# Synthesis and Characterization of Polyimide Thin Coatings Deposited by Means of a Standard RF-Magnetron Sputtering Equipment

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## ABSTRACT

A conventional radio frequency magnetron sputtering (RFMS) equipment has been employed to synthesize thin PMDA-ODA (pyromellitic dianhydride-oxydianiline) and BPDA-PDA (biphenyl tetracarboxylic dianhydride-paraphenylenediamine) polyimide (PI) coatings. Several polyimide coatings with thickness ranging from 200 nm to 3 µm have been deposited onto silicon single crystals, sapphire and polyimide substrates. SEM micrographs of these coatings show a homogeneous and crack-free surface. Fourier transform infrared spectroscopy (FTIR) reveals that the as-deposited films are made of polyamic acid and not-reacted monomers, while the imide peaks appear clearly only after a thermal treatment (typically 200°C, 1 hour, in air or argon). The electrical properties of the polyimide coatings (i.e. bulk and sheet resistivity and dielectric breakdown voltage) are those typical of an insulating material and comparable with the bulk material. The polyimide films are characterized by good adhesion to the silicon, sapphire and polyimide substrates. The friction coefficient of the deposited PMDA-ODA films, measured by the Micro-Scratch Test method, is very low, as compared with the vapor deposited polyimide coatings, making these coatings very interesting for low friction applications. The resistance to some chemicals like acetone, hydrogen peroxide, nitric and hydrofluoric acid has been also tested.

## INTRODUCTION

Polyimides are very attractive materials for applications in many fields of the chemistry and physics research, ranging from aerospace and medical applications to microelectronics, owing to their excellent thermal stability, dielectric properties and chemical durability.

Several methods are now used to prepare polyimide coatings. The formation of the films from a liquid solution [1], which can be considered the conventional method, suffers from several problems: the solvent is partially retained in the film and the control of the film thickness is difficult.

The deposition of polyimide films by vapor deposition polymerization (VDP) is an interesting alternative method [2] in that it enables a good control of the film thickness and provides coatings with superior electrical characteristics [3] as compared with the conventional method. However, the films have relatively low molecular weight (~13000) and contain considerable amount (≥20%) of isoimide [2,4].

The ionized cluster beam deposition (ICBD) technique [5] allows to obtain PI films with the maximum imidization, negligible impurities (~1% isoimide) and good crystalline structure.

The conventional sputtering technique, successfully employed by several authors to deposit polymeric films like polytetrafluoroethylene, failed when applied to deposit polyimide layers. Using a 13.56 MHz radio frequency power source (120-300 W), argon gas (0.133-13.3 Pa) and a 200 µm thick Kapton™ polyimide film as the target material, Kitoh *et al.* [6] obtained a sputtered film with a molecular structure very different from that of the target: the imide ring structure decomposed, the carbon component (as measured by XPS) increased and the nitrogen and oxygen components clearly decreased in comparison with the target ones. These results were confirmed by Hishmeh *et al*. [7] who found that both parts of the PI molecule (imide group and ether) are completely destroyed. Moreover, they discovered that the target structural damage depends on the sputtering $Ar^+$ ion energy in the energy range 0.5-2.0 keV: below 500 eV the PI molecule appears to maintain its integrity and the damage of intramolecular bonds is negligible. This dependence was previously recognized by Sengupta *et al.* [8] who observed a preferential sputtering of carbonyl groups with a relatively small loss of nitrogen, and a decrease of the concentration of imidic groups accompanied by an increase in the isoimide and amide functional groups concentrations. Using $Kr^+$ ions at low energy and low pressure the creation of an undamaged polyimide structure has not been possible [7].

With a different approach to the ion-solid interaction process we succeeded in obtaining polyimide films using a conventional magnetron sputtering equipment. One of the most important effects of the ion and electron bombardment is, indeed, the target surface heating: it is in fact necessary a continuous target cooling to prevent the demagnetization of the permanent magnets or, in extreme cases, target melting. Because target heating induces the sublimation of volatile species [9], we used pyromellitic dianhydride (PMDA) and



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4,4'-oxydianiline (ODA) powders as target material instead of a polyimide film or bulk disks. Due to their weak bond the monomer molecules sublime and deposit onto the substrate producing a film constituted by a mixture of polyamic acid and not-reacted monomers. During the following curing treatment carried out at 200°C for 1 hour in air, the as-deposited film becomes a polyimide coating through the condensation reaction. Our FTIR results [10] indicate that the monomer molecules are not damaged during their travel through the plasma region from the target to the substrate.

In this work we present some preliminary physico-chemical properties of the PMDA-ODA polyimide films obtained by this method that will be named "Glow Discharge induced Vapor Deposition Polymerization" (GDVDP): in particular we report the friction coefficient and critical load, the bulk and sheet electrical resistivity, the dielectric breakdown voltage and the chemical durability of the coatings.

## EXPERIMENTAL

The experimental set-up used for the polyimide coatings deposition consisted of a stainless steel vacuum chamber evacuated by a rotary pump to a base pressure of 0.1 Pa. The glow discharge device was constituted by a 2-in. diameter planar magnetron sputtering source, connected to a radio frequency power supply (600 W max, 13.56 MHz), through an automatic matching box. The PMDA and ODA (97% purity, provided by Sigma-Aldrich®) powders were mixed and uniformly placed on the surface of a copper target, positioned on the conventional sputtering source. The substrates (silicon single-crystals, sapphire and polyimide) were placed on an aluminium sample holder at ground potential. The target-substrate distance could be modified in the range from 2 to 15 cm. Helium gas was chosen as glow discharge gas because of its very low erosion rate and high chemical inertness. The direct sputtered particles flux is thus minimized. The pressure in the chamber was measured by means of a capacitive gauge.

The curing treatments of the as-deposited films were performed in a pyrex-glass tube furnace at 200°C for about 1 hour in argon or in air.

The films thickness was determined by means of a stylus profilometer (Tencor Instruments, model Alpha-Step 200). Infrared analysis on films deposited on double sided polished 500 mm thick silicon wafers was performed using a FT-IR Nicolet 5DCX spectrometer with 2 $cm^{-1}$ resolution.

The mechanical properties of PI films (friction coefficient and critical load) were determined by a CSEM Micro Scratch Tester instrument (MST), which generates scratches on the sample to be tested using a diamond hemispherical indenter drawn under either constant or increasing load in the range 0.02 to 30 N. The measurement of the acoustic emission, frictional force and penetration depth of the indenter permits to study the adhesion of the coating-substrate system.

The electrical measurements were performed in a vacuum chamber ($5x10^{-4}$ Pa) at room temperature with an electrometer (Keithley Instruments, model 237 High Voltage Source Measure Unit). For the volume resistivity and dielectric breakdown voltage measurements a polished silicon substrate was coated by a thin (400 nm) evaporated gold film. Then a GDVPD polyamic acid film was deposited on the sample and, after curing, circular gold electrodes (1 mm diameter) were evaporated on the polyimide film surface. Each measurement was performed by biasing each circular electrode at positive voltage with respect to the lower backplane electrode. For the sheet resistance measurements gold parallel rectangular electrodes (0.57 mm far apart) were evaporated on the polyimide film deposited on a sapphire polished substrate.

The chemical tests were performed by using as a guideline the ASTM D1239-92 prescriptions. A temperature and humidity controlled chamber (BLUE M Electric, model VP-100RAT-1) was used for carrying out the experiments. Both the prepared chemical solutions and the samples were kept at the fixed temperature and humidity conditions of the treatment before immersion for at least one day. Each test was performed in such a way to keep constant the ratio solution-volume/sample-surface (8 $ml/cm^2$) with 400 ml of each chemical solution.

A precision micro-balance with sensitivity 0.01 mg has been used for weighing each sample before coating, before and after curing and after the chemical treatments.

The surface morphology has been inspected by optical and scanning electron microscopy (SEM) before and after each chemical treatment.

## RESULTS AND DISCUSSION

The FT-IR spectra of a PMDA-ODA coating before and after curing are reported in Figure 1: the peaks at 1240 $cm^{-1}$ (aromatic ether C-O stretching) and at 1500 $cm^{-1}$ (aromatic ring stretching) are clearly visible. The broad band around 1650 $cm^{-1}$ (amide groups) clearly decreases after curing indicating a progressive formation of imide groups. This fact is confirmed by the appearance of the typical imide peaks at 1780, 1725 and 1380 $cm^{-1}$.

Several 2.0±0.2 μm PMDA-ODA thick films have been deposited in order to perform the dielectric breakdown tests and the other electrical measurements. The deposition parameters are summarized as follows: He pressure 8 Pa, target-to-substrate distance 6 cm, DC self-bias -20V÷-30V, obtained by applying a RF power of 12.6 W for 2 min followed by 4 min at 17.6 W and 4 min. at 26.6 W for a total time

duration of 10 minutes. The results of the breakdown tests indicate that the dielectric strength of the deposited films is $2.9x10^2$ V/μm (± 20%), this being the average datum over many tests in different sample regions. At a polarization voltage of 100V the steady state volume resistivity of the coatings resulted $9.5x10^{15}$ Ωcm (±10%). The sheet resistance obtained following the ASTM D257-93 prescriptions resulted $2x10^{15}$ Ω/square. These results show that the GDVDP PMDA-ODA films have electrical properties comparable to those obtained by other methods and thus can be used as insulating thin layers in many technological applications.

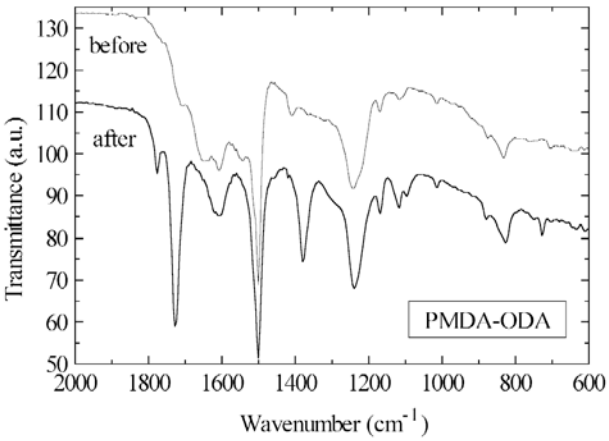


Figure 1. FT-IR spectra of a PMDA-ODA polyimide coating deposited by GDVDP, before and after curing.

The mechanical properties of the GDVDP layers show clear improvements over those of the VDP PI films [11]. The results obtained by means of the micro-scratch tester with a Rockwell C diamond tip of 800 μm radius at 50% relative humidity at room temperature, indicate that the friction coefficient was 0.12, at least four times lower than that of the VDP coatings (Figure 2). The critical load $L_C$ for coatings of thickness of 1.3 μm, ranges from 7 to 10 N for the GDVDP coatings while for the VDP films of comparable thickness it was between 1.0 and 1.5 N. Above the critical load the film visibly detached from the substrate. A variation of friction coefficient of the VDP coatings was observed once the film detached from the silicon substrate. For GDVDP coatings, this variation was not so clear due to the comparable friction coefficient of coating and substrate.

The improved mechanical features of these layers can be attributed to the particular method of synthesis characterized by the presence of a plasma containing several forms of radiation including UV photons, low and high energy electrons and helium ions. The presence both in the plasma and in the coatings of fragmented carbon-rich radicals or sputtered hydro-carbon groups must not be excluded because of the interaction with the mentioned radiation either in the solid or gas phase. These species, partially removed by the curing step, can allow for a composite microstructure with improved wear resistance and hardness. The low energy bombardment of the growing film surface by the plasma ions and electrons can influence the balance of polyamic acid, not-reacted monomers and carbon rich fragments that can be partially retained by the following curing process; thus the adhesion and hardness properties of these layers can be easily tailored to the specific needs by controlling the electric potential of the samples with respect to the plasma potential. This can be accomplished by RF biasing the sample holder during the deposition or at the early stages of the deposition.

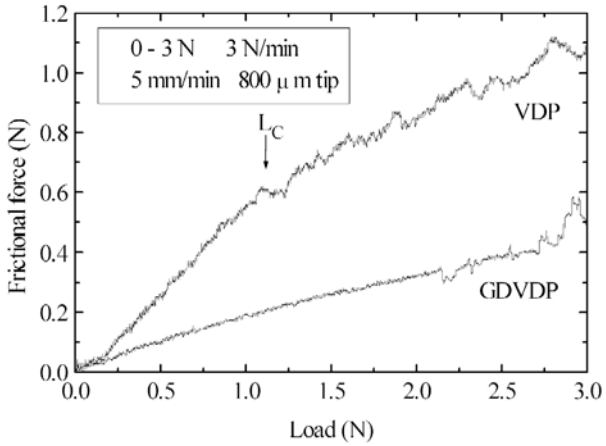


Figure 2 Frictional force *vs* normal load for a VDP and a GDVDP PMDA-ODA polyimide coating deposited on Si. The critical load indicating the film detachment from the substrate for the GDVDP is not shown because it was observed at loads between 7 and 10 N.

The resistance to chemicals of the GDVDP PMDA-ODA coatings has been investigated by analyzing the performance of a PMDA-ODA film deposited on Si single crystals (2 cm x 2 cm x 0.5 mm) and on Upilex-R™ substrates (2 cm x 2 cm x 40 μm). The films deposition were carried out with the following parameters: 8 Pa helium pressure, 6 cm target-to-substrate distance, -60V÷-70V DC self-bias obtained with a stepwise increase of the RF power from 15.8W to 29.7W for a total time duration of 10 minutes for Si substrates and -70V÷-180V DC self-bias obtained with a stepwise increase of the RF power from 27.5W to 39.4W for a total time duration of 8 minutes for Upilex-R™ substrates. After the deposition the samples have been cured at 200°C in air for 1.5 hours. Both coated and uncoated Si samples have been exposed to a 3% m/v aqueous solution of $H_2O_2$ and to a 6.5% m/v solution of $HNO_3$ at 28 °C.

Each immersion lasted 24 hours; after each immersion the samples have been rinsed in deionized water and dried in air

(for 77 h in the case of $H_2O_2$, and 40 h in the case of $HNO_3$). After each treatment no microscopic variation of the surface morphology has been observed in the samples. No mass variation has been detected after exposure to $H_2O_2$, while the films exposed to $HNO_3$ underwent an average +15% mass increase. Both coated and uncoated Upilex-R™ samples have been immersed in acetone 99% and in a 20% m/v HF solution at 25°C. Each immersion lasted 24 hours; after each immersion the samples have been heated in air at 50°C for 24 h. No change in the surface morphology has been detected and, with respect to the uncoated Upilex-R™, no loss of mass has been observed.

## CONCLUSIONS

By using a standard magnetron sputtering apparatus using a He glow discharge it was possible to deposit thin solvent-free polyimide PMDA-ODA layers. The target material was a mixture of the monomer powders. The PI formation process required a curing of the deposited layers at about 200°C.

After this treatment the electrical properties of the layers are comparable to those obtained by other methods and in particular by means of the solvent-free VDP process.

The adhesion of the GDVDP layers is much better than that of VDP coatings. The friction coefficient against diamond is 0.12 (a factor of 4 lower than that of VDP coatings).

The chemical durability of the GDVDP layers has been tested. These tests showed no weight loss after immersion for 24 h in acetone and in aqueous solutions of either $H_2O_2$ or HF.

The GDVDP synthesis method has been successfully used to grow also other kinds of polyimide coatings [12] like BTDA-ODA, BPDA-ODA, BPDA-PDA. As an example in Fig. 3 are reported the FT-IR spectra of a BPDA-PDA coating before and after curing.

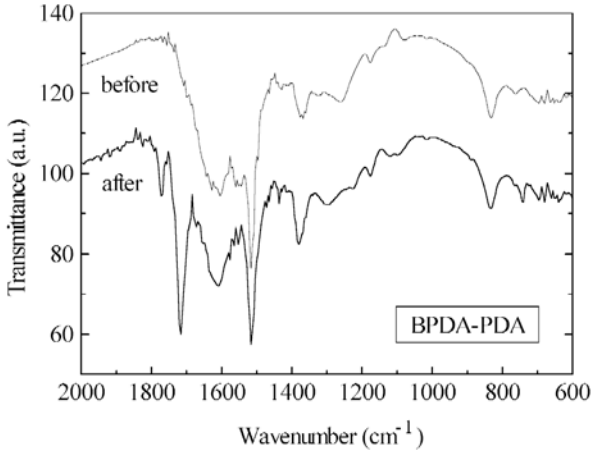


Figure 3. FT-IR spectra of a BPDA-PDA polyimide coating deposited by GDVDP, before and after curing.

The GDVDP method can be successfully used for preparing polyimide co-polymers and quite easily can be used in a conventional co-sputtering system for co-deposition of PI with metals or ceramic materials.

**REFERENCES**


1. C.E. Sroog, J Polym Sci: Macromol Rev, 1976, 11, 161.

2. Y. Takahashi, M. Iijima., K. Inagawa and A. Itoh, J Vac Sci Technol, A5, 2253 (1987).

3. J.R. Salem, F.O. Sequeda, J. Duran, W.Y. Lee and R.M. Yang, J Vac Sci Technol, A4, 369 (1986).

4. R.N. Lamb, J. Baxter, M. Grunze, C.W. Kong and W.N. Unertl, Langmuir, 4, 249 (1988).

5. K.W. Kim, C.E. Hong, S.C. Choi, S.J. Cho, C.N. Whang, T.E. Shim and D.H. Lee, J Vac Sci Technol, A12, 3180 (1994).

6. M. Kitoh and Y. Honda, Thin Solid Films, 271, 92 (1995).

7. G.A. Hishmeh, T.L. Barr, A. Sklyarov and S. Hardcastle, J Vac Sci Technol, A14, 1330 (1996).

8. K.S. Sengupta and H.K. Birnbaum, J Vac Sci Technol, A9, 2928 (1991).

9. J.L. Vossen and J.J. Cuomo, "Glow Discharge Sputter Deposition," in Thin Films Processes, ed. by J.L. Vossen and W. Kern, Vol. 1, p. 22, Academic Press, New York, 1978.

10. G. Maggioni, S. Carturan and V. Rigato "Polyimide Films by Glow Discharge Vapor Deposition Polymerization," submitted to Mater. Lett. (1998).

11. G. Maggioni, S. Carturan, D. Boscarino, G. Della Mea and U. Pieri, Mater Lett, 32, 147 (1997).

12. Italian Pat. Application #PD97A000244 (October, 1997).