flux (1:1) for ODA and PMDA was ensured. The co-deposited monomer layers were transformed into PI films by a two-step thermal treatment - 1 hour at 170 °C followed by 1 hour at 350 °C in air atmosphere [14,15].

Deposition windows for each monomer were determined, i.e., the rates beyond which changes in the structure, morphology and defects of the deposited layers take place. These rates do not exceed 15-20 Å/s. The dynamic state of the substrate allows the best mixing conditions of both precursor gas streams.

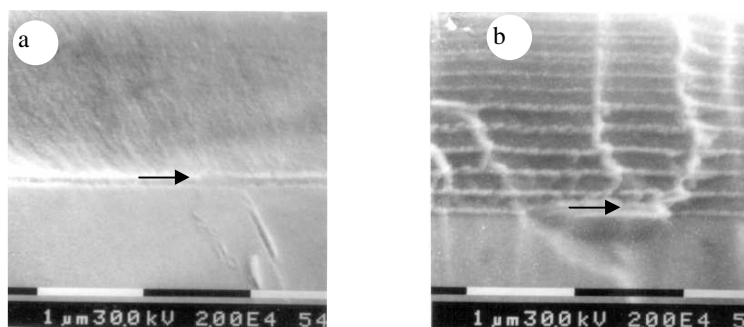


Fig. 10. Cross-sections of thermally treated VDP layers, deposited: a/ on PR substrates; b/ on LM substrates. The arrows show the boundary of the substrate and film.

The linear moving substrate shows a uniform structure, but the cross-section is clearly layered (Fig. 10). Obviously, interfacial thin layers are created by the penetration of the substrate in the zone of one or another gas flux. Most probably, the adsorbed molecules from the residual atmosphere in the vacuum chamber play the role of separators.

The obtained PI layers are optically uniform and clean. They have a high transmission ($\geq 80\%$) in the range of 500-800 nm and negligible reflection (5-10%). Our experiments showed that the shape of the curves and the optical parameters do not depend on the dynamic state of the substrates.

The created PI films show excellent chemical resistance in solution.

The electrical characteristics of the layers – relative dielectric constant (ϵ_r) and breakdown field (E_b), show the major role of the stoichiometry and the influence of the thermal treatment conditions. The investigated data are comparable to those of the commercial (solution-cast) films [15].

The excellent chemical characteristics of the polyimide layers make them quite attractive protective and insulating media in various processes. The possibilities of these layers to be effectively structured with short wave, excimer laser treatment, and with reactive plasma (O_2 , CF_4) or ion-beam influence are of particular interest.

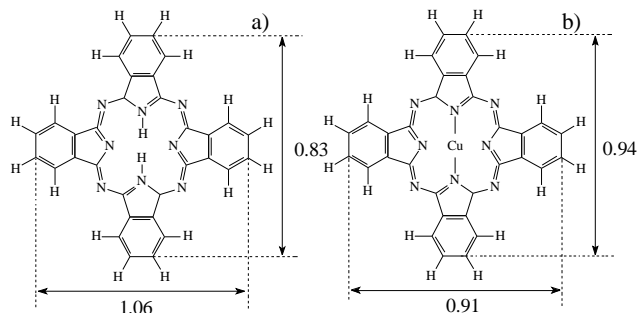


Fig. 12. The chemical structure of molecules of: a) - H₂Pc and b) - CuPc. Dimensions are in angstroms.

The experiments show that a so-called “lithographic window” exists (structure with best sharpness, high-accuracy edge, and reproducibility) for 308 nm and 248 nm lasers with the energy boundary of 0.375-0.625 J/cm². By plasma etching, the observed surface is very rugged. By the use of pure oxygen plasma, the etching rate attains 140-150 nm/min, but the image obtained is extremely loose (“polyimide grass”) [15]. The gradual introduction of CF₄ from 20 to 100% leads to gradual changes in the image. The etched surface smoothens and the etching rate decreases to 50-60 nm. The data obtained reveal the possibility of creation of effective lithographic systems by the use of a “solventless” process (Fig. 11) [16].

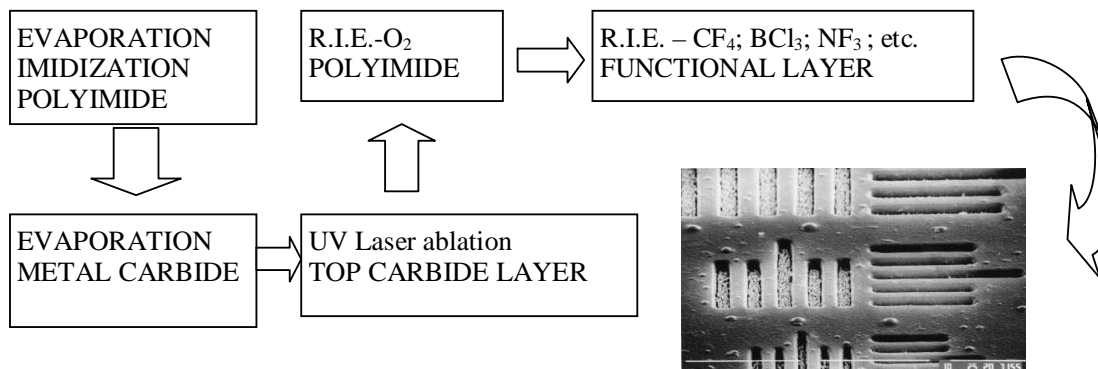


Fig. 11. All-dry and in-situ microstructuring of carbide/polyimide layers.

Nanocomposites

Nanocomposites, consisting of a PI matrix and dispersed nanoparticles of salts, metals, carbon, dyes or metal-organic are materials with good prospects for different high-tech applications. These materials show excellent mechanical, gas sensing, optical, magnetic, and transport properties. The most promising approach in the development of new materials is the possibility to combine the advantages of organic materials with those of inorganic solids, either in a pure form or to which organic or organometallic side groups are attached. The side groups control the refractive index, surface properties, non-linear optical properties, such as hydrophobicity, hydrophilicity, adhesion, or biological compatibility. Four different types of optical properties can be designed in this way – optical absorption in the UV or visible spectrum; tailored refractive index; non-linear optical behavior, photochromism. We studied several nanocomposite systems based on the co-evaporation of a polyimide matrix (ODA-PMDA) and embedded metal (aluminum), copper phthalocyanine (CuPc); or metal-free phthalocyanine (H₂Pc) as “guest” components. The following technique was applied: The evaporation of the separate components was carried out from a Knudsen-type source with careful thermal and deposition control. This system is developed and realized from our young collaborators. Two types of composite layers were prepared – the “sandwich” type – PI/guest/PI -

layer-by-layer and “cake” type -- by co-evaporation of both the precursors (ODA-PMDA) and the “guest” (metals, or CuPc and H₂Pc). [17-21]. The results obtained with “guest” phthalocyanines are of particular interest. These are organic semiconductors also distinguished by a high thermal and chemical resistance. They are stable in vacuum at high temperatures and can be embedded in the polyimide matrix by vacuum techniques. It was established that the layer properties are determined both by the “guest” type and by the way in which the composite layer is built up. The nanocomposite phthalocyanine thin films are of practical interest. The poor mechanical properties of phthalocyanines require their embedding in a more stable matrix. The possibilities of application of vacuum technologies in the preparation of such composite materials are extremely attractive. We have established that the polyimide/phthalocyanine system is very sensitive not only to the “guest” concentration, but also to its distribution in the bulk matrix.

The conductivity and photoconductivity of Pcs can be modulated upon exposure to certain ambients, thus making them attractive as potential gas sensors. Chemisorption of a gas capable of inducing donor-acceptor interaction produces an ionized state and deforms the energy band gap. Me-Pcs have two possible sites for gas adsorption: one is the central metal itself and the other is the π -electron system. Because the refractive index of an organic compound varies with the number of π -electrons in the molecule, the adsorption properties of Pcs towards oxidative gases can be optically determined.

The PcS are macro-cycled ligand-ring systems. The Pc is relatively chemically inert, thermally stable, and possess a p-type molecular conductivity. They find application and are promising materials in many fields of industry, e.g., semiconducting devices, photovoltaic and solar cells, rectifying devices, liquid crystal devices, gas sensors, and low-dimensional conducting materials. An extensive review of these materials has been reported by Leznoff and Lever [22].

The effects of adsorbed electron-acceptor or electron-donor gases on the surface of organic semiconductors have been recognized for many years and widely studied for sensor applications [23].

The performance of MePcs as gas sensors is based on large changes in the dark conductivity which are directly related to the absorption of strong electron acceptor or donor gases on the surface of the p-type Pc films. It is known that the changes in conductivity are primarily a surface effect, and so the sensors configuration should have a high surface area-to-bulk volume ratio. The optimum concentration of Ps – as CuPs and H₂Pc (Fig.12) is 14% in the PI matrix volume. The optimal thermal treatment conditions for the obtained composites were 60 min at 170 °C plus 60 min at 200 °C. By these conditions, we obtained minimal changes in film composition and good surface quality.

In order to avoid critical values of the substrate temperature (40 °C), resulting in re-evaporation, the precursor trimethyl aminalan (TMAA) was used in the case of aluminum. TMAA sublimates easily at temperatures of about 150 °C and is embedded in the ODA-PMDA layer. During the imidization process, under the action of temperature and water molecules, TMAA decomposes to gaseous products and aluminum clusters. Probably the formation of a single Al-O-C bond, as a result of Al / C=O interaction, decreases the reactivity of the symmetrical C=O site as well. In addition, diffusion of Al into the PI together with formation of small metal clusters is observed.

3. Conclusions

The physical methods of deposition of thin layers of organic materials represent a key solution in the various modern technologies or they could be regarded as an important and promising alternative in many cases. Their application is only possible by profound knowledge of the organic materials used and by adaptation of the vacuum technologies to these materials. The evaporated polyimide layers are a very convincing example in this respect.

The creation of key technologies in this field is the very way for rapid development of new and diverse devices.

Our knowledge of polyimide deposition and the possibility for its application as a matrix with improved electrophysical properties permitted us to create the following strategy:

Incorporation of diamine and dianhydride reactants with large substituting groups into the molecular skeleton, such as PMDA/OTD and BPDA/OTD, which minimize polarizability.

Incorporation of diamine and dianhydride reactants impart a high degree of free volume. The addition of pendant groups and bulky groups, which limit the chain density will enhance the free volume. By another approach based on evaporation in the presence of noble gases, one could expect the formation of free volumes in the layer, i.e., creation of a layer structure with a minimal dielectric constant or with high porosity suitable for embedding of active organic or metallo-organic nanoparticles.

Incorporation of fluorine atoms into the molecular structure of the polyimide. Incorporation of fluorine into PI has shown that the dielectric constant decreases with symmetric fluorine substitution.

Continuation and broadening of the studies related to the introduction of suitable "guest" materials with nano-size.

Acknowledgements

The financial support of the National Fund of the Ministry of Education and Science, Bulgaria - contract X-1322 is gratefully acknowledged.

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