**Polystyrene-TiO\textsubscript{2} thin films produced in a hollow cathode**

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**Abstract:** Plasma polymerization can be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions as such processes involve electron impact dissociation and ionization for chemical reactions. The objective of this investigation was to obtain a polystyrene film in mixture with titanium oxide (TiO\textsubscript{2}) groups in a hollow cathode discharge (HC). Monomer vapour was propagated by argon gas flow into the HC at a working pressure of about 0.1 mbar. The substrate was a silicon wafer.

**1. Introduction**

Recently plasma polymerization has gained importance as a tool to modify material surfaces. Organic vapours can be polymerized at low temperatures using plasma enhancement. Plasma polymerization can also be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions since such processes involve electron impact dissociation and ionization for chemical reactions. The most frequently used experimental set-ups to obtain polymer films under plasma condition are dielectric barrier discharges (DBD) at atmospheric pressure or radio frequency discharges (RF) at lower pressure (around $10^{-2}$ mbar).

The production of thin films is one of the most important technological applications of plasma physics. Various techniques are in use such as magnetron discharges, laser ablation, thermionic vacuum arcs (TVA), hollow cathodes (HC) etc. All these techniques require certain conditions to obtain suitable thin films such as magnetic field, ultra high vacuum or high current acceleration. One of the least expensive techniques to
obtain thin films are hollow cathode discharges, which do not need a magnetic field and are thus particularly useful for ferromagnetic material sputtering [1], light sources [2], spectroscopic light sources [3] and electron beam sources [4].

The goal of this work was to obtain polystyrene films in mixtures with titanium oxide (TiO₂) groups in a hollow cathode discharge.

2. Experimental set-up

The experimental set-up is very simply (see the photo of Fig. 1). The hollow cathode (HC) is manufactured of a Ti cylinder with a length of 40 mm, with an inner diameter of 5 mm and an outer diameter of 10 mm. This was inserted directly into a ceramic tube with an inner/outer diameter of 10/15 mm, respectively, through which the working gas was employed to the chamber. In this case no cooling of the cathode was provided. The plasma jet was oriented vertically; a grounded copper ring (5 cm in diameter, positioned coaxially 17 mm above the nozzle outlet of the hollow cathode) served as the anode.

Fig. 2 shows the current-voltage characteristic of the HC for two different pressures (black symbols: 2 Pa and red symbols 20 Pa). We see the strong hysteresis of the system which for voltages above \( V_{HC} > 500 \text{ V} \) very suddenly jumps from the normal glow discharge mode into the hollow cathode mode with a much larger current, electron density, ionization and thus efficiency of sputtering. This mode of operation is preserved for lower voltages down to about \( V_{HC} \approx 330 \text{ V} \).

Vapours of monomer were inserted into the argon gas and transported by its flow into the hollow cathode. The working pressure was kept around at 0,1 mbar. The discharge current was varied between 20 mA and 40 mA. The substrates were silicon wafers and the time of deposition was about one hour.

The deposited films were analysed by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction for the investigation of the chemical composition and the chemi-
cal structure of the thin films. Scanning electron microscopy (SEM) was used for calculating the thickness of the films and to see the topography.

Fig. 3. (a) Typical optical spectra of the HC discharge with Ti disks as cathodes and Ar and styrene. (b) ATR (Attenuated total reflectance)-FTIR spectra of the thin films produced by the HC discharge.

3. Results and discussion

Optical spectra of the hollow cathode discharge show the presence of a C-line at 391.4 nm and also lines corresponding to titanium and argon are observable. Argon was the working gas (see Fig. 3(a)).

In infrared spectra (Fig. 3(b)) also the presence of TiO$_2$ peaks is observed as well as the C-H and CH$_2$ bounds corresponding to polystyrene. The Si-H$_2$ originates from the silicon wafer which was used as substrate for the deposition.

Fig. 4 shows typical X-ray diffraction spectra of the thin TiO$_2$ films and the polystyrene-Ti films. After introducing styrene into the discharge the structure of the TiO$_2$ deposition does not change but remains in two crystalline phases (anatase and rutile) [5]. For the new polymer obtained in the HC discharge, the thickness of the substrate does not change when the discharge current is increased, but remains in the range of 80 nm.

Fig. 5 presents the results of SEM measurement for two kinds of
surface: TiO$_2$ layer (a) and polystyrene- TiO$_2$ layer (b). The topography of the thin films is granular both for TiO$_2$ and polystyrene-TiO$_2$ films, but the grain size becomes smaller in the presence of polystyrene.

![SEM image](image_url)

Fig. 5. SEM image for TiO$_2$ thin film (a) and polystyrene- TiO$_2$ (b).

4. Conclusion

By using a hollow cathode discharge sputtering source, we have obtained new thin films of Ti and polystyrene mixtures which can have more applications in biomedicine such as protein absorption. This kind of deposition technique can also be used very well for obtaining conductive polymers for industrial applications.

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References