Synthesis of gold/polymer thin films in atmospheric-pressure dielectric barrier discharges

F. Massines[1], A. Perdrau[1,2], B. Plujat[1,2], A. Najah[1], N.Barros[1,2]
[1]*CNRS PROMES, Rambla de la thermodynamique, 66100 Perpignan, France*
[2]*Université de Perpignan Via Domitia, 52 Avenue Paul Alduy, 66100 Perpignan , France*

Abstract: The aim of this work is to find a new process to synthetize nanocomposite thin films. The solution explored is based on an aerosol of gold salt diluted in isopropanol and injected in a Ar dual frequency DBD. The higher frequency plasma reduces the salt to form gold nanoparticles (NPs) and polymerizes the isopropanol while the low frequency transports the NPs on the surface. The effect of 2 salts, 2 gases and 2 high frequencies on the thin film properties is compared.

1. Introduction

Atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) is a low temperature process used for the growth of thin films. Unlike low-pressure PECVD, it does not require the use of vacuum systems and is suitable for the treatment of large surfaces. Another interesting aspect of working at atmospheric pressure is that liquids or colloidal solutions can be easily injected in the form of an aerosol into the plasma. This can lead for instance to the growth of nanocomposite thin films through proper selection of the precursors of the matrix and of the nanoparticles (NPs) embedded in it. One of the main benefits of this method is that NPs are not in any case directly manipulated, making the process safe by design.

In this work, the aerosol of a solution of gold salt (i.e., NPs precursor) in isopropanol (i.e. polymerizable solvent acting as a matrix precursor) is explored using a dual frequency dielectric barrier discharge (DBD) [1]. A previous study [2] using an aerosol of a colloidal solution of TiO2 NPs highlighted the benefits of alternating a high plasma frequency, responsible for the matrix polymerization, and a low one, to control the transport of NPs onto the substrate. In this research, both high and low frequencies are alternated; the low frequency is continuously applied while the higher is modulated.

2. Methods

The effect of the process parameters on the nanocomposite morphology, chemical composition and optical properties are studied. Furthermore, the aerosol formation and the evolution of the aerosol-droplet size are also characterized prior to the plasma entrance.

In this study, the low frequency is always 800Hz, while the high frequency is 60 kHz or 13.56 MHz. As a 60 kHz DBD is filamentary in Ar and could be glowing in Ar+NH_3 Penning mixture, these two atmospheres are considered, by adding 133 ppm of NH_3 to Ar. However, as the lower rate of isopropanol allowing proper functioning of aerosol is 1.7 %, even in Ar/NH_3 the DBD is filamentary. The rate of salt and gold is 11 ppm.

3. Results and Discussion

First, properties of thin film made from $HAuCl_4$•H_2O in Ar and Ar+NH_3 DBDs are compared [3]. Gold NPs are formed in the two cases, however, the presence of NH_3 drastically reduces the plasmonic resonance related to electron oscillations in the NPs. One explanation could be a reaction between the salt and NH_3 before entering the discharge cell. To check it, thin films are made with NH_4AuCl_4•H_2O in an Ar DBD. Results confirm that the gold nanoparticles are formed with this salt without allowing any plasmonic resonance. The analysis of the thin film morphology allows linking these observations to the aggregation of the nanoparticles formed from NH_4AuCl_4•H_2O.

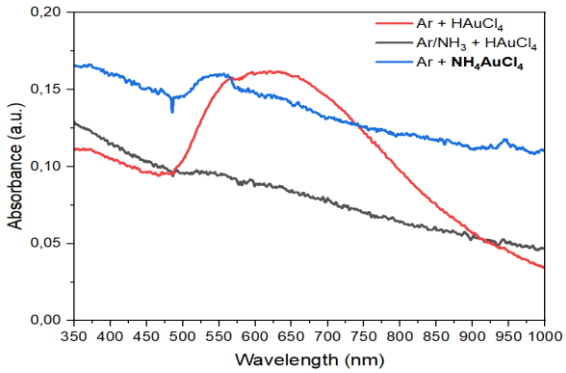

Fig. 1. Comparison of the light absorption of thin film deposits made from an aerosol of isopropanol and $HAuCl_4$ in Ar or Ar+NH_3 DBDs and from isopropanol + NH_4AuCl_4 in an Ar DBD.

The interest of radiofrequency voltage is to significantly increase the DBD power and its homogeneity. The deposit of a nanocomposite thin film with a RF-BF dual frequency DBD is shown and work is in progress focussing on the relationship between the DBD regimes and the film properties.

Acknowledgement

This work was supported by the National Agency for Research (ANR) under the project ANR-21-CE08-0038.

References

[1] E. Nadal et al. Nanotechnology 32, 17 (2021) 175601.
[2] P. Brunet et al. Langmuir 34, 5 (2018) 1865–1872
[3] A. Perdrau et al. Plasma Chem. and Plasma Proc., 2023, 43 (6),1749.