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Abstract- In this research we describe the preparation of polyimide with pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (PDA) thin films by physical vapor deposition. For this study, FTIR Spectrometer has been used to measure the effect of imidization temperature on the chemical structure of vapor-deposited thin films of the aromatic PI. When temperature increases, a general increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. The surface topology of the PI films was further examined by using AFM atomic force microscopy as a function of the imidization temperature at 150,200,250°C for 1 hour each, it can be clearly seen that the surface became rougher with increasing imidization temperature.

The thermal stability of polyimide was also improved by using Thermo gravimetric analysis (TGA).

Keywords: polyimide thin films, thermal imidization temperature, thermal evaporation, polycondensation reactions.

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SYNTHESISANDCHARACTERIZATIONOFPOLYIMIDETHINFILMSBYTHERMALEVAPORATIONANDSOLIDSTATEREACTIONS

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Synthesis and Characterization of Polyimide Thin Films by Thermal Evaporation and Solid State Reactions

Ikram Atta AL-Ajaj [α] & Aseel A. Kareem[σ]

Abstract- In this research we describe the preparation of polyimide with pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (PDA) thin films by physical vapor deposition. For this study, FTIR Spectrometer has been used to measure the effect of imidization temperature on the chemical structure of vapor-deposited thin films of the aromatic PI. When temperature increases, a general increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. The surface topology of the PI films was further examined by using AFM atomic force microscopy as a function of the imidization temperature at 150, 200, 250°C for 1 hour each, it can be clearly seen that the surface became rougher with increasing imidization temperature.

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I. Introduction

Polyimides are one of the most important classes of high temperature polymers available today. They find wide spread application due to the wide range of chemistry and properties accessible [1]. Innovative polyimide design has led to their use in aerospace, microelectronics, automotive and packaging industries [2]. Polyimides have become important materials in the manufacture of a large number of technical products, e.g. varnishes, coatings etc, due to their excellent thermal stability and mechanical strength, high stability to ionizing, good film forming ability, and superior chemical resistance [3]. Since the excellent properties of polyimides are a result of combination of both chemical structure and final morphology of the products, it is important to understand the structural evolution within the material during imidization process, which directly affects the final thermal, mechanical and optical properties [4]. Polyimides are step or condensation polymers derived from both aliphatic or aromatic dianhydrides and diamines[5].

In this research polyimide films prepared by the vapor deposition, which are prepared by the reaction of a dianhydride and diamine mixture, which by solid state reactions is converted to polyimide by thermal treatment usually below 300°C.

Vapor deposition of the precursors and solid state reactions of imidization are of a greater priority than the spin coating and dipping methods.

The physical vapor deposition as a "dry" method provides high purity for producing thin polymer films of controlled thickness, ratio of precursors and composition control of the so prepared layers [6]. The aim of the present work is to study, FTIR Spectrometer has been used to measure the effect of imidization temperature on the chemical structure of vapor-deposited thin films of the aromatic PI PMDA–PDA. AFM has been used to elucidate the effect of heating subsequent to imidization of PI.

Thermal degradation processes were also investigated through dynamic thermogravimetric analysis at different heating rates.

II. Polyimide Synthesization

Polyimide is synthesized by a two-step reaction, as shown in Fig. 2. In this work, pyromellitic dianhydride (PMDA) and p-phenylene diamine (PDA), which are commercially available from Sigma-Aldrich. These two monomers, 2 gm each, were evaporated from two separated boats to form a poly(amic acid) (PAA) thin film on substrate. The substrates used were silicon wafer and glass.The deposition process began at vacuum of 2 X 10^{-5} mbar. Figure 1 shows the scheme of the PVD apparatus. The resultant polyamic acid PAA film was then soft baked to remove nH_2O from the substrate followed by a thermal treatment at (150, 200 and 250°C) for 1 hour each in an air circulating oven.

In the case of PI the purpose of the thermal treatment is the run of polycondensation reactions in solid state till completion of the PI formation. As a consequence of these reactions leading to a release of water and imidization also a certain pack of the layer is achieved. The final thickness of films is 5±0.1 μm.

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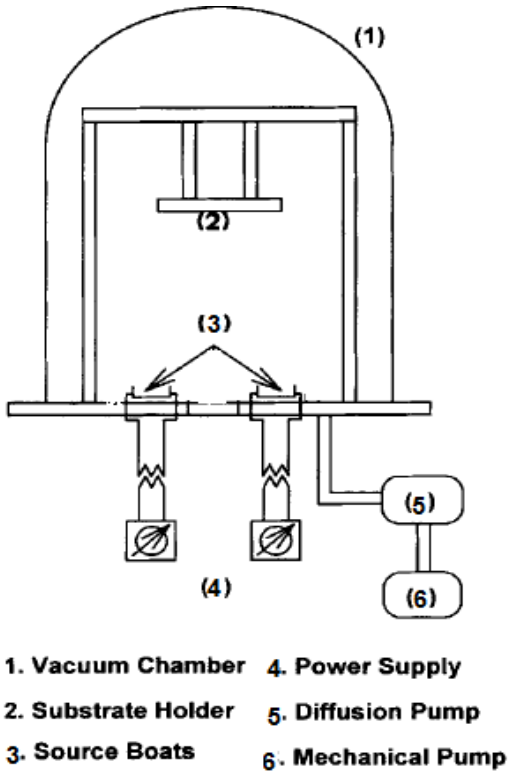

Figure 1 : schematic illustration of the PVD chamber

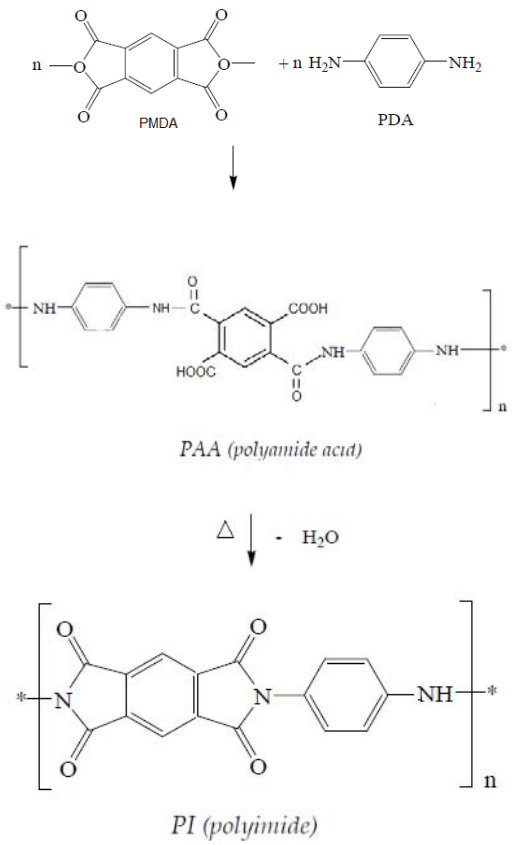

Figure 2 : Synthesis of Polyimide in two steps

III. Results and Discussions

a) FTIR Analysis

FTIR measurements have been performed for different imidization temperatures to determine the completion of the imidization reaction of the polyimide films. This analysis rests on the transmission peak magnitude changes in the functional groups or in the characteristic linkages during the reaction. Figure 3 shows the changes in FTIR spectra of PMDA-PDA for different imidization temperatures(150, 200 and 250°C) for 1 hour each.

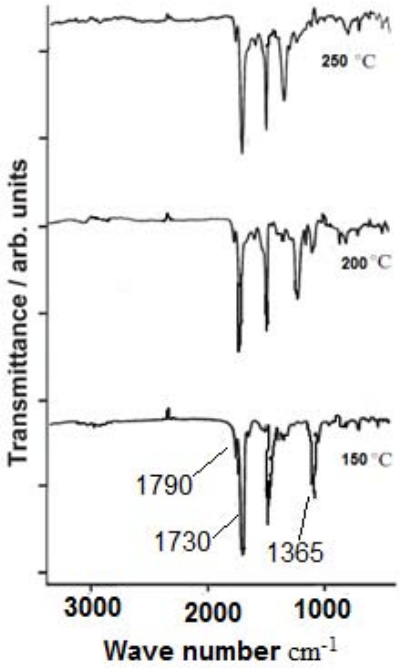

Figure 3 : FTIR spectra of PMDA-PDA for different imidization temperature

When temperature increases, a general increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. This evolution is stabilized after exposure to temperature above 250°C[3,7].

Spectra have been normalized to the classical aromatic ring C=C absorption band appearing around 1500 cm^{-1}, and the absorption peak at 1365 cm^{-1} (C-N) stretching vibration of imide ring was monitored during the curing from PAA to PI. The absorption peaks at 1790 cm-1 and 1730 cm^{-1} indicated that there was asymmetry and symmetric stretching vibration of C=O bondings. The absorption peak at 710 cm^{-1} was the flexural vibration of C=O bonds. [8,9].

b) Atomic Force Microscopy (AFM)

The AFM analysis also provides information on the changes in the surface morphology and roughness introduced by the heat treatment. Fig. 4 shows the AFM

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topographic images of the polyimide films and those subjected to imidization temperature150, 200 and 250°C for 1 hour each.

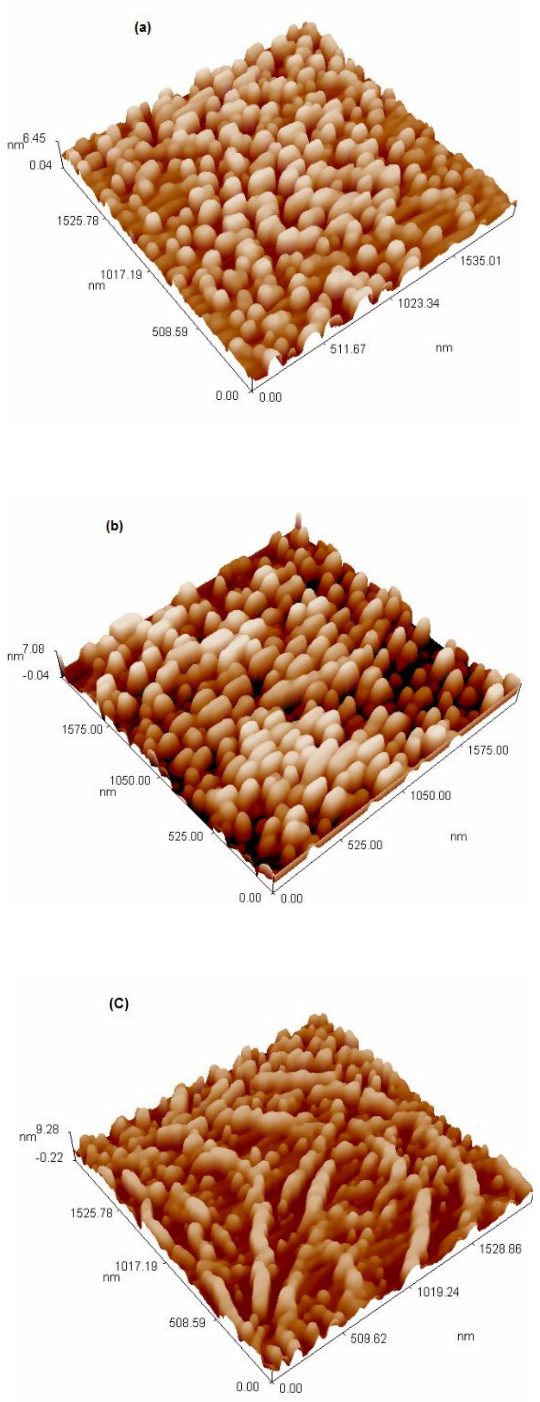

Figure 4 : 3-D AFM images PI thin films The respective imidization temperatures from (a) to (c) are 150, 200 and 250°C

It can be clearly seen that the surface became rougher with increasing imidization temperature, creating a distinctive surface structure[10]. This indicates that films of PAA and fully cured PI have comparable roughness and thickness uniformity; i.e. curing does significantly roughen the surface for the conditions used in this work.

The surface topology of the PI films was further examined by using AFM. nodular aggregates are aligned in several row[11]. Moreover, the area of the dark spots, indicating the troughs on the surface increased when the imidization temperature increase, for instance, some kind of decomposition occurs at the elevated temperatures before the imide chain decomposition [6,12].

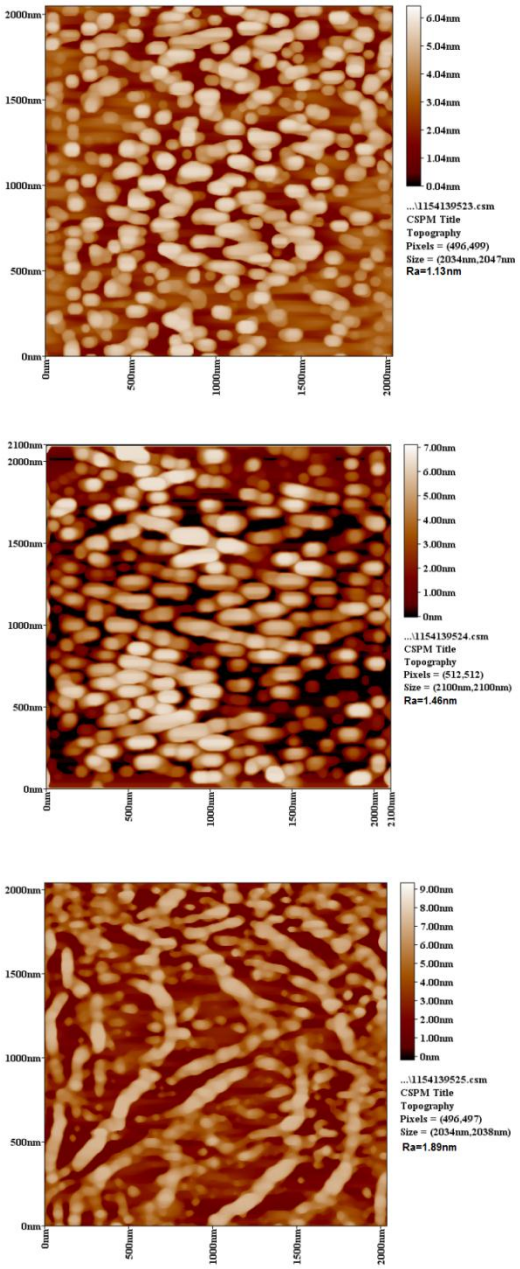

Figure 5 : 2-D AFM images PI thin films The respective imidization temperatures from (a) to (c) are 150,200 and 250°C

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c) *Thermal Stability*

Figure 6 showed the weight loss of the PI with temperature at a heating rate of 10℃ /min as measured by TGA in air

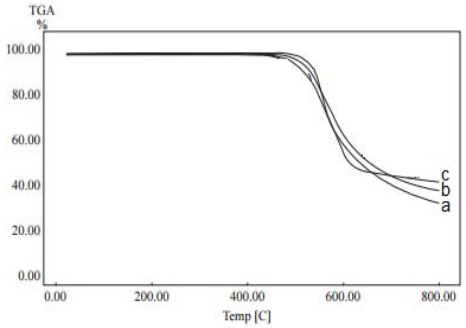

Figure 6 : TGA curves of PI thin films The respective imidization temperatures from (a) to (c) are 150,200 and 250°C

The three curves in the figure indicate the thermal stability of PI which had a thermal imidization temperature at 150℃, 200℃ and 250 ℃ for a,b and c respectively

It can be observed from Figure 6 that the temperature, at which weight loss of occurred, 490℃, 520℃ and 542℃ for PI-a, PI-b and PI-c respectively, a continuous weight loss in the initial stage may be attributed to the evaporation of the preabsorbed water and solvent in the film[9]. It was also found that the temperature of thermal weight loss of was raised with the increasing of thermal imidization temperature of PAA. weight loss becomes more marked, indicating the occurrence of imidization.

The result implied that imidization temperature had a significant influence on thermal weight loss [13,14]. At above 580oC, the sample starts to decompose drastically. For the conventional film, as shown in Figure 6, the rapid weight loss at above 490°C may result from ongoing solvent evaporation and imidization. until decomposition takes place at 585°C[4,15].

IV. Conclusions

In this research polyimide films prepared by the vapor deposition, which are prepared by the reaction of a PMDA-p-PDA mixture, which by solid state reactions is converted to polyimide by different imidization temperature . When temperature increases, a general increase in all the absorption peaks is observed by FTIR. The AFM analysis also provides information on the changes in the surface morphology and roughness introduced by the heat treatment. The thermal stability of polyimide was also improved .The thermal properties of all polyimides were varied, depending on the structure of the monomer and following the stiffness of the polymer backbones makes the polymer thermally stable with increased solubility.

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