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THIN FILMS FORMED BY PLASMA POLYMERIZATION ON SOLID SUBSTRATES*

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Polymeric thin film deposition in a capacitively coupled rf discharge has been investigated. A variety of volatile monomers have been used; thin films formed on different solid substrates show interesting physical and chemical properties.

ТОНКИЕ ПЛЁНКИ, ОБРАЗОВАННЫЕ ПЛАЗМЕННОЙ ПОЛИМЕРИЗАЦИЕЙ НА ТВЁРДОТЕЛЬНОЙ ПОДЛОЖКЕ

В работе исследовалось нанесение тонких полимерных слоёв в ёмкостно связанном высокочастотном разряде. Использовались различные летучие мономеры. При этом оказываится, что тонкие слои, образованные на подложках, обладают интересными физическими и химическими свойствами.

I. INTRODUCTION

During the past ten years there has been a steadily growing interest in the plasma polymerization processes. Many organic chemical substances are used as monomers for producing polymeric films by plasma polymerization. One outstanding advantage of the plasma process for the formation of organic polymer films is the wide variety of organic compounds that may be polymerized by this technique [1, 2, 3].

Thin polymeric films are usually formed in non-isothermic discharge plasma excited at pressures from 0.1 to 500 Pa. The best results are obtained with capacitively coupled rf discharge plasma, where the plasma column has been more homogeneous than that in other experimental arrangements. The application of plasma — polymerizded films to any purpose will undoubtly require them to be prepared with uniform thickness. In [4, 5] it is shown that the flow rate can have a significant influence both on the rate of polymer deposition and the quality of the polymer. It is possible to deposit uniform polymer films through the proper

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selection of flow rate, total pressure, rf power input and inlet configuration. The best approximation to the plasma polymer deposition process is found to be the following model [6]: monomers are activated in the gas phase by electron bombardment and subsequently diffuse to the substrate where they propagate and terminate, while the adsorption of monomers on the substrate plays an important role.

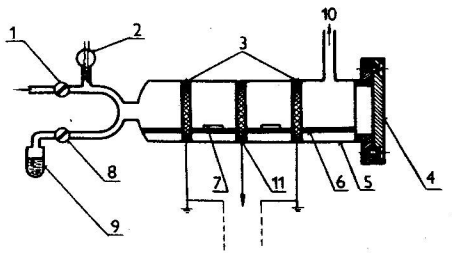

Fig. 1. Flow system for plasma polymerization with external electrodes. 1 — needle valve for argon or nitrogen inlet, 2 — pressure gauge, 3 — external cylindrical electrodes, 4 — metal flange with seal, 5 — discharge tube, 6 — glass plate, 7 — substrates, 8 — needle valve for monomer inlet, 9 — monomer, 10 — to oil pump, 11 — external cylindrical electrode connected with rf generator.

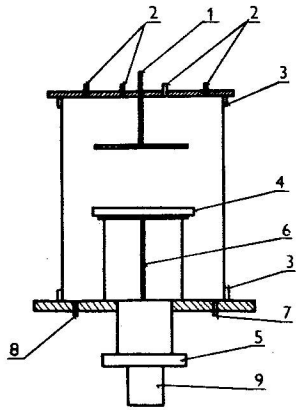

Fig. 2. Container for plasma polymerization with internal electrodes. 1 — electrode connected with rf generator, 2 — monomer and buffer gas inlet, 3 — seal, 4 — substrate, 5 — valve, 6 — electrode connected with earth, 7 — to LKB vacuum gauge, 8 — to Baratron MKS vacuum gauge, 9 — oil pump with cold trap.

II. EXPERIMENT

A schematic drawing of the apparatus is presented in Fig. 1 and Fig. 2. In the glass discharge container the substrate was placed (glass, silicon, aluminium, steel plates). The discharge container was initialy evacuated by an oil pump. Argon was introduced first into the discharge container at a fixed flow through a variable needle valve. Pressure was continuously measured by a Pirani vacuum gauge (LKB Autovac) and a membrane manometer (Baratron MKS). By the system of needle valves, the required pressure and gas flow of argon and monomer were established. The discharge were operating at a variety of total pressures and partial pressures of the monomer.

The capacitively coupled rf discharge was established by coupling an rf generator (27 MHz) to external (Fig. 1) or internal (Fig. 2) electrodes. The power output of

the rf generator used during the polymer formation was 80—120 W, which means 0.20—0.40 W/cm^3 of the discharge volume. The best results were obtained at an argon pressure 15—40 Pa and a monomer partial pressure 10—15 Pa. The discharge was first excited in pure argon or nitrogen and the polymer formation began immediately after the increase of monomer partial pressure. The clear and smooth polymer films of good quality are deposited on the soubstrate surface if the

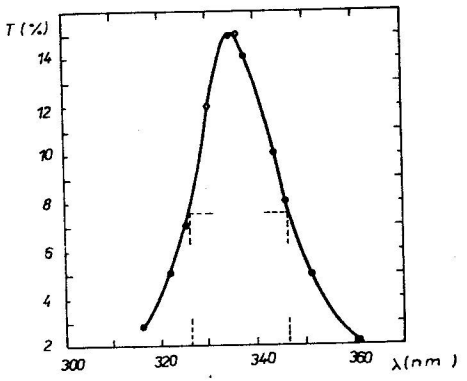

Fig. 4. Sandwich system used as hygrometric element.

Fig. 3. Transparence versus wave length for interference filter with polymeric dielectric layer.

partial monomer pressure is relatively low. At greater monomer pressures polymerization is very intensive and hence in the discharge volume „snow flakes" — like polymer particles form [7, 8]. In all cases where the rf power input and total pressure are high enough the polymerization products may be observed in the gas phase [9]. The temperature of the neutral gas does not exceed 90 °C if argon is used as a buffer gas. The presence of nitrogen increases the temperature of neutral gas and at higher pressures the polymeric film is not smooth.

III. RESULTS

Thin polymeric films were gradually formed from the following volatile monomers: octamethylcyclotetrasiloxane (OMTS), benzene, toluene, xylene, pyridine, picoline and allylamine.

The poly-OMTS films prepared by a plasma polymerization process are clear, smooth, oprically transparent from 370 nm to 800 nm, pin-hole free, thermally stable up to 160 °C and exhibit a very low loss for light-wave propagation. The measured index of refraction is 1.39—1.40. From the IR spectra of poly-OMTS films we conclude that by plasma deposition of OMTS a cross-linked polydimental conditions is 30—50 nm/min. The poly-OMTS thin films show excellent optical properties and may be used as protective coatings on special mirrors and other optical devices. These films ranged in thickness between 0.4 μm and 1.5 μm. The

poly-OMTS films can be washed in water without damage, but they are frequently scratched by contact with hard materials. Poly-OMTS films may be used also as dielectric layers in interference filters — Fig. 3. Poly-OMTS coating deposited on glazed metal surface reduces the coefficient of friction and thus these films are considered as possible protective coatings on special medical devices.

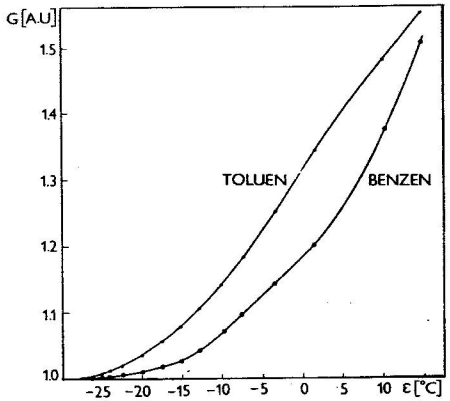

Fig. 5. Graduation curve for sandwich system with polymeric function layers. Capacity of the system versus dewing point.

The poly-benzene, toluene, xylene, pyridine, picoline and allylamine thin films are yellow-brown. Benzene, pyridine and toluene thin films show interesting changes in the water permeation rate. By the help of sandwich system — Fig. 4 there have been measured changes of capacity and resistance of these polymeric thin films, the sandwich system having been placed in a gaseous atmosphere with varying moisture. The greates dependences of capacity and resistance on water concentration in gas exhibit poly-toluene, pyridine and benzene films. The sandwich system presented in Fig. 4 can be used as a very sensitive hygrometric element. Repeated measurements of the hygrometric graduation curves given in Fig. 5 even after several months indicated no noticeable changes.

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