

LOW TEMPERATURE PLASMA AND PLASMA TECHNOLOGIES ON THE SYNTHESIS AND PROCESSING OF NANOPARTICLES BY PLASMAS

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A gas aggregation system combined with a magnetron discharge is used to produce nanoparticles (NPs) from metal targets. Here, we present an overview of the role of different parameters in the TiOx NP synthesis and available challenges in this technique. Particularly, considering the role of duty cycle in the TiOx NP formation at pulsed DC regime indicates that only at a certain duty cycle (for the given condition) a stable NP generation can be achieved. Furthermore, the critical role of oxygen (as a reactive admixture gas) in launching and controlling of the NP synthesis process is studied in detail. Employing an RF hollow electrode discharge for processing of silver NPs leads to charging of most of the NPs, and surprisingly, we found that at high RF plasma powers the contribution of charged NPs in the primary NP beam vanished in the treated beam deposition.

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INTRODUCTION

Synthesis and processing of nanoparticles (NPs) for different applications have received numerous attentions during the last years due to the extraordinary characteristics of NPs and the exclusive role of this type of materials in tuning the properties of advanced functional materials [1]. Although in advanced technologies, plasmas with different configurations are frequently employed for various aims, due to the complexity of the phenomena, several aspects of the observed behaviour in the NP generation process and materials treatment are still unexplored.

Controlled synthesis of NPs is an interesting challenge in nanotechnology. Among several plasma based techniques for NPs production [2], a gas aggregation source (GAS) combined with magnetron sputtering is one of the most desired systems to generate NPs from various materials [3-6]. Adjusting the NPs properties by tuning the operating conditions is the biggest advantage of this method.

Due to the interesting chemical activities and a wide variety of applications [7, 8], many researchers have focused on understanding and optimizing the synthesis process of titanium based NPs by the gas phase route [5], [9-12]. Previously, Marek et al. [10] showed that adding oxygen (as a reactive admixture) to the aggregation zone can considerably accelerate the TiOx NPs synthesis process. Next, experiments by Peter et al. [11] approved that the NP generation from a pure Ti target is impossible by the conventional DC sputtering in a pure noble gas atmosphere. Furthermore, in the given conditions, the TiOx NPs generation is launched only when the oxygen admixture is selected from a certain range. Recently, we have indicated that by adjusting the amount of oxygen admixture, a stabilized TiOx NPs generation rate for a long term can be achieved [12]. The physics beyond the synthesis and also the stabilized generation of TiOx NPs is very complicated. Here, we overview the key role of the plasma species and also the discharge properties in the NP synthesis from a reactive metal.

In most cases, the synthesized NPs should be treated by a proper technique in a characterized environment to show the desired properties. Hence, understanding the interactions between NPs and processing medium is very important and plays a crucial role in the fabrication of advanced nanomaterials and also adjusting of their properties. Nowadays, modification of physical and chemical properties of NPs is one of the biggest challenges in technological breakthroughs [13]. To avoid undesired effects and also complexity, the NP modification should be performed in a separate environment. However, when a complex medium, such as plasma, is employed for processing, interpreting the observed phenomenon will often be complicated. Nevertheless, the outstanding properties of plasmas with different configurations could convince many researchers to employ them for processing a wide range of materials. Here, we investigate the interactions between an RF hollow discharge and a metal NPs beam produced by the GAS. For this purpose, an extra plasma system was added to the setup and the titanium target was replaced by a silver target.

1. EXPERIMENTAL

The experimental setup used here was already described in previous articles [12, 14, 15]. A home-constructed GAS combined with a 2 inch planar magnetron was applied to generate NPs from a silver and/or titanium target. Argon was used as a working gas, while in case of the titanium target a small amount of oxygen (as reactive admixture) was added to the aggregation chamber. The GAS was connected to the deposition chamber via an orifice, 3 mm in diameter. The pumping system (includes a turbo molecular pump supported by a scroll pump) connected to the main chamber reduced the whole system pressure to 10^{-5} Pa as base pressure [12]. To process the formed Ag NPs, a fairly small hollow electrode working at low pressures and RF regime was lastly installed in the main chamber [14]. It was connected to the GAS through an electrical deflector. The deflector system includes two plate

electrodes with a small rectangular slit on each. These electrodes were connected to the separate DC power supplies with opposite polarities at a fixed voltage (70 V) to remove all charged NPs from the NP beam. More details of the used experimental setup can be found in Ref. [15].

2. RESULTS AND DISCUSSION

For the study of the stability of TiOx NP generation, a set of experiments was performed by running a DC magnetron discharge in the GAS to generate NPs from a pure titanium target. To get comparable results, all experiments were started with the pre-cleaning process by running the discharge for several minutes in a pure argon atmosphere to remove all impurities in the system (mostly from the target surface). The pre-cleaning was continued as long as a certain magnetron bias voltage was recovered at a given pressure (50 Pa). After the pre-cleaning process (at $t = 0$), a small amount of oxygen admixture was added to the GAS, and the NP deposition rate (D.R.) was measured by a quartz microbalance monitor (QCM) which was mounted in the deposition chamber. Primary findings at DC regime showed that only under a certain oxygen admixture a highly stable TiOx NP generation can be achieved at the relatively low pressure (50 Pa) [12].

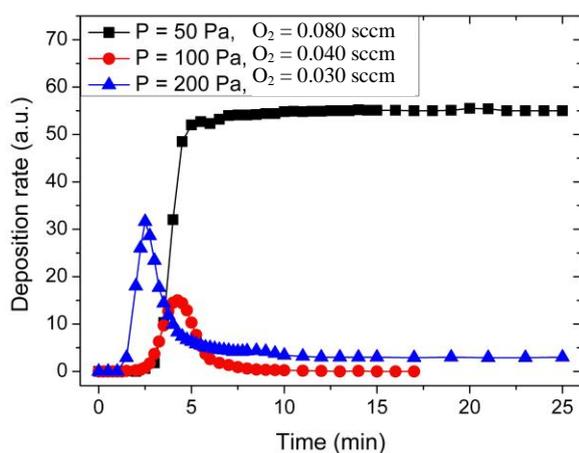


Fig. 1. Evolution of TiOx NPs deposition at different pressures after optimizing the oxygen admixtures. Only at low pressure (50 Pa) a highly stable deposition rate was found [12]

The oxygen admixture is needed to increase the bonding energy of the seeds by changing their chemistry [11]. On the other hand, oxygen can reduce the sputtering rate by forming (and then developing) the poisoned area on the target. Competition between these two mechanisms determines the evolution of the TiOx NP generation rate in the GAS.

Switching to higher pressure not only shifts the range of working oxygen admixture to a lower level, but also can dramatically decelerate (and finally suppress) the NP formation process by reducing the sputtering rate (Fig. 1). In the high pressure regime, returning many of individual sputtered atoms to the target surface, after oxidation in volume (due to the collisions with the background gas), is the main factor to accelerate the

poisoning process. Therefore, the NP D.R. drops to zero (or very low level) after increasing for some minutes.

As already seen, the oxygen admixture plays an important role in controlling of different mechanisms in the GAS. Thus, considering the role of reactive species in different processes is very instructive. Particularly, in the current research, understanding the channels of oxygen consumption in the GAS is of interest. When oxygen is injected into the chamber, it starts to diffuse into the volume. During this process, some of the oxygen species can meet the sputtered atoms and bond to them. These oxidized species (metal oxide molecules) are the main constituents for the nucleation and growth of NPs in the GAS [13]. The rate of oxygen consumption by free sputtered atoms depends on the concentration of oxygen species, the density of free sputtered atoms, and specially the diffusion rate in the buffer gas. Furthermore, the flux of oxygen, the working pressure, and the temperature are considered as important parameters which can indirectly influence on the rate of oxygen-sputtered atom reactions. The non-reacted oxygen particles in the above mechanism can reach the walls and also the target surface. Those oxygen particles that reach the walls can be bound by the available metal atoms on the GAS walls through chemical reactions, or stick to the walls individually. Furthermore, the arrived oxygen particles on the target can react with upper atoms of the target surface and poison the target by forming a dielectric oxide layer on it. Finally, the remaining oxygen, which does not participate in the above processes, can escape from the GAS via the small orifice.

The rate of oxygen consumption by each mechanism depends on how the oxygen is introduced into the GAS. Since in the used setup the gases stream into the GAS from a channel near the target, the poisoning process is more pronounced in a short period after the oxygen injection.

A study on each possible scenario of oxygen consumption provides useful knowledge to understand the physics of synthesis in the GAS. As it was previously addressed in detail [5, 12] the escaped oxygens from the GAS can be monitored by a mass spectrometer in the deposition chamber. The mass spectrometer signals clearly manifest the evolution of the oxygen consumption in the GAS [12]. In-situ measurement of chemical composition of the formed NPs can give some information about the content of oxygen consumed in the clustering process [5]. Furthermore, the evolution of the bias voltage (of the magnetron discharge) is proportional to the development of the poisoned regions on the target [12]. Fig. 2 displays a chart of possible scenarios for oxygen in a GAS. Although the highlighted green route is the desired scenario that leads to the NP generation, the optimized NP formation can be achieved only by controlling all scenarios.

It is well known [17] that forming of poisoned areas on the target reduces the active area in the sputtering process by creating a strong local electric field in the poisoned regions. For solving this problem, the pulsed DC sputtering was developed [16]. Preliminary

experiments confirmed that switching to the pulsed DC regime can significantly increase the rate of TiOx NP generation [17] which is promising for stabilizing the NP formation at high pressures. The frequency and the duty cycle of the pulse are crucial parameters in this regime [5], [16]. They should be adjusted in a way that the electrons can neutralize the total charge on the target, and also the strength of the delivered power

should be sufficient to remove the poisoned area on the target surface.

To optimize the pulsing parameters for getting the stabilized TiOx NP generation, several experiments were performed at different operating conditions. This part is devoted to study the influence of the duty cycle on the synthesis process at 100 Pa working pressure, while the oxygen admixture and frequency are kept constant at 0.055 sccm and 40 kHz, respectively.

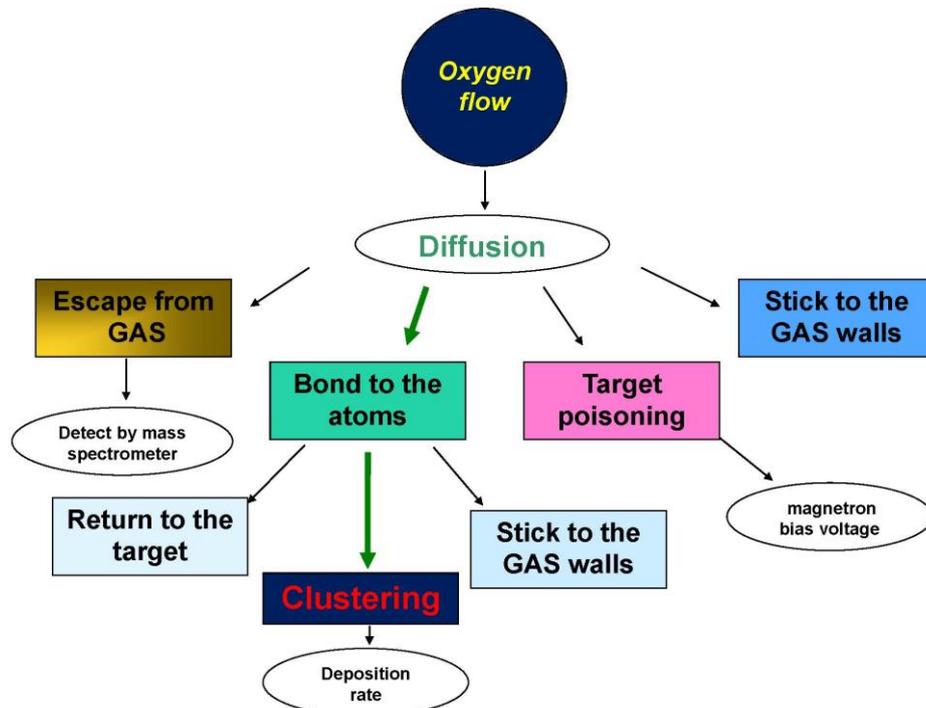


Fig. 2. A schematic chart of different possibilities for oxygen consumption in the GAS. The green line is the favored route leading to the NP generation

As shown in Fig. 3, immediately after oxygen injection to the chamber no deposition was recorded. As found in the DC regime, during a short period after oxygen injection, most of the oxygen is absorbed by the highly reactive pure titanium atoms on the target and the walls of the GAS. This prevents forming sufficient seeds in the volume to launch the TiOx NP. Thus, the D.R. of NPs remains at the zero level during a short period after the oxygen injection. As soon as the gettering process ceases, some of the oxygen species can participate in the clustering process by oxidation of the sputtered atoms. However, sputtering the oxide species during the *plasma on* period has a main contribution in launching the NP synthesis in this regime. According to the obtained data (see Fig. 3), only at a certain duty cycle (50 % for the given operating conditions), the stabilized TiOx NP formation was achieved. This means, only at unique operating parameters the area of the poisoned zones on the target (and then the sputtering rate) is constant. In this case, the rate of the poisoning process and the rate of the cleaning process in the *plasma on* period are in equilibrium.

Switching to the lower duty cycle led to an unstable D.R.. At this condition, a shorter *plasma on* period increases the power density which improves the sputtering rate during the *plasma on* period.

Additionally, a longer *plasma off* period results in more oxide formation on the target. These oxide species have an opportunity to participate in the NP formation process after sputtering off in the next *plasma on* period. At such a duty cycle, the cleaning process overcomes the poisoning process. Higher seed density accelerates the NP formation rate, which shifts the knee of the D.R. to a higher level. However, by continuous surface cleaning, the target gradually turns to a pure metal target. This increases the number of pure Ti atoms in the volume, and then the NP nucleation process will be decelerated (due to low bonding energy of pure Ti atoms). In the opposite direction, by switching to a higher duty cycle, the NP D.R. falls to the zero level after initial increasing. In this case, the longer *plasma on* period reduces the power density which leads to a lower sputtering yield. On the other hand, a completely oxidized TiO₂ layer has a tendency to release oxygen under energetic ion bombardment and convert to a titanium sub-oxide layer [18], [19]. Therefore, in reactive sputtering of titanium, the energetic impacting ions have a critical role in the cleaning process and subsequently, in increasing the conductivity of the target surface. At a lower power density, the magnetron discharge includes less energetic ions which reduces the rate of the cleaning process. Additionally, a shorter

plasma off period reduces the available time for the incoming electrons (to the target surface) to neutralize the ions on the target. Both above mentioned factors decrease the seed density continuously. Then, after several cycles, the number density of seeds in the volume cannot meet the supersaturation condition, and the NP formation process will be totally suppressed. As it recently has been reported, a similar behavior can be found for the repetition frequency [5].

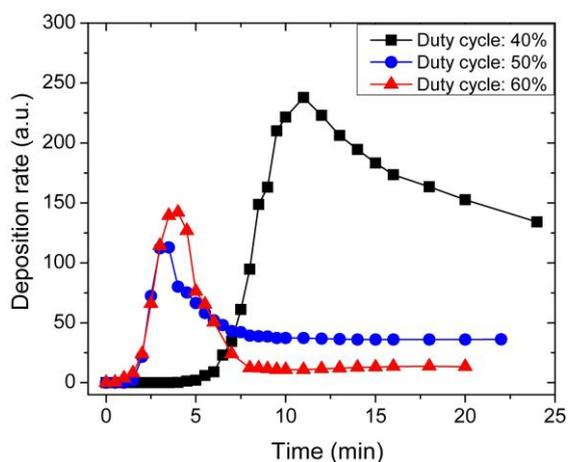


Fig. 3. Evolution of TiOx NPs deposition at different duty cycles in the pulsed DC regime. The repetition frequency and oxygen admixture were fixed at 40 kHz and 0.055 sccm, respectively

The role of oxygen in the NP synthesis process in the pulsed DC regime was previously studied [5]. Several experiments confirmed that a small change in oxygen admixture does not disturb the stability of the TiOx NP deposition, but can significantly change the size of the formed NPs in a nonlinear way. However, the physics of this behavior is not understood yet.

In the last section of this work, a fairly small RF hollow electrode working in the low pressure regime was added to the setup to modify the NPs before deposition. The target was also replaced by a silver target to be able to have a stable NP generation in the conventional DC regime. The hollow electrode was installed in the deposition chamber and connected to the GAS via an electric deflector. The deflector was employed to remove all the charged NPs coming from the GAS [12]. Due to the novelty of the hollow electrode geometry, a set of plasma diagnostics was used to characterize the ignited RF discharge at different operating conditions. Details of the obtained data have been reported by Ahadi et al. [14]. The RF plasma interestingly resembles a DC hollow cathode discharge. Furthermore, the high electron density at different operating conditions promises to be a suitable system for different materials processings. Previous investigations [15] showed that the geometry of the deposited spot varied with the RF power. Furthermore, the lateral size distribution of Ag NPs in the beam changes with plasma power. These observations can be explained by the charging of NPs in the plasma and trapping of the negatively charged NPs in the plasma volume. Additionally, the results clearly indicated that

most of the NPs are negatively charged by the plasma, while the contribution of the positive NPs increases with increasing the RF power [15].

Here, we explored the influence of the hollow electrode discharge (with different powers at fixed pressure (2 Pa)) on the D.R. of Ag NPs generated by the GAS operated at 200 Pa. The measurements were performed two times, once for a pure neutral NP beam (after purification by the deflector) and once for the primary NP beam generated by the GAS (without purification). The obtained data are summarized in Fig. 4. As a general trend, treatment by the RF plasma significantly reduces the NP deposition (a sharp drop in the curve). At low RF powers, this reduction is more pronounced, and the D.R. reduces more than one order of magnitude in the presence of the RF discharge. Increasing the plasma power, increases the D.R. gradually, and finally the rate of NP deposition reaches a stable level. Losing NPs in the plasma volume (particularly at low applied powers) and the electrostatic repulsion force between NPs after charging by plasma can explain this reduction. Moreover, increasing the plasma bias voltage by the plasma power [14] enhances the trapping of negatively charged NPs in the bulk plasma, which results in a greater D.R. at higher RF power. As expected, the D.R. of the pure neutral NP beam (blue markers) at very low powers is lower than the D.R. of the unfiltered beam (black markers). However, by increasing the RF power this difference becomes smaller, and eventually at high powers an identical D.R. was found in both cases. In other words, the existence of the charged NPs in the unfiltered beam was concealed by the RF discharge at high applied powers. Reflection of the negatively charged NPs by the plasma sheath (which can be changed by power) and then losing the positively charged NPs in the RF plasma volume, can explain the observed behavior. However, more experiments should be done to clarify the physics behind this trend.

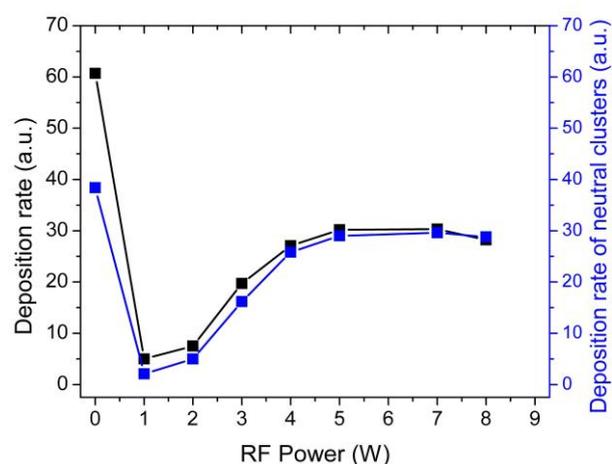


Fig. 4. The deposition rate of the filtered (blue) and unfiltered (black) Ag NPs after processing by a hollow electrode discharge at different powers

CONCLUSIONS

Synthesis and deposition of oxide metal NPs were investigated experimentally by employing a GAS combined with reactive DC and/or pulsed DC

magnetron sputtering. The role of reactive gas admixture, pressure, and pulsing parameters on NP formation was studied in detail. In the DC regime, due to the continuous enlarging of the poisoned area at high pressures, the highly stabilized TiO_x NP generation was found only at low pressure (50 Pa). The analyzed data demonstrated that, at given conditions, the stable NP production is limited to a narrow range of oxygen admixture and certain pulsing parameters.

Considering the interaction between Ag NPs and an RF hollow electrode discharge showed that most of the NPs are negatively charged in the plasma. The NP deposition was considerably reduced under plasma treatment. Furthermore, the losing of charged NPs from the unfiltered beam is more pronounced in the high plasma power regime.

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СИНТЕЗ И ОБРАБОТКА НАНОЧАСТИЦ С ПОМОЩЬЮ ПЛАЗМЫ

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Использование систем агрегации газа и магнетронного разряда позволяет получать наночастицы (НЧ) из металлических мишеней. Представлен обзор различных параметров, влияющих на синтез TiO_x НЧ, и существующих проблем этого метода. В частности, влияние рабочего цикла на формирование TiO_x НЧ в импульсном DC-режиме указывает на то, что стабильное образование НЧ может быть достигнуто только в определённом рабочем цикле (при данных условиях). Кроме того, детально изучена ключевая роль кислорода (в качестве газовой реактивной добавки) в инициировании и контроле процесса синтеза НЧ. Использование ВЧ-разряда с полым электродом для обработки НЧ серебра приводит к зарядке большинства НЧ. Также показано, что в режимах с высокой ВЧ-мощностью, вводимой в плазму, заражённые частицы в первичном пучке НЧ не вносят вклад в осаждение.

СИНТЕЗ І ОБРОБКА НАНОЧАСТИНОК ЗА ДОПОМОГОЮ ПЛАЗМИ

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Використання систем агрегації газу і магнетронного розряду дозволяє отримувати наночастинки (НЧ) з металевих мішеней. Представлено огляд впливу різних параметрів на синтез НЧ TiO_x та існуючих проблем цього методу. Зокрема, вплив робочого циклу на формування НЧ TiO_x в імпульсному DC-режимі вказує на те, що стабільне утворення НЧ може бути досягнуто тільки в певному робочому циклі (за даних умов). Крім того, детально вивчена ключова роль кисню (в якості газової реактивної добавки) у ініціюванні та контролі процесу синтезу НЧ. Використання ВЧ-розряду з порожнім електродом для обробки НЧ срібла призводить до зарядження більшості НЧ. Також показано, що в режимах з високою ВЧ-потужністю, що вводиться в плазму, заряджені частинки в первинному пучку НЧ не мають впливу на осадження.