# PRODUCTION OF THIN FILMS BY CATHODIC PLASMA ELECTROLYSIS

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**Abstract**: This paper deals with the production of thin films using a new plasma process, called Atmospheric Pressure Plasma Deposition (APPD). The films produced are titanium oxide and carbon films and have been characterised by visible and some UV micro-Raman spectroscopy.

A new deposition method, Atmospheric Pressure Plasma Deposition (APPD), has been developed, which combines galvanic processes and plasma-chemical phenomena. Unlike other plasma deposition techniques, the process occurs in liquid precursors and the plasma is confined to the cathode in a superheated vapour sheath surrounded by the liquid phase. This method, previously used in anodic configuration for the deposition of oxide films, [1,2] allows (in cathodic configuration) the production of a wide range of films, such as carbon, titanium and silicon films.

The basic process of APPD is the electrolysis of a solvent at high voltage. In our test facility, we use a direct current power supply (Bertran 105-02R) with a maximum voltage of 2000 V and a maximum electric power of 1 kW. The electrodes are flat or cylindrical. The anode area is significantly larger than the cathode area (30 times) to concentrate the current density and create the vapour sheath and the glow discharge around the cathode. The cathode area is 1 $cm^2$. Titanium oxide films and carbon films have been deposited on the cathode using this technology. For the production of titanium oxide films, the electrolyte consisted of absolute grade ethanol, with a maximum water content of 0.2%, and tetraisopropoxy titanium (IV) (TPT). The anode and cathode materials are respectively titanium and copper. For the deposition of carbon films, the electrolytic solution is composed of ethanol (90% in volume), potassium chloride and phosphate buffer. Potassium chloride and phosphate buffer are used to increase and adjust the electric conductivity and the pH of the solution. Here, the anode and cathode materials are respectively graphite and aluminium (grade 6061). The operating temperature is kept at around 70 °C. The current density is respectively equal to 200 $mA/cm^2$ and 400 $mA/cm^2$. Raman spectra of the solid samples were measured using either 633 nm or 325 nm excitation with a Renishaw Raman microscope. No sample preparation was necessary.

## Production of titanium oxide films

The films produced with ethanol and TPT have been analysed by Raman spectroscopy. The analysis reveals that titania ($TiO_2$) and carbon are present in all films. The D and G peaks at 1360 $cm^{-1}$ and 1600 $cm^{-1}$ correspond to the presence of graphitic carbon. They are due respectively to the disorder in graphite and the Raman active mode in the graphite plane. All three phases of titania (anatase, rutile and brookite) were found to be present in the films, with the phase present affected by various factors, such as the applied voltage and the electrolyte composition. These phases correspond to the peaks between 200 and 900 $cm^{-1}$.

The film deposited at 2000 V contains a mixture of rutile and anatase crystallites, whereas the film deposited at 1700 V contains anatase with a trace of brookite (fig.1). The film deposited at 1000 V is comprised of amorphous titania. The phase differences may indicate that the energy of the conditions of film deposition is imparted to the film, which relieves these stresses on formation

of oxides. The sparking in the 40% TPT solution was much more intense than that in the 20% TPT solution at the same potential, indicating higher energy was involved. This is confirmed by the Raman spectra (Fig. 2), which indicated that the film deposited from 20% TPT contains amorphous titania, whereas the film deposited from 40% TPT contains anatase, with a trace of brookite.

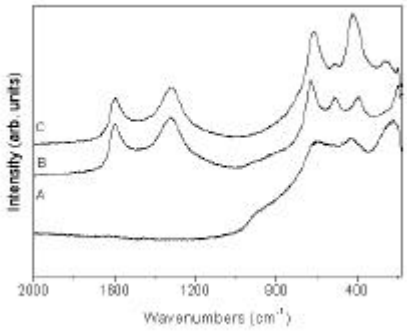


Fig. 1: Raman spectra of films deposited from 40% TPT in ethanol by applying 2000 V for 600 s (a) 1000 V (b) 1700 V (c) 2000 V

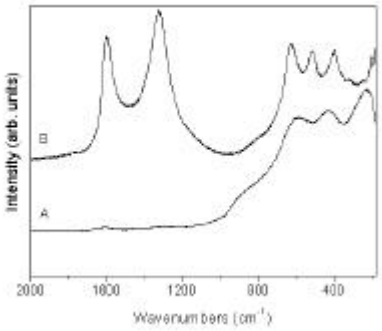


Fig. 2: Raman of films deposited at 2000 V for 600 s from (a) 20 % TPT in ethanol (b) 40% TPT in ethanol

**Production of carbon films**

The films produced with a solution composed of ethanol, potassium chloride and phosphate buffer reveal the presence of carbon only. We can observe the presence of the D and G peaks. The relative intensity and width of these two peaks is a characteristic of graphite nano-crystallites. This carbon films present the same carbon structure as in the titanium oxide/carbon films. The energy provided by the plasma discharge is used to decompose ethanol in a large amount of liquid products and in carbon nanoparticles [3]. These carbon nano-particles diffuse then in the vapour sheath to be deposited on the metallic substrate but carbon does not react with the implanted ions, since no TiC bonds have been observed in the first case. The carbon films have also been characterised by UV micro-Raman spectroscopy. The carbon films show three peaks (Fig. 4): the G and D peaks, located near 1600 and 1400 $cm^{-1}$, and the T peak, located at 1010 $cm^{-1}$, corresponding to the vibration of the $sp^3$ sites. The carbon films are therefore composed of $sp^2$ sites with a small amount of $sp^3$ sites.

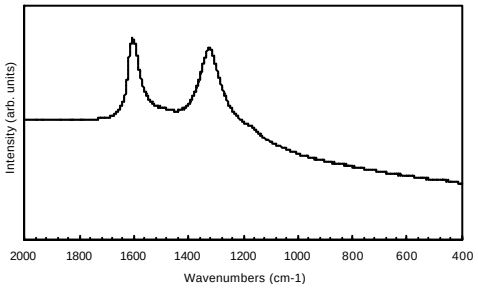


Fig. 3: Raman spectra of films deposited from absolute ethanol (350 ml), phosphate buffer (10 ml) and potassium chloride (5 g) by applying 1000 V for 1800 s

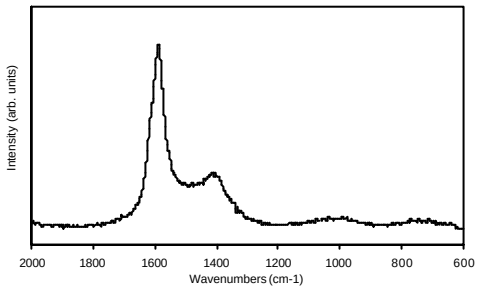


Fig. 4: UV Raman of films deposited from absolute ethanol (350 ml), phosphate buffer (10 ml) and potassium chloride (5 g) by applying 1000 V for 1800 s

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