Dual frequency DBDs
or
how to design an atmospheric pressure plasma for surface treatment

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Abstract: The aim of this work is to play with two sinusoidal frequency voltages to manage the properties of thin films made in a DBD. The two frequencies are alternatively applied at the time scale of the thin film precursor residence time in the plasmas or simultaneously applied to the electrodes. The first configuration is of interest to make nanocomposite thin films of controlled morphology from nanoparticles and reactive gases or liquid, the second one allows to control the ion bombardment and thus the densification of the thin film.

Keywords: nano composite, glow, Townsend, biased RF, DBD, PECVD, FSK, aerosol

1. Introduction

Well-controlled multifunctional coatings are now the challenge in the field of plasma thin film processing. Composite thin films adding the properties of two materials like ZnO for antiUV and SiO_2 for barrier layers [1] or modifying the roughness to get a hierarchical multiscale surface texture [2] are good solutions to reach that goal. Such materials are obtained by mixing gas or liquid precursors able to form particles in the gas phase and thin film or by mixing nanoparticles (NPs) and gas or liquid thin film precursors. The advantage of the last solution is the control of the size, shape and chemical composition of the NPs. However, the plasma should be adapted to control the gas or liquid polymerization and the NPs transport to the surface. It is from there that the idea of coupling different plasma frequencies during the same process came. This coupling can be done at different time scales of the process: ns to ms for the discharge and the transport of the species created by the discharge, tens of ms for the interaction of the thin film precursors and the plasma and minutes for the process.

At atmospheric pressure, dielectric barrier discharge (DBD) is the most useful discharge to avoid gas temperature increase. Numerous configurations are developed. However, the simple plane/plane DBD is still the most useful for in-line treatment of two-dimensional materials like polymer films, silicon wafers, glass glazing, foams… This simple configuration generates different discharge modes in the same configuration and gas atmosphere.

In a Penning mixture, like Ar/NH3 or He very different low temperature discharges are obtained in a plane/plane DBD configuration with a millimetric gap [3-4]. In addition to filamentary discharges, homogeneous glow, Townsend, radio frequency DBDs are observed when the frequency increases. Typically, for sinusoidal voltage of frequency lower than 20 kHz the discharge is filamentary, thus it is a glow discharge thanks to the higher memory effect from a discharge to the following. Around 200 kHz for a 1 mm gap, the ions begin to be trapped in the gas and the discharge becomes a Townsend discharge. The transition to the RF mode occurs around 1 MHz. In the radio frequency range, the uniform mode is usually an alpha RF mode. If the RF voltage amplitude increases, the gamma mode is reached but the discharge tends to become filamentary. This is avoided by adding a polarization.

The increase of the frequency always increases the DBD power with a step of a factor two related to the transition from glow to Townsend and a step of a factor 10 between the Townsend and the RF discharges. The transition from Townsend to RF is characterized by a drastic decrease of the gas breakdown voltage (factors 4 to 5). The density of electrons increases to 10^{10}-$10^{11}/cm^3$ while that of metastable decreases by a factor 10 to become of the same order of magnitude as the electrons. The possibility to get all these discharges mode in a given configuration and with the same gas mixture, offers great potential in controlling thin film growth and properties.

Another point is that in a usual DBD configuration, the reactive gases are introduced in one side of the plasma and their residence time in the gas is tens of ms. Uniform thin films are usually obtained if the density of the precursor is always high enough to control the chemistry of the reactive species interacting with the substrate. This is obtained by the modulation of a high-power discharge. The high power ensures a rapid activation of part of the initial precursor, the modulation ensures a density of the initial precursor high enough to have the same chemical composition of the thin film whatever the precursor residence time in the plasma.

Having in mind all these points, the aim of this work is to explore how to manage the morphology of a composite thin film, or the density of a thin film coating with two frequencies DBD. After a rapid description of the different discharge modes obtained by changing the voltage waveform, the effect of the combination of different voltage waveforms on the discharge physics, the transport of different species to the surface and the final properties of the thin film will be presented.

2. FSK double modulation: nanocomposite thin film morphology

A solution more and more considered to make nanocomposite coatings is to use nanoparticles (NPs) and polymerisable molecules (gas or liquid) to make the matrix. The growth rate of the matrix is proportional to the discharge power which increases with the frequency. Thus the question is how to deposit NPs with a high frequency discharge. The drift is the highest force acting on NPs in a DBD as far as the voltage frequency is low enough, typically 1 kHz. So two different frequencies should be used, one to control the matrix thickness, the other one to control the density of NP.

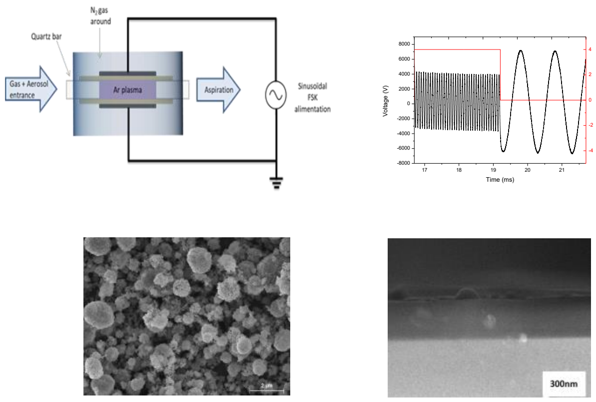

Fig. 1. Schematic representation of the discharge cell. Example of frequency shift keying (FSK) double modulation waveform applied onto the electrodes: the FSK frequency (f_{FSK}) is 200 Hz, the high frequency (f_H) is 15 kHz, the low frequency (f_L) is 1 kHz and the duty cycle (DC) is 50%. SEM observation of the surface of a superhudrophobic composite thin film realized with a DC=20% and SEM cross-section of the nanocomposite deposited with f_{FSK} = 200 Hz, f_{fH} = 15 kHz, f_{fL} = 3 kHz and DC = 20%.

Both frequencies could be applied simultaneously, however, we know that in a roll to roll DBD configuration, the plasma should be modulated to get homogenous thin film coating. As the precursor dissociation is really limited with a 1 kHz DBD, the aim is to alternate a period for the matrix growth rate (high frequency) and a period for NPs deposits (low frequency). An easy way to test this solution consists of using a FSK mode [5]. Fig. 1 presents one cycle of a typical FSK high voltage waveform applied to the electrodes. Frequency-shift keying (FSK) is a method of transmitting digital signals. The two binary states, logic 0 (low) and 1 (high), are each represented by an analogic waveform. Logic 0 is represented by a wave at a specific frequency and logic 1 is represented by a wave at a different frequency. It is defined by 4 parameters: the FSK frequency (f_{FSK}=1/T_{FSK}), with T_{FSK} the period of the signal which is the binary signal frequency, the frequency associated to the logic state 1 (f_H), the frequency associated to the logic state 0 (f_L) and their duty cycle (DC) defined as TOn_{FSK} /(T_{FSK}): higher is DC the longer the application of f_H.

Results show that alternating between two frequencies using Frequency Shift Keying (FSK) modulation waveform is a solution to control the morphology of the nanocomposite thin film [5] as illustrated by the SEM image of Fig. 1. Nanocomposite thin films of TiO_2 in a polymer-like matrix are made in an argon dielectric barrier discharge (DBD) from a suspension of TiO_2 nanoparticles in isopropanol (IPA). The sinusoidal voltage, which produces the plasma, is designed to separately control the matrix growth rate and the nanoparticles ~~(NPs)~~ aggregates transport to the surface. The design is based on the observation that a frequency higher than 10 kHz is needed to obtain a plasma power high enough to polymerize the IPA and a frequency lower than 10 kHz is needed to efficiently drift NPs aggregates to the surface. The useful FSK modulation mode (Frequency Shift Keying) is chosen to successively generate two sinusoidal voltages: a high frequency equal to 15 kHz and a low frequency ranging from 0.5 to 3 kHz. The duty cycle between these two signals is varied from 0% to 100% keeping constant the FSK period or the low frequency duration. According to the coating surface covering by the NPs and the thickness of the matrix determined from SEM images and in agreement with water contact angle measurements, in a filamentary DBD with a 1 kHz low frequency, the matrix thickness is basically correlated to the high frequency plasma power with a slope decreases at 0.43 $W.cm^{-2}$ related to the coating of the NPs in the gas bulk, while the NPs quantity in the composite thin film is basically proportional to the duration of the application of the low frequency signal. The FSK waveform is basically a double modulation: during the high frequency period the gas flow carries the NPs farther in the plasma and during the low frequency period the gas flow carries IPA molecules farther in the plasma. When it is close to the cutting edge, the low frequency acts like a NPs aggregate filter: higher the frequency smaller the size of the aggregates transferred to the surface. The others are trapped in the gas bulk. By only changing the FSK modulation parameters the thin film made from the same precursors is changed from superhydrophobic to superhydrophilic.

3. Low frequency biased RF DBD: thin film coating density

It is well known that an ion flux onto the surface helps in densifying a thin film coating. To benefit of both the high ionization level of the RF discharge and the ion bombardment of the surface associated with the LF voltage, each electrode is powered by a different power supply: 5,5 MHz and 1 to 100 kHz. The lower breakdown

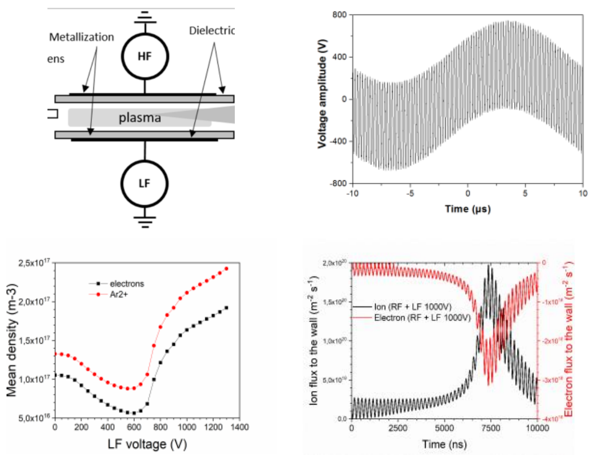

Fig. 2: Schematic representation of the discharge cell. Example of dual frequency DBD voltage. Variation of the mean electrons and ions density as a function of the 50 kHz bias amplitude for a 5 MHz and 350 V RF discharge.

voltage of the RF discharge allows to maintain a RF discharge while applying rather high LF voltages. The influence of the amplitude and the frequency of the two voltages is studied by optical methods [6] as well as by a numerical model using a fluid model developed by Gerjan Hagelaar that well describes the LF and the RF discharge [7].

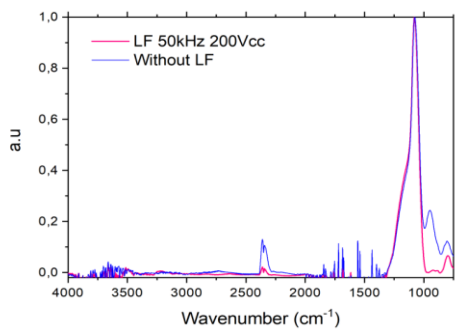

Fig. 3: Infrared absorption spectra of SiO:H thin film made at room temperature from SiH_4 in Ar/NH_3 with and without a bias added to the RF-DBD (f_{DBD} = 4.8 MHz) showing that the bias remove Si-OH.

Fig. 2 illustrates the two main behaviors. For RF discharge, first the LF voltage decreases the density of ions reducing the power of the discharge up to the point where the discharge is pulsed at 2LF as it is only on when the LF voltage is equal to zero. If the LF voltage amplitude increases more, the discharge turns off in pure Ar while it is enhanced in a Penning mixture. Its light becomes very intense with a large Ar emission and its intensity varies like in LF DBD. In this regime the gamma mode is reach part of the time. The LF/RF dual frequency discharge is a uniform mode [8]. As illustrated by the Fig 2., the model shows that this behavior is related to the enhancement of the electron secondary emission characteristic of gamma RF. The large secondary emission is related to a high ion flux to the electrodes which increases thin film density as shown by the drastic decrease of Si-OH bounds shown by IRTF spectra (Fig. 3).

4. Conclusion

This work illustrates how, in a DBD, the difference of the species mobility is easy to use to modify thin film properties keeping constant the thin film precursor, the gas and the set-up. Plasma frequency appears as a key parameter and the mix of frequencies pave the way to a better process control.

The rather long residence time of the gas and the thin film growth rates allow to alternate different discharge keeping and even enhancing the thin film homogeneity. The advantage of using a FSK double modulation mode is that the advantage of two different discharge are added to optimise the process without any modification of discharges physics.

When the aim is to control a short life time specie like ions, the two frequencies should be simultaneously applied leading to new discharge mode that should be studied to optimise the process. A very promising mode to enhance the ion bombardment and thus the densification of the thin film is the very stable and homogeneous gamma RF mode alternating with an alpha mode.

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