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Polyimide (PI) films by chemical vapor deposition (CVD): Novel design, experiments and characterization

Jaime Puig-Pey González *, Alain Lamure, François Senocq

CIRIMAT CARNOT UMR-CNRS 5085. INPT/ENSIACET, 118 route de Narbonne, 31077 Toulouse Cedex 04, France

Abstract

Polyimide (PI) has been deposited by chemical vapor deposition (CVD) under vacuum over the past 20 years. In the early nineties, studies, experiences and characterization were mostly studied as depositions from the co-evaporation of the dianhydride and diamine monomers. Later on, several studies about its different applications due to its interesting mechanical and electrical properties enhanced its development.

Nowadays, not many researches around PI deposition are being carried. This paper presents a PI film deposition research project with an original CVD process design. The deposition is performed under ambient conditions (atmospheric pressure) through a gas flux vector. Design of apparatus, deposition conditions and preliminary characterizations (IR, SEM and surface analyses) are discussed.

Keywords: Polyimide; CVD; Flux vector; Thin films

1. Introduction

Chemical vapor deposition (CVD) can be defined as a deposition technique, in which chemical components react in the vapor phase on a surface, to form a solid film. CVD techniques offer unique advantages as deposition process like: excellent film uniformity and conformality, high purity, ease of deposition over large substrates, ease of fabricating multi-layered and heterojunction films, compatibility with manufacturing technology, and many others [1].

In the last several years, polymer thin film deposition using chemical vapor deposition (CVD) has become increasingly popular. CVD of polymers offers numerous unique advantages over other polymers synthesis techniques and has been exploited for diversified applications in microelectronics, optical devices, biomedical industry, corrosion resistant and protective coatings, and even in the automobile and aerospace industries. Micro fabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial [1–4]. Thin films of polymeric materials are of growing importance in technical applications for insulation, isolation and passivation in microelectronics [5].

* Corresponding author. Tel.: +33 5 62 88 56 55; fax: +33 5 62 88 56 63.
E-mail address: Jaime.PuigPey@ensiacet.fr (J.Puig-Pey González).

Polyimides are a class of high temperature polymers that exhibit a unique combination of thermal stability, high softening point or glass transition temperature, and easy processibility into coatings or films. The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies for synthesis [2].

Polyimides are usually prepared by a two-stage synthesis; firstly, solution condensation of an aromatic dianhydride with an aromatic diamine yields a soluble polyamic acid; afterwards, thermal or chemical dehydration of this polymer yields an insoluble and intractable polyimide. Polyamic acids prepared by vapor deposition polymerization (VDP) offers an alternative process for the fabrication of high temperature polymeric films [3,4].

In the present work, we report an introduction to the preparation and characterization of polyimide films at ambient conditions (atmospheric pressure) by two gas flows as deposition vectors, pyromellitic dianhydride (PMDA) and oxydianiline (ODA).

2. Experimental

Most of CVD processes follow these different steps: 1. Transport of gaseous chemical reactants to the surface. 2. Adsorption of the species on to the surface (condensation). 3.

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Reaction of the species on the surface. 4. Desorption of gaseous by-products of the chemical reaction. 5. Transport of by-products away from the surface. 6. Incorporation of the reaction products into the bulk of the film.

Particularly, CVD of polymer thin films as polyimides requires the following conditions: 1. Initiation of the reaction must occur exclusively on the surface, to eliminate polymerization in the gas phase. 2. Rate of propagation must greatly exceed the rates of initiation and termination. 3. The surface mobility of the monomers must be high. 4. The monomers must be stable under depositions conditions [1].

2.1. Fabrication materials

Polyimides are typically synthesized from the reaction of diamines and dianhydrides. Pyromellitic dianhydride (PMDA) (1,2,4,5-benzenetetracarboxylic dianhydride; 97% purity) and 4,4′-oxydianiline (ODA) (99+% purity; zone refined) were purchased from Aldrich Chemical and used without further purification. The monomers react in solution to form the polyamic acid, precursor which is thermally converted to a poly (4,4′-oxydiphenylene pyromellitimide) film, (Kapton ™) [4,6]. (Fig. 1).

2.2. Deposition equipment and conditions

The polymer deposition system (Fig. 2) consists of the deposition chamber, two identical evaporation bubblers (one each for PMDA and ODA), the radiators and the gas lines; the control and measure equipments are also considered, as temperature regulators, mass flow controllers, thermocouples, heating resistors lines and blankets.

The deposition chamber (Fig. 3) is a pyrex cylinder ($\varnothing = 8$ cm and 20 cm long) closed on the top (with two adapted entries), and open downside, to position the samples support with its heating resistor. The system is pumped by a helium flow which carries monomers through the system (the specific principle of our CVD deposition). The helium flow is controlled by a

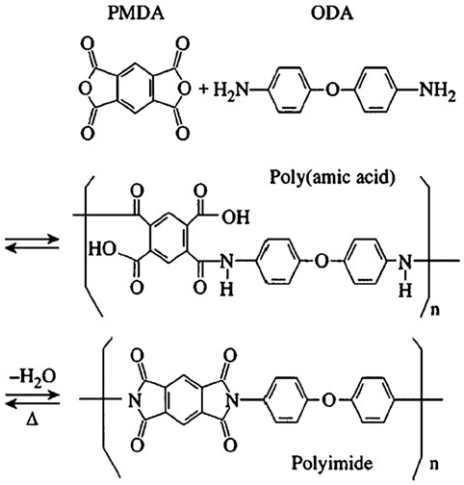


Fig. 1. Polymerization of PI by reaction between ODA and PMDA precursors.

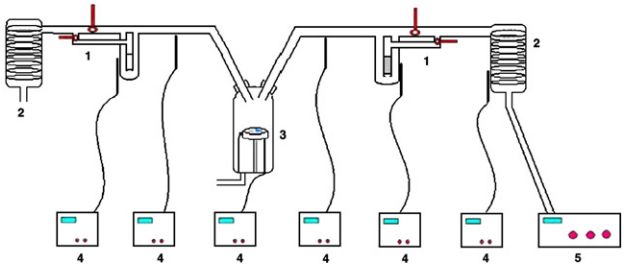


Fig. 2. Deposition system 1. Precursors' bubblers 2. Radiators. 3. Deposition chamber 4. Temperature regulators with its thermocouple 5. Mass flow controller.

Mass Flow Controller Brooks 5850 TR Series. Flow calculations are simulated considering the initial temperatures, the steam pressures, the volume and the chemical compounds used in the experiences (See Section 3.1.2.).

The samples holder is stainless steel made, so thermal conductivity is induced. As heating device, a temperature cartridge is placed inside the holder. Its working conditions, going up to 350 °C are controlled by a thermocouple. This entire device is inserted in the deposition chamber, to regulate the samples temperature during all the deposition process.

The temperatures (radiators, evaporating sources, samples' surface and gas flow) are real time regulated during all the process. The complete process is understood as the coordinated sequence of different cycles: 1. Preheating 2. Evaporating 3. Deposition cycle and 4. Curing cycle.

The process starts with a pre-heating cycle. The radiators and the gas lines are heated to 115 °C and 100 °C respectively, to maintain the system temperature and to facilitate the monomers' evaporation process. Once the system is balanced, the deposition process begins with the monomers' evaporation in the bubblers.



Fig. 3. Deposition chamber (heating resistor inside the sample's support).

Bubblers containing ODA and PMDA precursors are heated till the evaporation temperature (135 °C and 145 °C respectively) [7,8] and once it is reached, bans are open to let the flow get to the deposition chamber. Through the gas lines, the evaporated monomers get into the chamber, where the deposit is made on the samples' surface.

Deposition takes place during 3 h, in which temperature and atmospheric pressure conditions are balanced, to obtain a homogenous film. The samples' support is maintained at 50 °C during the whole deposition process. Once the process is finished, heating devices and gas flow are stopped; then, a curing process takes place during another 3 h, to obtain polyimide from the polyamic acid deposition. This curing process takes place inside the deposition chamber. In this way, there are no changes in the reactions conditions, which damage the resulting deposition.

Depositions are realized on different supports. First depositions are done on quartz and crystal supports, to analyse optical properties easily. As possible applications for depositions are integrating them into microelectronics devices, processed Si supports are chosen. Depositions have also been done on KBr pellets, to facilitate FTIR analyses.

3. Experiment process parameters and characterization methods

The presented system shows a performance PI thin films dry deposition process. The system equipments are available in most of CVD laboratories, with an interesting relation price–performance. The characterization methods demonstrate properties of the films, looking into microelectronics applications. These tests serve to guarantee chemical composition of the films, and mechanical, electrical and optical properties.

3.1. Deposition parameters

3.1.1. System pressure and process

Most articles in bibliography [1,3–5,9] talk about the deposition of PI from a molecular flow by direct evaporation of monomers, always working under vacuum (pressures $<7.5\times10^{-6}$ Torr). Working at reduced pressures accelerates the monomers' evaporation process, initializing the molecular transfer of the system.

Using a gas flow vector avoids complicated proceedings to maintain low steams in the system. Chemical interactions between the gas and the monomers, which can damage the samples deposited, are eliminated choosing inert Helium as gas vector. Gorham Process [1] demonstrates how weak vector gas flows can initialize the evaporation and the deposition. This type of dry process allows depositions of polyimide and others polymeric films, preventing from possible sealing problems.

3.1.2. Precursors' flow rates

Initial gas flow conditions are calculated based on a theoretical approximation of evaporation rates. System flow estimations are based on the concentration of each precursor in the mix so to obtain time-thickness' balanced relations on the polyimide film. Calculations consider Clausius-Clapeyron equations for the monomers at low temperatures [5], their molar masses ($M_{ODA}=218.1$ g/mol and $M_{PMDA}=200.24$ g/mol) and the initial temperature:

$$\ln P_{VAP} = -\frac{H_V}{R}\left(\frac{1}{T}\right) + C \tag{1}$$

With H_V [ODA]=130 Kj/mol and H_V [PMDA]=120 Kj/mol [5]

The real flow of each precursor is:

$$D(\text{precursor})[\text{sccm}] = \frac{D_{\text{VectorGas}} \times P_{VAP}(\text{precursor})}{P_{ATM}} \tag{2}$$

And the concentration of this product in the deposit is:

$$\chi(\text{precursor}) = \frac{D(\text{precursor})}{\Sigma D_i} \tag{3}$$

Stoichiometric balanced quantities for the PI film are calculated with these working conditions, to obtain monomers evaporation [8] rates for each manipulation:

$$m_{\text{CONSUMED}}\left[\frac{g}{h}\right] = \frac{D(\text{precursor}) \times M(\text{precursor}) \times 60}{22,400} \tag{4}$$

Different flows of precursors have been used, always keeping the same relation between precursors' concentrations. Table 1 shows conditions used in the final experiments, once optimized the deposition process.

3.1.3. Heating cycle

Films were thermally cured in a nitrogen-purged environment using the following program: ramp from deposition temperature (50 °C) to 150 °C in 30 min, hold at 150 °C for 30 min, ramp to 300 °C in 1 h, and hold at 300 °C or 1 h, and cool to room temperature.

The codeposition of evaporated monomers onto a substrate maintained at temperatures bellow 50 °C, led to a mixture of reacted and unreacted material, which when subjected to a heat treatment process (curing) undergoes a cyclodehydratation, resulting in a uniform film of polymer [9,10].

Table 1
Working conditions, flow and evaporation rates

Training PMDA flow rate (sccm)	60
Training ODA flow rate (sccm)	76
χ_{PMDA}	6.10E−05
PMDA flow (sccm)	0.0083
PMDA evaporation rate [g/h]	0.0048
PMDA evaporation rate [mol/h]	2.22E−05
χ_{ODA}	6.10E−05
ODA flow (sccm)	0.0083
ODA evaporation rate:[g/h]	0.004451
ODA evaporation rate:[mol/h]	2.22E−05
Support temperature	50 °C
Curing temperature	Ramp to 300 °C
Curing time	3 h

3.2. Deposition analyses

3.2.1. Contact angle measures and surface energy

Fig. 4 shows water drops placed on the sample's surface. Contact Angle Measurements have been realised with a GBX-Digidrop. Image demonstrates how easily sticky polyimide films deposited, have an elevated surface energy. CVD deposited polyimide contains carbonyl and amine groups which generate hydrogen–water bonds. Medium sized angle measured is 62° for water drops. Measures were done for different samples, and in different days, obtaining stable results.

The values of surface free energy of the thin films measured by the contact angle method, were calculated accordingly to Young and Owens et al. equations.

$$\gamma_{LG} \cos \Theta = \gamma_{SG} - \gamma_{SL} \quad (5)$$

With γ_{LG} liquid surface energy, γ_{SG} solid surface energy, γ_{SL} inter-surfaces energy and Θ the angle between the liquid and the solid. Results obtained show that after PI deposition, surface energies were ranged between 38 and 42 mJ/m^2, values in good agreement with plastic materials characterized by low surface energy.

3.2.2. Fourier transform infrared FT-IR

Infrared spectrums were made using KBr-pellets with a PI film deposited. The analyses were made with FT-IR-Spectrometer Nicolet 5700 (see Fig. 5). PI characteristic bands are:

- The band at 1500 cm^{-1} is due to elongation of the ODA C═C bonds
- The band at 710 cm^{-1} is due to the symmetrical elongation of PMDA aromatic nucleus.
- The band at 1380 cm^{-1} corresponds to imide's concentration.
- The band at 1325 cm^{-1} corresponds to amide's carbonyl C-N concentration.
- The 1775 and 1850 cm^{-1} bands and the 1550 and 880 cm^{-1} bands, corresponding to the carbonyl anhydride peak, determine the excesses of ODA and PMDA respectively.

Fig. 5 shows the FTIR spectrum of PI film deposited during 3 h, after a ramp heating cycle of another 3 h. Surface deposited is 185 μm high and 6 μm roughness (measures realised with Mechanical Profiler KLA TENCOR P-15), for a deposition rate

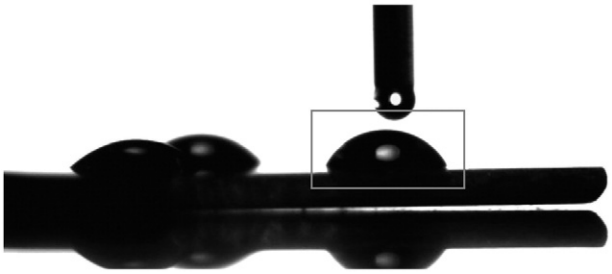


Fig. 4. Contact angle measures with water on PI film.

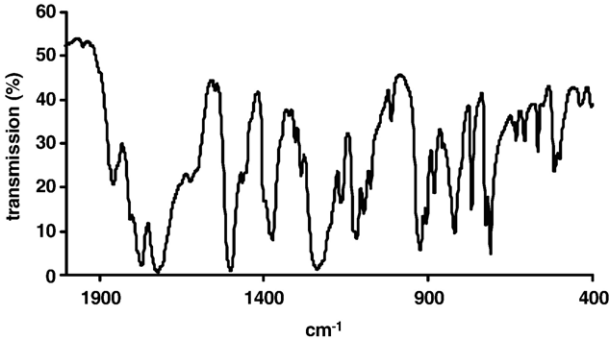


Fig. 5. FTIR spectrum of PI film deposited.

in the range 13–20 nm/s. The source-to-substrate distance was 80 mm. After curing at 300 °C, characteristic bands are: ODA C═C bonds (1500 cm^{-1}) and PMDA aromatic nucleus (710 cm^{-1}), 1380 cm^{-1} band defining imides' concentration, 1775 and 1850 cm^{-1} bands corresponding to the carbonyl anhydride peak, determining the excesses of ODA. It is also observed how the imides' absorption peaks are dominant: 1780 cm^{-1} (C═O asym. stretch), 1720 cm^{-1} (C═O sym. stretch), 1380 cm^{-1} (C–N stretch), and 725 cm^{-1} (C═O bend), and the amide coupling and carboxylic acid anhydride absorption peaks are disappeared.

The main problem in the characterization of films PMDA/ODA by FTIR is the quantification of ODA-concentration in the film. In fact, high intensity peaks corresponding to ODA are concomitant with aromatic nuclear vibrations, and are not affected by ODA evaporation rates in the reaction, which impedes the appreciation of ODA-excess in the film. Quantifying the PMDA is easier, as it is characterized by the vibration peaks corresponding to carbonyl anhydride [10,11].

3.3. Optical and scanning electron microscopies

Samples are observed with an Optical Microscope Leica DM 4000 M, to appreciate details of the thin film, and analyse homogeneity of the deposition. Fig. 6 shows the film of PI deposited on processed Si, where the effect of poly(amic acid) dehydration can still be appreciated. The figure shows an excess on the heating cycle speed, enhancing the traces of the reaction. The picture also shows that by-products of the monomers remained on the sample without reacting (monomers crystals surrounded by polyimide film).

SEM (model ZEISS DSM 940) lets observe depositions details clearly, and shows how crystals have remained on the films. Efforts in the deposition and curing technical have still to be done, to obtain optimal films (cf. Fig. 6 A and B).

4. Conclusions and perspectives

Experimental results showed a viable method to synthesize polyimide films from a CVD process. This technique does not involve any solvent operation. Polyimide films are experimentally prepared from a dry synthesis process, with the advantage of working at ambient conditions (atmospheric pressure). FT-IR

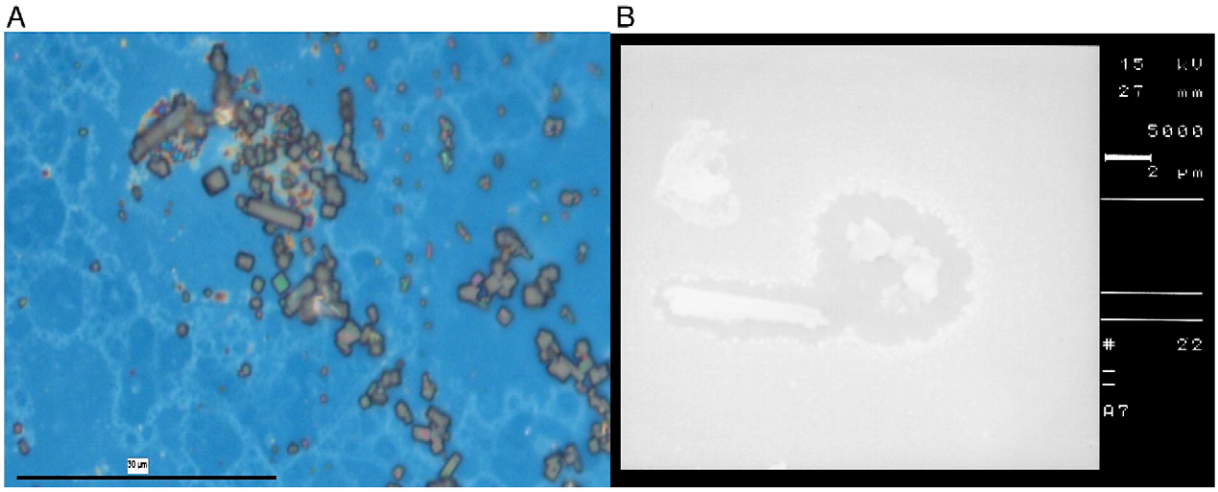


Fig. 6. A Microscope and B SEM pictures of the deposition. (Homogenous film and no reacted monomers on the surface).

spectroscopy and Microscopy analyses highlighted certain limits for the deposition (presence of crystallized monomers on the film); nevertheless, as contact angle measures show, samples surfaces were macroscopically homogeneous on planar substrates.

As it has been already done in other CVD deposition studies [1], overcoming experiments will evaluate gap-filling and step coverage characteristics of the deposited PI films on 3-D substrates. A complementary study by experimental design will be investigated to determine the range of deposition conditions guaranteeing an optimal deposition.

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