

The synthesis of DLC using a novel cathodic arc technique: Gas-TVA

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An original deposition technique was developed for the synthesis of DLC from methane and is presented here for the first time. The technique is based on the ignition of a cathodic arc plasma in the vapours of the material of interest, similar to the Thermoionic Vacuum Arc (TVA) method [1]. The novelty here consists in using a flow of methane as anode, instead of the carbon rod used in the classic TVA method. This extends enormously the applicability of the TVA technique for the synthesis of materials from **solid** precursors to the synthesis of thin films using **gas** precursors. A wider range of complex materials can be now obtained. The present paper presents the first results obtained with the Gas-TVA. Optical spectroscopy measurements of the methane plasma ignited using the Gas-TVA method have clearly shown dissociation of the CH₄ molecule into different radicals. The composition, adherence and morphology of the films deposited using this new technique were investigated. The DLC films were found to be made of hydrogenated amorphous Carbon with relatively high sp³ content, extremely adherent and smooth.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Gas-TVA, Arc plasma, Gas precursors

1. Introduction

DLC has some extreme properties similar to diamond such as high hardness and resistance to wear, high thermal conductivity, low specific heat, wide band gap and high refractive index, low static and dynamic friction, chemical inertness to both acids and alkalis, lack of magnetic response, optical transparency and high electrical resistivity. Virtually all applications of diamond exploit one or other of its interesting properties.

A variety of deposition methods are currently used for the deposition of DLC, either from solid or carbon-containing gas precursors.

The potentially attractive properties of DLC coatings will remain irrelevant on the industrial scale as long as the specific problems limiting the applicability of the material, such as adhesion, high sp³ content, uniform thickness over large areas and production cost are not addressed.

The structure, the texture as well as physical properties of DLC films depend on the growth conditions which determine the relative concentration of the sp³ and sp² bonds.

Various techniques are currently used to produce DLC coatings: ECR-VCD [1 and 2], DC and RF PECVD [3 and 4], RF magnetron [5 and 6], filtered cathodic vacuum arc (FCVA) and PLD. Generally, film deposition techniques

are divided into ion beam, reactive plasma and laser techniques. The characteristic feature of most processes for growing DLC is that energetic carbon-containing species of 50-500 eV are involved.

In this paper, an original deposition method of DLC, Gaseous Thermoionic Vacuum Arc (G-TVA) is presented. The method is a sister technique of the – now classical TVA. While TVA is the name of a deposition technique based on vacuum arc plasma ignited in vapours of the solid material, G-TVA applies exactly the same principle but uses gas precursors.

DLC films were successfully obtained with G-TVA using CH₄ as precursor. This paper presents the first results obtained with this technique.

2. Experimental setup

The method is based on the localized ignition of an arc plasma in vacuum. The arc is ignited by applying a high voltage on an activated gas flow. The gas activation is obtained by bombardment with thermoelectrons supplied by a heated Tungsten filament. A schematic view of the experimental arrangement is presented in Fig. 1.

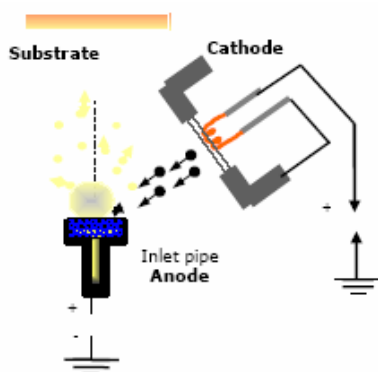


Fig. 1. Schematic view of the experimental arrangement.

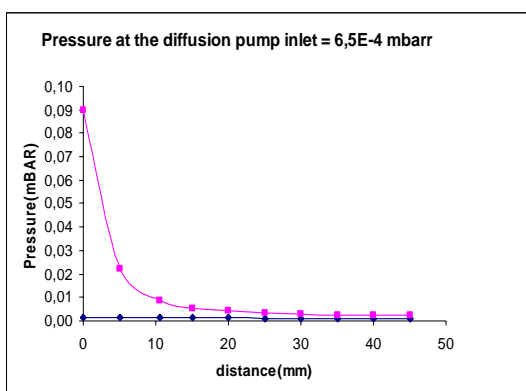


Fig. 2. Illustration of pressure gradient within the chamber with distance from gas inlet.

The most important part of the experimental arrangement is the gas inlet, which is provided with a special sieve capable of limiting and simultaneously spreading spatially the flow of gas.

Thus, a high pressure gradient is obtained between the end of the gas inlet and the chamber walls. The spatial distribution of the pressure within the chamber is presented in Fig. 2.

The plasma is localized just above the gas inlet, as can be observed in Fig. 3 where an arc plasma ignited in CH_4 is presented.



Fig. 3. Photo of the GTVA plasma ignited in methane.

3. Results

The optical emission spectrum of the methane plasma ignited using the Gas-TVA method has clearly shown the dissociation of CH_4 into hydrogen and CH radicals: H lines $\lambda_1 = 434.05 \text{ nm}$, $\lambda_2 = 486.14 \text{ nm}$, $\lambda_3 = 656.28 \text{ nm}$ and CH radical molecular band of the transition $A^2\Delta - X^2\Pi$ (Fig. 3).

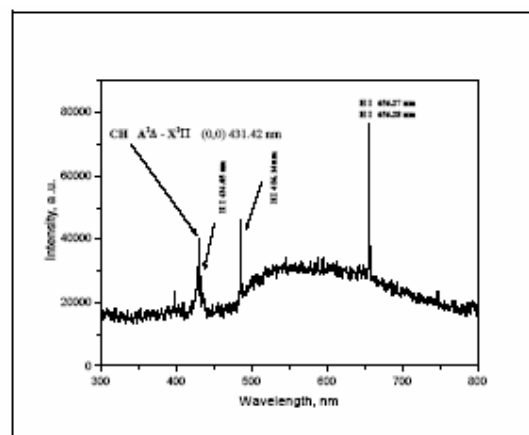


Fig. 4. Optical emission spectrum of the G-TVA arc plasma ignited in methane.

The composition, adherence and morphology of the films deposited using this new technique were also investigated.

The DLC films were found to be made of hydrogenated amorphous carbon with relatively high sp^3 content.

The thin films obtained are very smooth (roughness under 5 nm), compact and highly adherent. The grain size found was 4 nm. The HRTEM results indicated a 0.288 nm d-spacing corresponding to rhomboidal lattice of C8 structure.

XPS analysis revealed a high sp^3 content of the a-C:H films. The deconvoluted XPS spectrum of the films is presented in Fig. 7. Fig. 8 shows the appearance of the sp^3 peak reflected in the enlarged width of the spectrum compared to the width of the graphite spectrum (black).

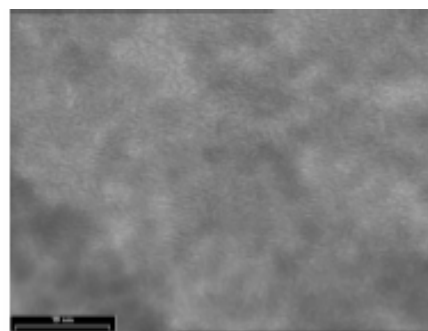


Fig. 5. HRTEM image of the carbon film.

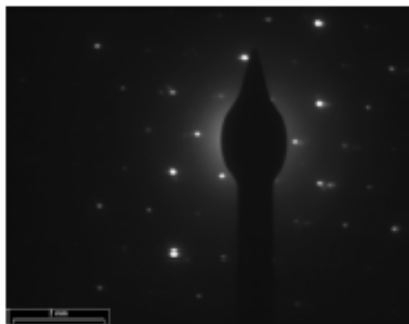


Fig. 6. SAED image of the carbon film.

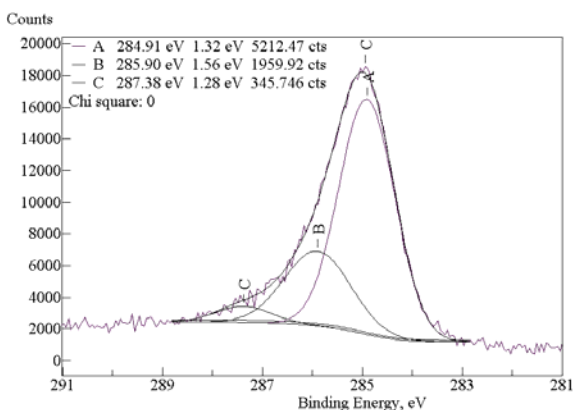


Fig. 7. XPS peak deconvolution.

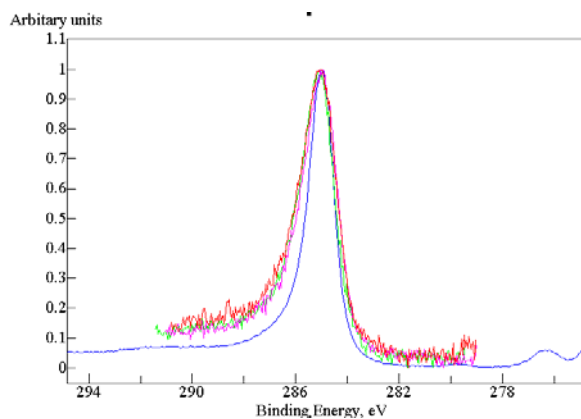


Fig. 8. XPS spectra, comparison of DLC with graphite.

4. Discussion and conclusions

The Gas-TVA is the only deposition method using precursor material in the gas state that forms a localized plasma in vacuum. This is a very important feature of the technique, as the substrate material can be placed away from the plasma, thus avoiding overheating.

In this work it was demonstrated the capability of the Gas-TVA technique to produce adherent, hydrogenated DLC films of relatively high sp^3 content.

The G-TVA extends the applicability of the classical TVA technique to the deposition of thin films from gas precursors.

The G-TVA deposition technique has opened up a new area of research for the synthesis of new materials. Further work on plasma diagnosis and also on surface characterisation of the films obtained using this technique is envisaged.

References

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