Partially ionized beam deposition of parylene

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Abstract

Conventionally deposited parylene C polymer thin films have excellent properties, including moisture barrier, toughness and electrical insulation characteristics. However, their use has been restricted by poor adhesion to most smooth or non-porous substrates characteristic of earlier deposition processes [H. Yasuda, B.H. Chu, D.L. Cho, T.J. Lin, D.J. Yang, J.A. Antonelli, Corros. Sci. 52 (3) (1996) 169. [1]]. In spite of this adhesion problem, parylene C has the proven ability to provide excellent environmental protection on electronic circuit boards for computer and general industrial products for which adhesion is enhanced by separate means. In addition to environmental protection, parylene will also encapsulate any solders that may be present and prevent them from causing shorting problems, and it is effective in very thin layers [R. Olson, Society of Vacuum Coaters, in: Proceedings of 31st Annual, May 2–6, 1998. [2]]. The work here shows that the adhesion between parylene C films and substrates can be greatly improved by ion-assisted deposition in which the parylene monomers are ionized and accelerated to the substrate during film growth. Solid parylene C is vaporized at 134 °C to a dimeric gas, and pyrolyzed to cleave the dimer to a monomer at 680 °C. The monomeric gas is ionized and accelerated toward the substrate by an electric field, and finally parylene is polymerized with some penetration into the substrate surface to improve the adhesion.

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1. Introduction

Strong, stable adhesion of polymer thin film coatings is of vital technical significance in a great diversity of applications. Polyimides have been used widely in the past as a good dielectric for multilayer printed wiring boards [3–5]. Another such coating material is parylene, which is a general term used to describe a class of poly-p-xylylenes derived from a dimer precursor having a structure of two benzene rings. Due to their ability to form thin films that can conform to substrates of varied geometric shapes, parylene polymers are ideally suited for conformal coatings in a wide variety of fields [6]. Conformal coatings can serve as protective electronic assemblies where high reliability and long switching life is required [7,8]. Parylene has also found its way into commercial and industrial uses because its material properties suit it to serve as a protective coating. The most important application of parylene is a conformal coating for printed wiring assemblies. The coatings exhibit stable dielectric properties over the wide range of temperatures in which military hardware is expected to perform. They also possess a low dielectric constant minimizing the unwanted loading of high frequency tuned circuits [9,10].

One of the problems that has restricted previous use of parylene C was its poor adhesion to most metals and non-metal surfaces. Poor adhesion lowered the life and stability of films and did not protect surfaces from abrasion, wear and corrosion. Prior work has successfully improved the adhesion between copper and parylene N using partially ionized beam (PIB) of copper atoms [11,12]. However, in most applications, parylene films need to be deposited onto smooth and metallic materials. The prime objective of this work is to improve the adhesion of parylene C onto smooth metallic surfaces and thereby protect the surface.
There are three common commercial forms of the parylene polymers. There are parylene C (C₈H₈Cl), parylene N (C₈H₈) and parylene D (C₈H₈Cl₂). Parylene C is selected for the work presented here. The newly developed parylene deposition system and method can also be used for the other forms of parylene. Fig. 1 shows an existing industrial type of parylene coating system used with parylene C, D, and N. It typically consists of three chambers. In the vaporization chamber, parylene vaporizes and forms a dimeric gas and subsequently enters into the pyrolysis chamber where the dimeric gas is cleaved into monomer form. The monomer vapor is deposited onto a substrate and polymerizes into a thin film coating.

![Fig. 1. The conventional parylene deposition system.](image)

2. Experimental

Fig. 2 shows the design of the new parylene deposition system. The main elements of the system are the evaporator, pyrolysis tube, ionizer, accelerating plates, and substrate mounting assembly.

The evaporator is located completely within the vacuum deposition chamber. It is a cylindrical container made of stainless steel with an inner diameter of 20 mm and height of 15 mm. The evaporator can be filled with up to 3 g of parylene C dimer. The evaporator is heated by means of a surrounding tungsten filament that is powered by a dc voltage supply. The desired evaporation temperature is 134 °C for evaporation into dimeric gas. The pressure in the deposition chamber is maintained at 3 × 10⁻⁶ torr.

The pyrolysis tube is a 2 mm diameter tungsten tube through which the evaporating dimer vapor escapes. This tube is also surrounded by a filament that is used to heat the tube to 680 °C to enable pyrolysis (thermal decomposition) of the dimers into monomers. The pyrolysis tube has an outer diameter of 4 mm and a total length of 115 mm.

Pyrolized monomers escape from the pyrolysis tube and enter the ionizer located immediately above it. The ionizer consists of a cylindrical housing carrying a tungsten grid of fine wire surrounding the center. The grid stands on four steel rods attached electrically as well as mechanically to the bottom of the ionizer. A heated tungsten filament sur-

![Fig. 2. The new ion-assisted parylene deposition system.](image)
Fig. 3. The electrical connections of the new ion-assisted parylene deposition system.

Fig. 4. The flow of parylene molecules from the evaporator to the substrate.
rounds the grid and emits electrons that are attracted to the grid by an applied ionizer bombardment voltage of 200 V. Some electrons encounter the grid, but most of them pass through it to interact with the monomer beam to form positive monomer ions and background gas.

The ionized monomers are accelerated toward the substrate by applying accelerating voltage to the ionizer housing. It is possible to deflect the accelerating ions by applying voltage to the deflection plates shown in Fig. 3. However, in this experiment, the ionized beam was not deflected and, neutral and ionized parylene monomers followed a direct path toward substrate.

There are three substrate wires that are located right below the substrate. They may be used to detect ionized molecules arriving at the wires. Fig. 3 shows the electrical connections of partially ionized system.

![Image](image.png)

Fig. 5. The roughness comparison of ionized and accelerated parylene film with conventionally deposited parylene film.
Fig. 4 shows the flow of parylene molecules from the evaporator to the substrate. A fraction of the parylene monomers are ionized and accelerated toward the substrate at high energy. The remaining, neutral fraction arrives at the substrate at the low energy characteristic of evaporation processes. With the deflection voltage set at zero, the ionized and neutral molecules both follow straight paths to the substrate. It is expected that the ionized, accelerated monomers with have some penetration into the substrate.

3. Results

The surface analysis of films deposited using the conventional and ionization methods was analyzed by the atomic force microscope (AFM). The change in chemical compositions and cross-linking of partial ionized methods were investigated using Fourier transform infrared spectroscopy (FTIR) and ellipsometry. An adhesion test on both films was also conducted.

Fig. 5 shows 2 μm x 2 μm atomic force microscopy (AFM) scans of two different parylene C films deposited identically except for ionization and acceleration. The films are approximately 200 nm thick. The upper image (5(b)) shows a parylene C film deposited without ionization (as in conventional methods), and the lower image (5(a)) shows a film deposited using ionization and acceleration. The surface of the film deposited with ionization and acceleration appears much smoother than that of the film deposited without using accelerated ions.

Parylene monomers were partially ionized by electron bombardment.

In order to be certain that these high energy electrons did not cause any ion fragmentations resulting the deposition of other forms films, Fourier transform infrared spectroscopy (FTIR) parylene films was conducted (Fig. 6). A Scotch tape test method was used to compare the adhesion of the two different parylene C depositions. The outcome of the test was grossly divided into three levels of adhesion as follows: (a) weak adhesion – the film completely removed from the substrate, (b) median adhesion – the film is partly removed or removed in patches and (c) strong adhesion – no observable part of the film is removed from the substrate. Scotch tape was pressed onto the film and then pulled up while the substrate was held firmly. The films deposited without ionization and acceleration were weakly adherent and were completely removed from the silicon substrate on all tests. By contrast, ionized and accelerated films were strongly adherent and were not removed at all from the silicon substrate. Fig. 6 shows both ionized/accelerated and conventionally deposited parylene spectra.

Ellipsometry was also used to find the index of refraction of ionized and accelerated parylene films. The index of refraction of the ionized and accelerated film was 1.648 at the wavelength of 632.8 nm compared to 1.639 for the conventionally deposited films at the same wavelength.

4. Discussion

Closer investigation of the conventionally deposited parylene film (Fig. 5(b)) reveals that the vertical height between the lowest valley and highest peak is more than 150 nm which is very rough as it is approximately 75% of the maximum film thickness (Fig. 5(a)). The roughness of
ionized parylene file is much less, on the order of 20 nm. Note that both images are displayed at the same vertical scale.

FTIR of both ionized/accelerated and conventionally deposited films shows a slight difference in energy level between these two spectra (shown in Fig. 6), but the exact location of each peak is very close to the same wavenumber which reveals very similar types of chemical bonds for the two parylene films confirming that significant fragmentation did not take place.

The difference in the index of refraction of ionized/accelerated and conventional films was very small, about 0.5%, which indicates a very similar optical property and also comparable the degree of cross-linking and types in the structure of ionized and accelerated parylene films.

The results of Scotch tape demonstrate that the partially ionized and accelerated parylene films had much better adhesion than ones deposited without ionization. Further testing to establish a quantitative measure of adhesion is called for.

5. Conclusions

1. Ionized parylene C was deposited in a vacuum by ionizing pyrolized monomers.
2. An accelerating voltage of 100–200 V achieved super-thermal condensation of the ionized monomers.
3. The partially ionized parylene C deposition improved the adhesion between the film and substrate.
4. This work showed that the ion-assisted parylene C results in smoother films in comparison to conventionally deposited films with significant enhancement in the surface roughness.
5. FTIR and ellipsometry of the ion-assisted parylene C revealed similar chemical compositions and optical property.

References