

論文内容の要旨

論文題目 : **Parylene thin film directly deposited on liquid**

(液体への直接蒸着有機膜の研究)

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1. Introduction

This work aims to study the Parylene thin films that are deposited directly on liquid surfaces (hereafter referred as Parylene-on-liquid-deposition Parylene thin films or POLD Parylene thin films). Compared to conventional application of Parylene, in which, Parylene is deposited on solid substrates often for coating purposes, the most important distinction of POLD Parylene thin films is that they are formed on liquid surfaces, which largely modifies their mechanical and surface properties.

The objectives of this work are:

- Studying the formation of Parylene thin films in POLD process by monitoring the evolution of film tension during the deposition.
- Studying the surfaces of POLD Parylene thin films, especially the surface that contacts with liquid during the deposition in order to understand the mechanism of the film formation on liquid.

The ability to perform Parylene deposition, which is a chemical vapor deposition process in a vacuum, on liquid leads to a surprisingly simple method to encapsulate liquids by sub-micrometer-thin polymer films. From the micro technology point of view, it create a whole new class of micro structure that are transparent, flexible and electrically drivable, and have micro- and sub-micrometer thin walls and smooth surface. These structures can make important changes to many MEMS and μ TAS devices, especially the new field of liquid MEMS.

This work is the first to study the formation of POLD Parylene thin films. POLD is expected to pave the way for broader integration of liquids in micro devices and micro technologies because it is a simple yet powerful method for liquid encapsulation. Recently, many applications of POLD are reported. This work is expected to establish a foundation for further applications of this POLD technique in micro devices by providing more information on the formation of POLD Parylene thin films.

In POLD, Parylene can be deposited directly on non-volatile liquids under conditions similar to Parylene CVD on solid substrates, which means at room temperature (25°C) and in a vacuum (about 25 mTorr). POLD therefore can cover a liquid surface with a flexible sub-micrometer-thin polymer film. The encapsulated liquid droplets still maintain certain important properties of bare, meaning non-encapsulated, droplets, such as their shape and surface flexibility, to a certain extent (**Fig.1**). POLD Parylene thin films are also smooth and transparent enough for optical use. Furthermore, thanks to the flexibility of sub-micrometer-thin Parylene films, the shape of the encapsulated liquid droplets can be altered to induce large deformations even by electrostatic interactions.

Encapsulating POLD Parylene thin films are sufficiently strong to prevent liquid droplets from being dragged down by gravity. POLD Parylene films take the form of a soft "skin" encapsulating a liquid droplet. Forming on the liquid surface, the films smoothly encapsulates the initial liquid volume. A Parylene-C coating film of 1 μ m in nominal thickness, meaning the film thickness measured on solid substrate area, is sufficiently strong to prevent the liquid inside a large droplet of silicone fluid (10 mm in diameter, 43 mg) from being dragged down by gravity.

Spherical encapsulated liquid droplets of sizes larger than the capillary length of the liquid can be fabricated by POLD. The capillary length of a liquid is the maximum dimension at which the effect of gravity distorting the spherical liquid droplets can be neglected. For droplets larger than this limit size, it is expected that the droplets take aspheric shapes, whose the center areas are flatter than the surrounding areas because of gravity. Depositions are conducted to encapsulate silicone oil droplets of circular base of diameters as large as 30 mm, which is about 17 times larger than the silicone oil capillary length of 1.8 mm, and results in spherical encapsulated droplets.

In POLD experiments, the Parylene films forming on the liquid surface are expected to exactly copy the shape of the surface profile and smoothly encapsulated the initial liquid volume. However, for many POLD experiments, an interesting phenomenon is observed in which the films modify the initial liquid droplet shape, making the surface of liquid droplets more spherical, though the shape of the liquid droplets prior to POLD process tends to corrupt to an aspheric shape due to gravity. This phenomenon suggests the existence of a tension that acts in the POLD Parylene thin films and has magnitudes comparable to gravity and liquid surface tension. This force creates an effect similar to that of a large liquid surface tension has on the liquid droplets (**Fig.2**).

Because surface forces play an important role in shaping the liquid body, this founding requires that in design of Parylene-encapsulated liquid structures, Parylene film tensions must be considered as one of the main factors that contribute to the final shape, together with other forces such as liquid surface tension and gravity (**Fig.3**). This observation also implies that the deposition process can fabricate surfaces with high surface tension and low surface curvature difference, which is in many cases a preferable characteristic for MEMS structures.

2. Surface force evolution during POLD

CVD experiments are conducted with droplets of silicone fluid HI-VAC 5 of less than 1 g in mass. The diameter of the droplet base is 30 mm. Experiments are conducted with about 0.5 g dimer, which means that a 1 μm thick Parylene film is expected to be deposited on the solid substrate area. Dimer vaporization is automatically controlled in order to keep the chamber pressure lower than 25 mTorr. Maximum vaporizer temperature is set at 175°C. Pyrolysis furnace is set at 690°C. The deposition chamber pressure at the beginning of the process is about 6-8 mTorr.

The deformation of liquid droplets during POLD is monitored. Photographs of a liquid droplet are taken during the process. These photographs, shown in **Fig.4**, reveal a continuous deformation of the liquid surface and the droplet shape. The droplet is of silicone fluid with volume about 910.48 mm^3 .

The profile data extracted from photographs requires appropriate smoothing before being able to be used for further calculation (**Fig.5**). A poly-nominal approximation and smoothing is used. Poly-nominal approximate profiles allow direct calculation of the surface curvature. The accuracy of profile calculation is high for testing patterns. Forces that act on the surface are calculated from the resultant profiles.

Change in the ratio of surface force σ to liquid surface tension γ during CVD is shown in **Fig.6**. Before POLD, this ratio equals to 1, which means that the surface force is liquid surface tension. This ratio increases rapidly during POLD time and reaches a final value around 20. These changes are attributed to the increase of surface forces acting on the surface, which, in this case, must be a result of Parylene film formation.

Fig.7 shows profile and surface mean curvature of sample droplets of different liquid volumes. Surface force σ calculated for droplet profiles after CVD reveals surface forces of magnitude 20-40 times larger than liquid surface tension γ of silicone fluid. Assuming that the thickness of POLD Parylene thin films is equal to their nominal thickness, the film stress is found to be smaller than 1.4MPa. Similar results are found with droplets of liquid paraffin, suggesting that the change of liquids only has minor effect on the formation of the POLD Parylene thin films.

Compared to reported inherent stress of Parylene of 18MPa, the tension of POLD Parylene thin films is one order smaller. This suggests a significant structural difference of POLD Parylene thin films compared to Parylene films deposited on solid substrates.

3. Properties of POLD Parylene

The thickness of a Parylene film deposited on a silicone liquid droplet sitting on a CYTOP coated glass substrate is measured in two areas: on CYTOP surface and on liquid surface. The deposited film is peeled off from its substrate, rinsed in iso-propanol and acetone, transferred to a new glass substrate and dried. The thickness is measured by a contact profiler (Dektak). The results are 0.7 μm and 1.9 μm , respectively (**Fig.8**). The different in thickness hints the different in the structure of Parylene films deposited on liquid compared to those deposited on solid substrates. That films deposited on liquid are thicker than those deposited on solid substrates can be a result of molecule diffusion in liquid, which is not possible in solid substrate, especially for long distances of diffusion (in the order of micrometer).

The roughness of the upper surface (the surface that does not contact with liquid) of POLD Parylene thin films is examined by atomic-force-microscopy (AFM) and compared with those formed on solid glass substrates. Approximately 2.5 nm of root-mean-square surface roughness is found for all nominal-1- μm -thick Parylene samples formed on glass (**Fig.9**), silicone fluid, and liquid paraffin. This roughness is similar to that of Parylene films deposited on solid substrates in similar conditions.

The lower surface (the surface that contacts with liquid) of POLD Parylene thin films are observed by scanning electron microscope (SEM). Parylene films are peeled off from its substrate, rinsed in iso-propanol and acetone, turned over (upside down), transferred and glued to glass wafers by UV-cured adhesive. The samples are coated with osmium for SEM observation. The SEM photograph is shown in **Fig.10**. The surface is rough, full of holes, bridges, hills and valleys. This is totally different from the SEM photograph of the upper surface of the same Parylene film. This geometry can be explained by the interaction between monomer molecules and polymer chains with the liquid and the diffusion of those molecules into liquid bulk volume. The photographs also show the surface with polymerization centers surrounding by bridging structures. This gives the hints about the formation of Parylene film on liquid.

The SEM photograph of a cross-section of a POLD Parylene thin film (**Fig. 11**) suggests that POLD Parylene films consist of two layers of different structures, one porous and one dense.

The evidence from Parylene deposit rate on liquid also supports this suggestion. **Fig.12** shows the thickness changes of Parylene films versus film nominal thickness. The red line shows the thickness of the film deposited on liquid area, the yellow line shows that of the film deposited on solid area on a same wafer. The process can be divided into 3 stages: "fast stage", "transitional stage", and "steady stage". In the "fast stage", the increment rate of the red line is much larger than that of the blue line, indicating the formation of the porous layer on liquid surface. In the "steady stage", the increment rates are almost the same for both 2 lines, indicating that similar polymers are formed on liquid surface and solid surface.

4. Conclusion

This work studies the deformation of liquid droplets during POLD process and the properties of Parylene films fabricated by POLD. It is found that the formation of Parylene film on liquid surfaces exerts force acting on the surface as a surface tension that shrinks the surface area of the encapsulated droplets. This effect is observed as the deformation of liquid droplets encapsulated by POLD towards more spherical shapes. This force causes the film stress. It is found that, different from reported inherent stress in Parylene films deposited on solid surfaces, which is compressive, the stress in Parylene films deposited on liquids is tensile. This is the consequence of the involvement of liquids during the polymerization and crystallization of the polymer. The existence of liquid in the vicinity of the reactions has significant effect on the morphology of the polymer on the side of the Parylene film contacting the liquid during deposition, which is observed in the investigation of the surface of the Parylene films. The morphology of the film suggests that the nucleation centers that appear in the early stage on deposition connect with one another by many polymer bridges. The force occurs in these bridges is the origin of the tensile film stress observed in the macro scale.

In this work, the POLD process and the resultant Parylene thin films, as well as the resultant encapsulated liquid structures were studied. Obtained results include:

- The observation of profile deformation of liquid droplets and the calculation of forces acting on the liquid surface during POLD process. A continuous profile deformation of liquid droplets during deposition is observed. A tension of about 700-800 $\mu\text{N}/\text{mm}$ is calculated for POLD Parylene thin films of nominal thickness of 1 μm , which means a film stress of 1.4 MPa. The film stress is tensile even though the stress in Polymer films deposited on solid surfaces is compressive.

- POLD Parylene films consist of two regions of Parylene significantly different in morphology distributing on the film depth direction. The one on the side contacting liquid during deposition is porous. The other one dense and have morphology similar to that of Parylene films deposited on solid surfaces.