

Gas Jet Deposition of Teflon-Like Films and Ultra-Dispersed Particles

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Abstract. Polymer gas jet deposition is proposed as a method to produce Teflon-like films that allows control on morphology and structures on different length scales including nanometer. Gasified Teflon is used as precursor and a computational modeling is proposed for better understand the gas dynamic occurring at the impact of the hypersonic C_2F_4 jet with substrate. The properties of the films produced are presented and discussed on the basis of their morphology as well as of AES, XPS and UPS electron spectroscopies, which are demonstrated. Gas Jet deposition is shown to be a quite promising method to produce and control the synthesis of Teflon-like and possibly of other polymers films.

INTRODUCTION

Gas jet deposition of thin polymer film ¹ is based on the idea of using gas-dynamical acceleration of the precursors to be deposited. From this point of view it is conceptually related to gas jet deposition of metals ² and of material by molecular beam extraction from jets ^{3,4,5}. This work is devoted to extending the gas jet deposition approach to Teflon-like films and to the synthesis of ultra-dispersed particles. The peculiarity of proposed method is using the gasification of polytetrafluoroethylene (PTFE) via sublimating the material at relatively low pressure in a reactor (stagnation chamber). Unrelenting interest to the formation of micro- and nano-sized structures from Teflon and Teflon-like materials is motivated by their unique combination of properties: low electrical conductivity, low heat conductivity, high hydrophobicity, low refraction and friction coefficients, biocompatibility, chemical stability, relative high strength.

A key feature of the deposition processes being studied in this work is the wide range of deposition conditions and the control achievable in synthesizing deposits with different structures as well as producing copolymer and metal-polymer materials.

As early as in 1947, it was shown⁶ that the destruction of PTFE at the pressure of about a few Torr and temperature of about 600°C, gives rise to PTFE gasification where the main product is tetrafluoroethylene C_2F_4 with an efficiency of up to 97% in optimal case. Keeping these conditions in the reactor and a background pressure in the expansion chamber at about 10^{-2} Torr, one gets a free jet behind the sonic nozzle with a free expansion region (as into vacuum) of about 15-20 nozzle diameters. The film deposition in the form of modified molecules of PTFE is performed on the substrate installed in the jet core.



FIGURE 1: Schematics of the experimental set: 1) body of the expansion camera; 2) substrate; 3) nozzle; 4) reactor.

EXPERIMENTAL

The Teflon growth on different substrates was performed in an equipment, specifically developed for this type of deposition at the low density gas dynamic facility “VIKA” of the Institute of Thermophysics, Novosibirsk. Fig. 1 shows the schematics of the experimental set up. It includes the expansion chamber (volume 30 liter), the reactor (volume 2 liters), the sonic nozzle (diameter 10 millimeters) and the aluminum substrate sample holder. The substrate is always located behind the Mach disk, so in subsonic flow conditions. The bulk Teflon is heated in reactor at about 700-900 K: sublimation generates monomers and radicals having a content of C_2F_4 (tetrafluoroethylene) of about 95%. By injecting helium in the reactor, a gas mixture is created that expands then in a free jet that accelerates the C_2F_4 molecules. Partial polymerization of C_2F_4 on the silicon substrate occurs in the chamber of expansion. Temperature of all important parts of experimental set is controlled by thermocouples, while the absolute pressure in the reactor is measured by a baratron type gauge. The conditions of experiment are: stagnation pressure in the reactor is about 15 torr, stagnation temperature is typically 700 K, pressure in the expansion chamber was kept at about 0.01 torr. The distance between nozzle and substrate is 300 mm. Two different kinds of substrate have been used: copper and silicon (SiO_2 native oxide on Si(100)), both kept at a temperature during deposition of about 450 K.

The sample has been studied ex-situ at the Institute of Thermophysics, Novosibirsk, by means of SEM microscopy by using a LEO-420 instrument. The electronic properties have been analyzed at the IFN-CNR lab in Trento, by using an UHV experimental set up (having a base pressure of $7 \cdot 10^{-11}$ mbar) devoted to surface science characterization by means of electron spectroscopies. X-Ray core level (XPS) and UV valence band (UPS) photoemission studies have been performed by means of a Mg $K\alpha$ source (photon energy of 1253.6eV) and Helium lamp (photon energy of 21.21eV), respectively. Auger analysis (AES) has only tentatively been performed, due to high charging effect of the analyzed films.

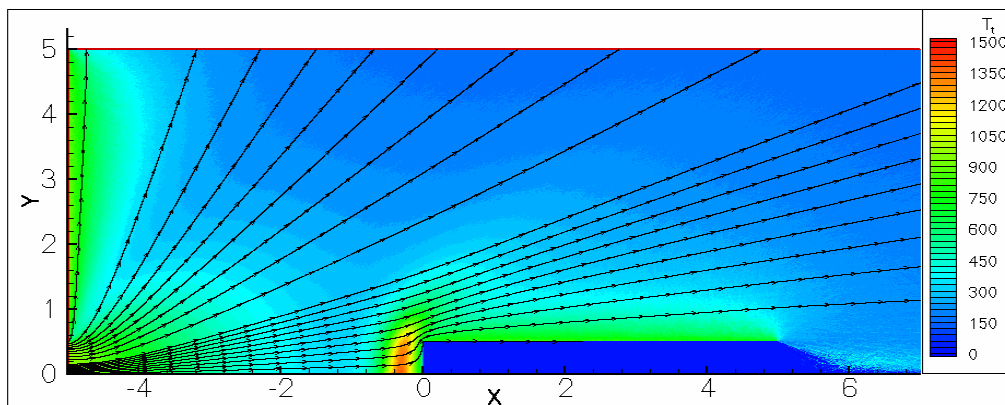


FIGURE 2: The figure of DSMC modeling result: translational temperature (shadows) and the stream lines. The axis are normalized to the nozzle diameter

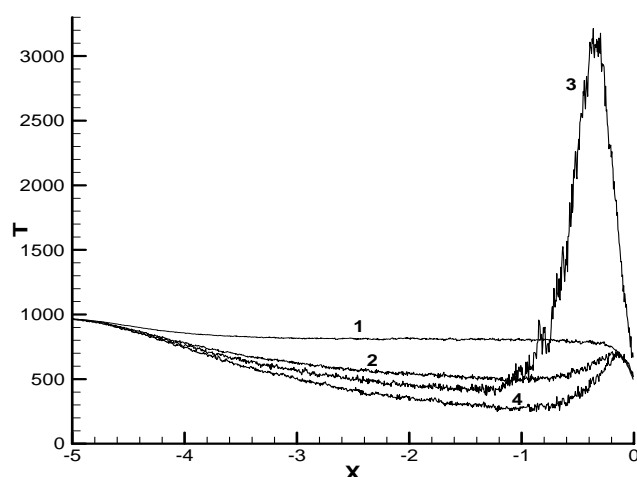


FIGURE 3: Computed temperature distribution along the axis:
1) vibrational, 2) rotational, 3) parallel, 4) two transversal ones.

COMPUTATIONAL MODELING OF JET DEPOSITION

The computational modeling was realized by Monte-Carlo method⁷. Details of calculation and of C_2F_4 molecule relaxation model are given in⁸. As an example, fig.2 shows the picture of the longitudinal axis-symmetrical C_2F_4 flow behind the sonic nozzle having a diameter of 10 mm past a flat face cylinder with the same 10 mm diameter. The stagnation parameters are: $P_0=10$ mm, $T_0=1000$ K, the temperature of cylinder is 400K, the cylinder is located at the distance of 50 mm, the probability of molecule to be deposited is 5%. On this figure one can see the stream lines and density distribution qualitatively illustrated by rendered image. Fig. 3 shows the distribution of temperatures along the flow axis up to cylinder face. Here are given: translational temperature in two directions (x-longitudinal and y-transversal), rotational temperature, vibrational temperature.

The results of computations unveil interesting aspects of poorly-investigated phenomena related to shock wave formation in non-equilibrium jet flow of polyatomic gas. For example, in this case, when the Mach number in front of the cylinder is close to 5, the longitudinal (parallel) temperature in the shock wave exceeds the stagnation temperature of more than 3 times. This is somewhat unpredicted if one considers only the more familiar phenomena occurring in the jet: strong freezing of vibrational temperature, partial freezing of rotational temperature, partial freezing of heat motion of molecules along the axis.

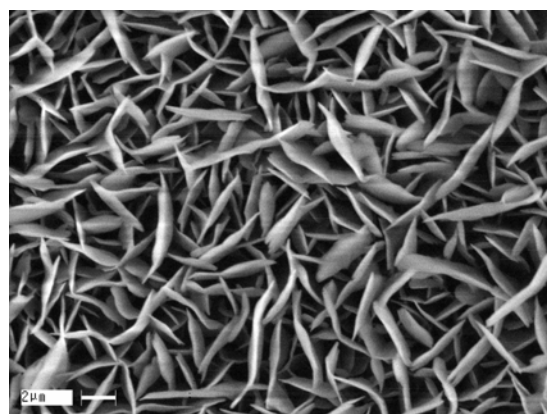
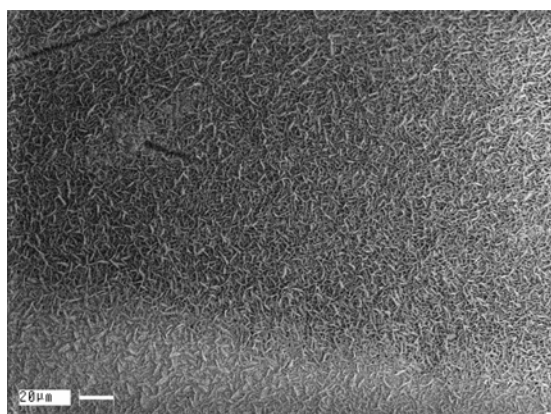


FIGURE 4: Morphology of the Teflon-like film deposited on copper

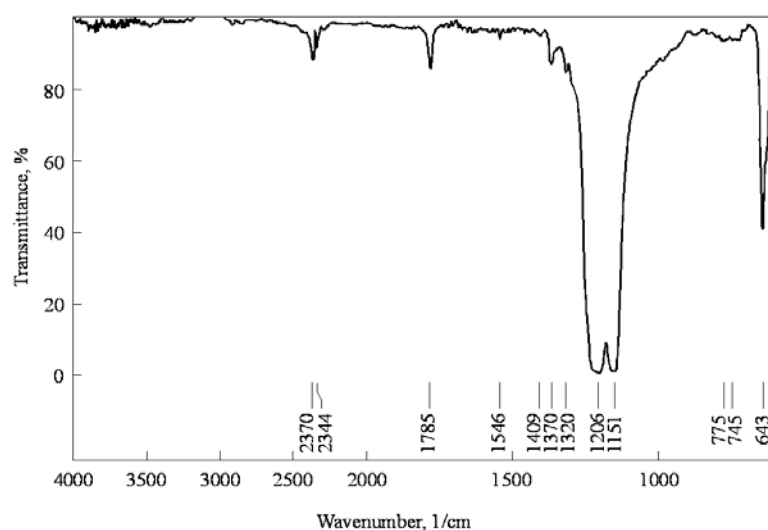


FIGURE 5: Spectrum of the Teflon-like film deposited on copper

MORPHOLOGICAL PROPERTIES OF TEFLON FILMS

The computational results presented above were obtained for the same experimental conditions used for the synthesis of the Teflon films described in the following. Fig.4 is a SEM micrograph showing the typical morphology of the Teflon film grown on a copper polished substrate at the temperature of about 150°C. The film is characterized by a somewhat uniform distribution of structures having all the same elongated shape on the scale of a few micron length. Fig.5 shows the absorption spectrum of such Teflon film. This spectrum differs from that of the bulk Teflon because of the presence of new absorption bands and different structures in the region of 1100-1200 cm^{-1} . This can be ascribed to a somewhat different molecular structure, that is to the formation of new molecular bonds and hence the appearance of new vibrational modes.

Teflon films deposited on a $\text{SiO}_2/\text{Si}(100)$ substrate (at a temperature of 450K) show a markedly different morphology, as shown in Fig. 6. Film appear to be formed by long fibers (tens of micrometer long), consisting of a net of smaller structures on a the lengthscales of μm and sub- μm (typically 1 – 3 μm , with thickness of 50 – 100 nm)

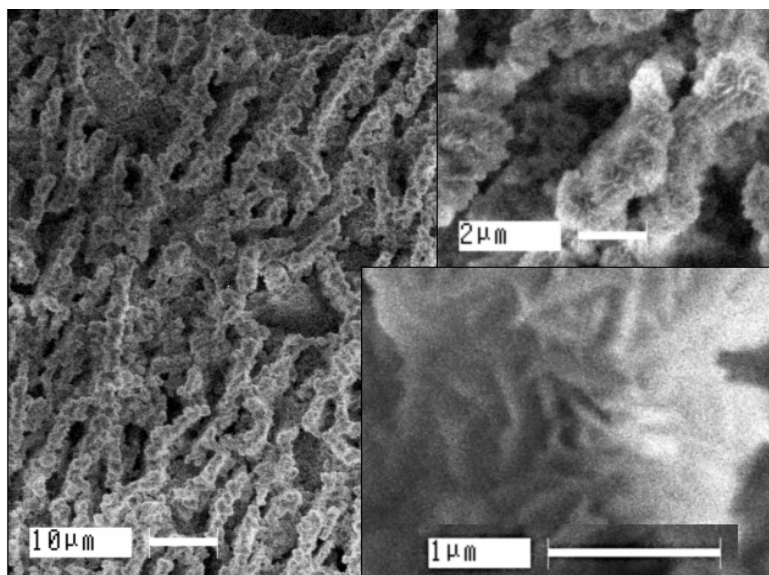


FIGURE 6: The morphology of the Teflon-like deposited film

SURFACE ELECTRONIC CHARACTERIZATION OF TEFLON FILMS

In order to better understand the properties of the Teflon film synthesised by gas-jet deposition, samples have been analyzed ex situ at the IFN-CNR lab of Trento. The two Teflon thin films have been deposited on SiO₂/Si(100) substrates, using gas-jet having the same gas mixture, C₂F₄ and He, at a total pressure of about 14.5 Torr. Two different gas temperatures in the source and substrate temperature have been used: 425°C and 178°C for the white film, 554°C and 156°C for the black film respectively. In order to test the uniformity of the whole film, two different zones have been tested for each film: the centre of the spot and its border.

The two films have been analyzed by using surface electron spectroscopies in UHV, namely AES, XPS and UPS. No serious pressure increase (up to $3 \cdot 10^{-9}$ mbar) has been observed due to the film presence: this is interesting if the typical Teflon properties in vacuum, i.e. high degassing (mainly water), is taken into account.

Both films showed high charging effects: this is why AES characterization has not been performed, due to electrons bombardment. Surprisingly, using UV photon as beam probe, we have not been able to obtain any spectra: this is quite difficult to explain, also taking into account that the valence bands of Teflon have been previously studied⁹. Anyway, also this behaviour can be probably ascribed to strong charging effects induced by the small spot/high photon flux of the helium lamp used in UPS experiments.

A reliable surface analysis has been possible only using the 1253.6eV photon of a Mg anode source. Due to the presence of a large amount of carbon contaminants, with a coverage that made impossible any accurate analysis, gentle sputtering by Ar ion beam at 0.6KeV and low density ($0.1 \mu\text{A} \cdot \text{cm}^{-2}$, $5 \times 5 \text{mm}^2$ rastering) has been performed in order to clean the surface. This procedure has been preferred to sample heating because temperatures significantly higher than those used for thin film deposition would have been necessary. Disorder effects have been reported^{10,11}, due to ion bombardment at higher energies and ion density. In our conditions we believe that the treatment did not cause any damage to the Teflon film.

Fig.7 reports the XPS spectra for the two films, after the cleaning procedure. As shown in the figure, the spectra are mainly due to the Fluorine signals, while the only other detectable peak is due to Carbon. No presence of Oxygen or Silicon has been found, suggesting that we are dealing with films having a thickness equal to or higher than 10-15nm. As shown, we are dealing with a strong charging effect, about +10eV in Binding Energy (BE, referring to the Au 4f signal at 84.0eV), as already reported¹².

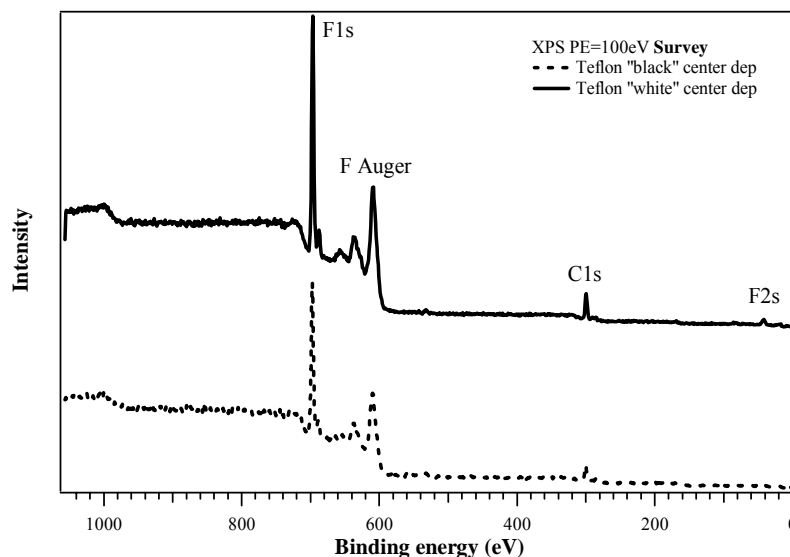


FIGURE 7: XPS spectra of the two Teflon film (named white and black).
The sample has been previously sputtered. Film zone: centre

Analysis of the F1s and C1s peaks are shown in Fig.8 and Fig.9, respectively. The analysis has been performed in two different zones of the film: in the centre of the original spot and in a border zone. The F1s core level is probably characterized by a single component in the white film, located at about 698eV, while for the black one a peak broadening suggests the presence of underlying other features. A significant energy shift (maximum about 1eV) is present in all films. The shifts are both, one with respect to the other, and also comparing emission from the centre and from the border of the films.

The C1s core level analysis reveals presence of two main components: the feature located at about 295eV is very weak, and can be ascribed to C-C bonds, i.e. to contaminants not removed by sputtering. The main component, located at about 301eV of BE and characterized by a large FWHM and a very low intensity, can be related to presence of C-F, C-F₂ and /or C-F₃ bonds⁹⁻¹³. A shift has been observed, comparing the two films / two zones spectra, as was for the F1s core level. This peak, in the black film, shows a larger FWHM with an evident lineshape broadening that can be attributed to the presence of several types of C-F bonds⁹⁻¹¹.

	White film, center dep	White film, border dep	Black film, center dep	Black film, border dep
$\Delta E(\text{F1s-C1s})$	396.7eV	396.8eV	396.5eV	397eV

TABLE 1: Energy difference between C1s (main component) and the F1s core level for the several cases

From the point of view of the chemical properties, due to the large variability of the absolute BE induced by charging effects, more reliable information can be extracted by evaluating the energy difference between C1s (the main component) and the F1s core levels, as shown in Tab.1. These values are very similar to the 397.2eV value reported for C-F₂ and 395.3 for the C-F₃ bonds, strongly indicating that the films have typical Teflon-like properties. From the point of view of stoichiometry, the theoretical concentrations should be 33% for C and 66% for F, with a C/F ratio of about 0.5. As shown in Tab.2, the black film in the centre zone has the best values while the other data are characterized by a weak C deficiency. Going from the centre to the border zone, in both films a C reduction has been observed.

	White film, center dep	White film, border dep	Black film, center dep	Black film, border dep	PTFE
C/F	0.47	0.44	0.52	0.47	0.50
C %	31.8	30.6	34.4	32.0	33.3
F %	68.2	69.4	65.6	68.0	66.6

TABLE 2: Stoichiometry for the two films / two zones as calculated from XPS data.

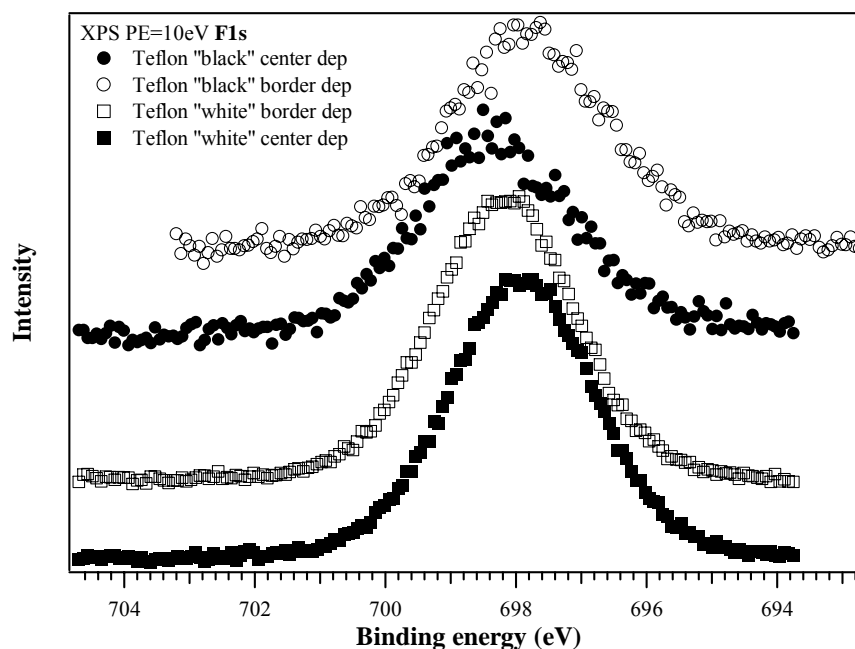


FIGURE 8: XPS high resolution F1s core level, for the white (squares) and black (circles) films. Two film zone have been analyzed: the spot centre (filled symbols) and in the border zone (open symbols).

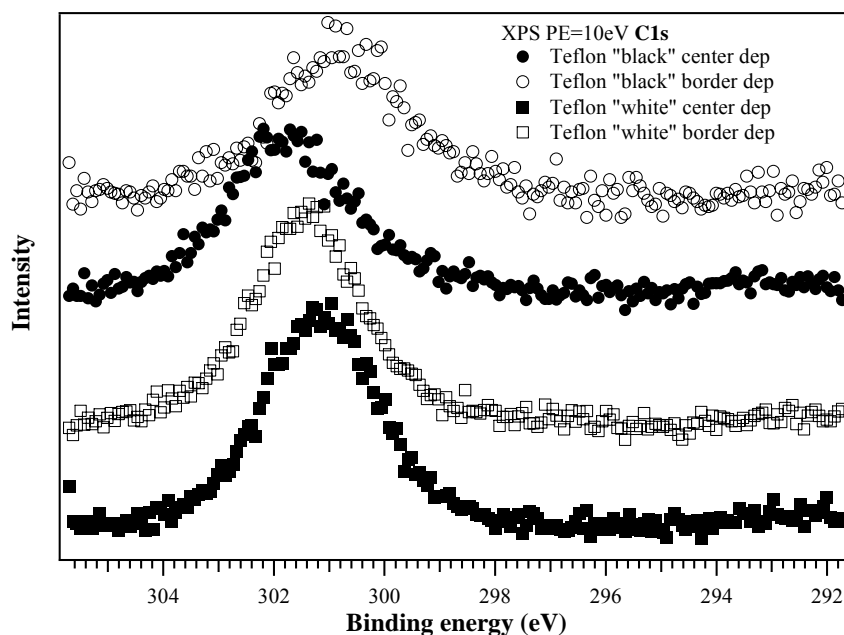


FIGURE 9: XPS high resolution C1s core level, for the white (squares) and black (circles) films. Two film zone have been analyzed: the spot centre (filled symbols) and in the border zone (open symbols).

STRUCTURAL CHARACTERIZATION OF TEFLON FILMS

XRD analysis has been performed on powder coming from the same films analyzed by surface electron spectroscopies. Measurement has been performed using a Cu K α X-ray emission, working in a Bragg-Brentano geometry. The 5°-90° angle range has been investigated.

Fig. 10 and 11 show the XRD spectra for white type and black type powders. They show very similar features: the main one of which is located at 17.8° while a second one, less intense, is present at 31.35° and a third, weaker one, is at 9.05°. Finally there is a broad large structure around 40°. No significant differences between the two films can be detected. The lines represent the typical structures of Teflon: as confirmed by the good agreement between experimental and theoretical data (sticks in the figures), suggesting that the powders have the same structure of Teflon. In conclusions, XRD analysis strongly indicates that the films are mainly composed of a material having the typical fingerprints of Teflon.

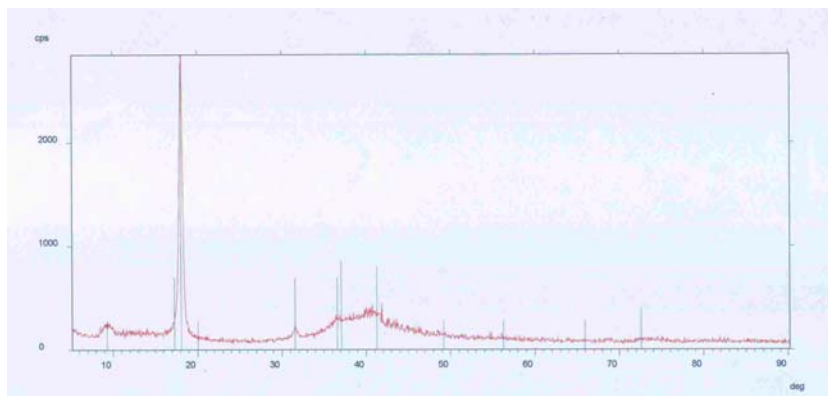


FIGURE 10: XRD analysis of powder coming from the white film.

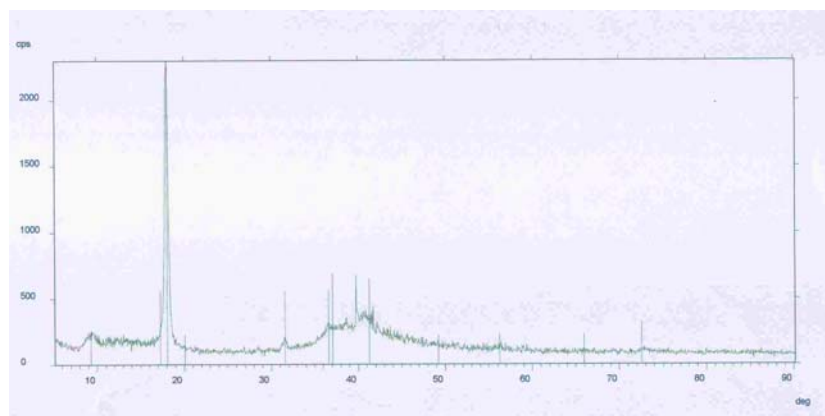


FIGURE 11: XRD analysis of powder coming from the black film.

CONCLUSIONS

The gas jet deposition is a controlled and viable approach to the synthesis of polymer films and nanoparticles as confirmed by the characterization of the films produced. This novel approach paved the way to the production of polymer materials with controlled morphology and structures at different length-scales down to the nanometer size making realistic the goal to preparing films and particles with a-priori tailored properties. We envisage applications in a variety of fields including devices and bio-related processes.

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