Operating domain for the formation of ZnO-DLC nanocomposite thin films in an aerosol assisted low pressure plasma

Z. Michon[1,2,3,4], G. Carnide[1,3], H. Klein[1,3], A. Girardeau[1,3], A. Paillet[2], M. L. Kahn[3], L. Stafford[4], R. Clergereaux[1]

[1] *Laboratoire Plasma et Conversion d'Energie, Laplace, Université Paul Sabatier, Toulouse, France*

[2] *Spaceship FR, CNES, Toulouse, France*

[3] *Laboratoire de Chimie de Coordination, LCC, CNRS, Toulouse, France*

[4] *Département de Physique, Université de Montréal, Montréal, Québec, Canada*

Abstract: Direct Liquid Reactor Injector (DLRI) enables the coupling of the synthesis of nanoparticles with the formation of nanocomposite thin films using a liquid spray injection. To control the formation of these thin films, the effects of injection parameters on the chemical synthesis and the thin film formation are of paramount. Here, we will describe these conditions for the formation of ZnO-DLC nanocomposites in a low-pressure RF plasma.

Introduction

Direct liquid reactor injector (DLRI) coupled with plasma processes is a safe-by-design method to form well-controlled nanocomposite thin films in a single process [1] It consists in the direct synthesis of nanoparticles (NPs) from liquid solutions prior to their injection in an aerosol phase into the plasma volume [2]. For example, it has been shown that nanocomposite thin films based on ZnO NPs dispersed in a DLC matrix can be produced in a low-pressure capacitively coupled RF plasma [2]. Indeed, in the DLRI, ZnO NPs are produced through the hydrolysis of zinc dicyclohexyl ($Zn(Cy)_2$) in the liquid droplets by a continuous flow of water vapor and transported in the plasma volume with the solvent, pentane, used as the matrix precursor through its plasma polymerization on the substrate (Figure 1).

a) b)

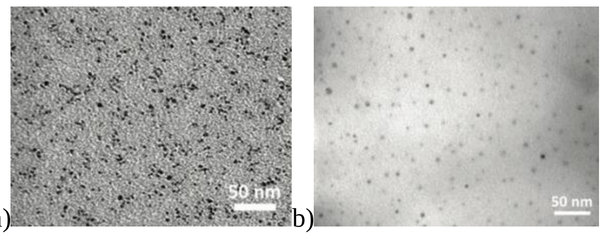

Figure 1 : TEM images of a) ZnO NPs formed in the DLRI and of b) a DLC-ZnO nanocomposite thin film. t_{liq} = 5 ms, t_{out} = 10 ms, Δt = 2 ms, $f_{liq} = f_{out}$ = 1 Hz

To further develop the process, a fine control of the injection times is needed. This study aims to report the operating domains of the DLRI coupled with a low-pressure plasma, i.e. the conditions were ZnO NPs are efficiently produced with a well-controlled composition of the ZnO-DLC nanocomposite.

2. Methods

Pentane solutions of $Zn(Cy)_2$ were prepared and injected through the DLRI:

1- to characterize the chemical reaction using ^{1}H NMR and to collect grids for microscopy.
2- to process in the plasma process and collect thin films for FTIR and TEM analyses.

Here, the operating domain for the ZnO NPs synthesis and the DLC-ZnO nanocomposite are determined for different injection times in the 2 to 10 ms (t_{liq}) and 2 to 20 ms (t_{out}) ranges.

3. Results and Discussion

^{1}H NMR allows to find the conditions for the full consumption of $Zn(Cy)_2$ during its hydrolysis. Indeed, for $t_{out} > t_{liq}$, zinc precursor is not further observed in the aerosol. TEM images highlight that it corresponds to optimal conditions for the synthesis of ZnO NPs. Their morphology does not significantly vary with an average size around 6 nm.

ZnO NPs formation is obtained for a stoichiometric condition of $Zn(Cy)_2$ and water vapor controlled by the injection parameters. It is expected that the quantity of ZnO NPs can be tuned by an optimal set of injection parameters (t_{liq} and t_{out}). However, with t_{out}, water vapor in excess can be introduced in the plasma process thus affecting the DLC deposition.

An operating diagram to form ZnO-DLC with controlled concentration of ZnO NPs will then be defined for the DLRI in low-pressure RF plasma.

4. Conclusion

DLRI is a well-controlled plasma assisted deposition process to form nanocomposite thin films. However, it needs to fully characterize the role of the injection parameters on both the chemical reaction and the plasma deposition process.

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References

[1] G. Carnide *et al.*, Coatings **13**, 630 (2023).
[2] G. Carnide *et al.*, Adv. Sci. **10**, 2204929 (2023).