Formation and growth of tungsten nanoparticles in a low pressure argon discharge

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Abstract

Tungsten dust particle were easily grown in a direct-current argon sputtering glow discharge. The effects of an oxide layer was directly observable on the evolution of plasma parameters. A dust particle size evolution was established for specific experimental conditions.

Introduction

The formation of metallic nanoparticles by sputtering has been investigated in rf discharges [1] and sputtering system using the inert gas condensation method [2, 3]. However, very few studies were devoted to the formation of tungsten particles by sputtering in plasmas. In this article, we report the growth of tungsten nanoparticles in a direct-current (DC) argon glow discharge by sputtering of a tungsten cathode. We show that tungsten nanoparticles were easily produced. A careful study at an argon pressure P=0.6 mbar and a discharge current I_d= 40 mA was performed for discharge duration up to 200 s. It was shown that the tungsten nanoparticle growth modifies the discharge properties such as the discharge voltage and argon line emission intensities. The collected tungsten particles were analysed with scanning electron microscopy (SEM) allowing the measurement of dust particle size distribution. A growth law was obtained.

Experimental Set-up

The experiments were performed between two parallel electrodes inside a cylindrical vacuum vessel (30 cm diameter and 40 cm length). The electrode assembly consisted of a tungsten cathode of 9.9 cm diameter and a grounded stainless steel disc (anode) below the cathode. The cathode was mounted on an insulating ceramic disc and kept parallel to the anode disc by two half glass cylinders at a distance of 10 cm. A regulated DC power supply was used to bias the cathode. The discharge current density was kept at a constant value and the discharge voltage was the free parameter. Different diagnostics were used during discharge operation (optical emission spectroscopy, microwave interferometry, measurement of the cathode voltage). A sample holder was placed below a hole at the centre of the anode in order to collect dust particle which were then studied ex-situ by SEM.

Tungsten nanoparticles obtained for different discharge currents

Experiments of tungsten sputtering for different discharge current have been performed. The argon pressure was fixed at P=0.6 mbar and the two values of the current have been chosen. The first set of experiment was performed for a discharge current I_d =40 mA. The second set of experiments was performed for a discharge current I_d =80 mA. The particles were collected for two plasma duration: 200 s and 500 s. An estimate of the expected sputtering yield Υ was done [4]. It was found $\Upsilon \sim 3.8$ % at $I_d = 40$ mA and $\Upsilon \sim 5.6$ % at $I_d = 80$ mA.

Dust particle collected during these experiments are shown in Fig.1. Dust particle size distributions have been measured. Independently of the discharge parameters the most probable diameter of the tungsten dust particles is $d_w = 20 - 50$ nm. There are however major differences between experiments at I_d=40 mA and I_d =80 mA. For a discharge duration of 200 s, at I_d =80 mA two peaks were observed ($\sim$17 nm and $\sim$33 nm). On the contrary, a log-normal distribution of dust particle size (most probable size $\sim$33 nm) was observed at I_d=40 mA. For a discharge duration of 500 s, two peaks were observed at I_d =80 mA ($\sim$17 nm and $\sim$47 nm). At I_d =40 mA, the most probable dust particle diameter was $\sim$27 nm. Larger dust particles with diameter up to 120 nm were observed.

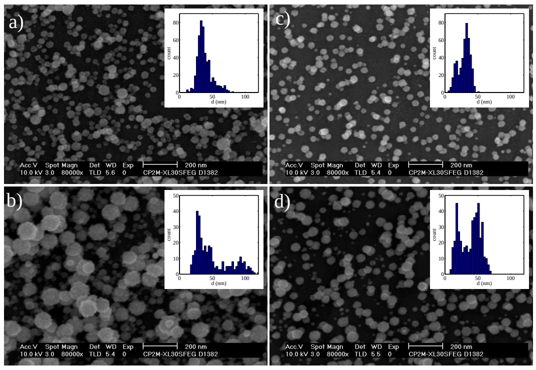

Figure 1: Scanning electron microscopy images of tungsten dust particle obtain in a discharge with $P_{Ar} = 0.6$ mbar. a) I_d=40 mA and t =200 s. b) I_d=40 mA and t =500 s. c) I_d=80 mA and t =200 s. d) I_d=80 mA and t =500 s. The inset in each images is the dust particle size distribution obtained from the micrographs.

Detailed studies at given plasma conditions

Discharges at P=0.6 mbar and I_d=40 mA have been performed. The dust particles were collected for different discharge duration up to 200 s and analysed with SEM. In Fig.2, the evolution of the different signals as a function of time is presented. Breakdown occurred for a cathode voltage slightly below 800 V. Then the cathode voltage decreased quickly (tens of milliseconds) to a value around $V_c \sim 500$ V and then it increased up to $V_c \sim 600$ V in 3-4 s. The electron density (Fig.2-f)was (except during the first second after breakdown) decreasing during this period. At this time a sharp drop of $\sim$15 V (in a time less than 0.5 s) was observed. This drop in the cathode voltage after 3-4 s was associated with the appearance of a luminous blue "secondary glow" at the center of the tungsten cathode and a stabilisation of the electron density. Then for 10 s to 30 s, the cathode voltage decreased very slowly while the electron density started to increase. With the naked eyes this corresponded to the expansion over the whole cathode surface of the "secondary glow". Afterwards the cathode voltage slowly decreased until the end of the discharge while the electron density increased.

The argon lines behaved differently. After the discharge break down, the signal intensity in-

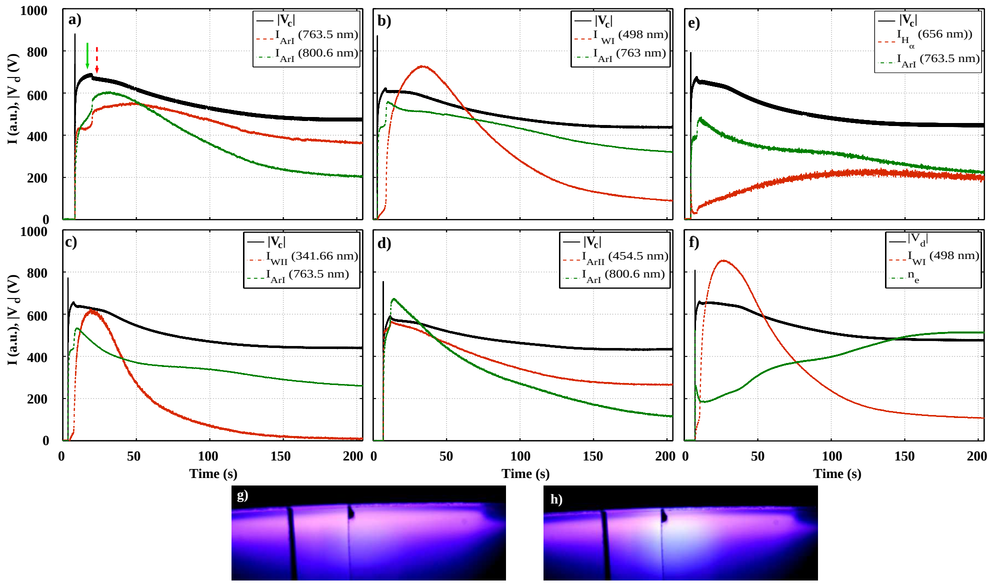

Figure 2: (a-f) Evolution of the cathode voltage, electron density and line intensities as a function of time. Each plot corresponds to an experiment with similar conditions. g) Picture of the cathode-fall region and beginning of the negative glow just before the sharp drop in the cathode voltage (indicated by the plain green arrow in a)). h) Same as g) just after the sharp drop in the cathode voltage (indicated by the dashed red arrow in a)). In g) and h) the contrast was increased (by the same amount in both picture) for a better visibility.

creased rapidly during the first tens of milliseconds. Then for 3-4 s, the intensity of the line continued to increase but at much slower rate. When the sharp drop in the cathode voltage occurred, the line emission increases again very rapidly for less than 0.5 s (duration of the cathode voltage drop, not a strong increase for argon ions). After this time, the behaviour of the emission intensity changed a little from one experiment to another. However there was a general trend to a diminution of the line emission intensity.

The tungsten lines shown another behaviour. After breakdown the signal increased almost linearly for 3-4 s. When the sharp cathode voltage drop occurred, the emission intensity of the line increased very strongly during 15 s to 30 s. Afterwards, the intensity decreased steadily until the end of the discharge.

A possible explanation for the observed behaviour is that the secondary electron emission coefficient of tungsten oxide is lower than the one of pure tungsten at the considered ions and fast neutral energies (∼70-80 eV) [5, 6]. A layer of tungsten oxide and other impurities at the cathode surface was sputtered away during the first few seconds of the plasma. When pure tungsten was exposed to the plasma, the secondary electron emission coefficient increased which engendered a small cathode voltage drop and a stabilisation of the electron density. This was in

contrast with the effect due to the formation of dust particle. The signal intensities of both argon and neutral tungsten lines increased at cathode voltage drop and were associated with the appearance of a luminous "secondary glow" in the center of the cathode. As the sputtering yield of tungsten is higher than the one of tungsten oxide [7, 8], the strong increase of the tungsten line intensities is in accordance with pure tungsten being exposed to the plasma.
Using the SEM images, it was possible to measure the dust particle diameters and obtain the evolution of the dust particle size distribution (Fig.3).

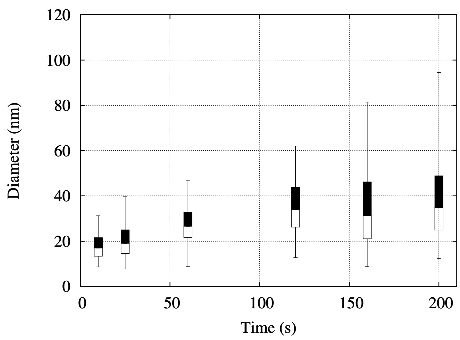

Figure 3: Evolution of the dust particle diameter in an argon plasma with $P = 0.6 mbar$ and $I = 40$ mA. The intersection of the black and white rectangle gives the mean diameter the top of black rectangle gives the multiplicative standard deviation at 1 $\sigma^{\star}$, the bottom of the white rectangle gives the lower one at 1 $\sigma^{\star}$. The upper and lower lines give the maximum and minimum measured dust particle diameters.

As can be seen, during the first sixty seconds, the dust particle diameter was increasing almost linearly and the multiplicative standard deviation was almost constant $\sigma^{\star} \simeq 1.3$. After that the dust particle mean diameter stayed around 35 nm but the width of the distribution started to increase. After 200s, dust particle with diameter up to 90 nm could be found and $\sigma^{\star} \simeq 1.4$.

Conclusion

In conclusion, we have shown that tungsten dust particle were easily grown in a direct-current argon sputtering glow discharge. The effects of an oxide layer was directly observable on the evolution of plasma parameters. A dust particle size evolution was established for specific experimental conditions.

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