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The influence of pressure and gas flow on size and morphology of titanium oxide nanoparticles synthesized by hollow cathode sputtering

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Abstract: Titanium oxide nanoparticles have been synthesized via sputtering of a hollow cathode in an argon atmosphere. The influence of pressure and gas flow has been studied. Changing the pressure effects the nanoparticle size, increasing approximately proportional to the pressure squared. The influence of gas flow is dependent on the pressure. In the low pressure regime ($107 \leq p \leq 143$ Pa) the nanoparticle size decreases with increasing gas flow, however at high pressure ($p = 215$ Pa) the trend is reversed. For low pressures and high gas flows it was necessary to add oxygen for the particles to nucleate. There is also a morphological transition of the nanoparticle shape that is dependent on the pressure. Shapes such as faceted, cubic and cauliflower can be obtained.

1. Introduction.

The synthesis of nanoparticles from highly ionized growth material is a versatile tool for fast nanoparticle growth,¹ with control of the particle size,² and oxygen stoichiometry.³ This approach can be used to decorate surfaces with mono dispersed particles without significant agglomeration.⁴ To further investigate and develop the process, the influence of the pressure and gas flow was investigated. Other authors have synthesized nanoparticles from weakly ionized growth material by sputtering and studied the influence of these two parameters. For the nanoparticles to be able to nucleate and grow in a sputtering system, a higher pressure is needed when compared to thin film synthesis. To achieve this, the magnetron is typically placed in a high pressure aggregation zone.

By increasing the gas flow or decreasing the size of the exit hole, the pressure in the aggregation zone can be increased. Previous studies on the effect of a pressure have been done by Drábik *et al.*⁵ on a Haberland style cluster source. They show a size increase when the pressure is varied from 50 to 100 Pa, but then a decrease from 100 to 150 Pa. Ayeshe *et al.*⁶ found a general size decrease with increasing gas flow when using a cluster source (Nanogen-50), however at certain aggregation lengths there were regions where the size increased with gas flow. Srivastava *et al.*⁷ used an identical cluster source to synthesize titanium dioxide nanoparticles. In their experimental setup, the pressure increases from 40 to 120 Pa when the gas flow increases from 20 to 60 sccm. They reported a decrease in the nanoparticle size with increasing argon gas flow which was attributed to a decrease in the nanoparticles residence time.

Typical magnetrons are designed for pressures in the order of 1 Pa, operating at higher pressure can lead to an unstable plasma and sputtering of the inside of the magnetron gun.⁸ In addition, the sputtering efficiency of magnetron discharges decreases with increasing pressure.⁹ This can make it difficult to separate the effect of increasing pressure from a reduction of the sputtering efficiency. Several authors have used other designs of cluster sources that can operate at higher pressures and studied the effect on the nanoparticle size.^{10 11 12}

Yamamuro *et al.*¹⁰ utilized a cluster source where two magnetrons faced each other. This setup was operated up to 360 Pa and the mean size of chromium clusters increased from 8.6 to 13.2 nm when the pressure was increased from 120 to 280 Pa accompanied by an increase in the width of the size distribution. This was attributed to an increased volume where nanoparticles could nucleate and grow at higher pressures. When the gas flow was increased and the pressure was kept constant, there was no increase in the mean nanoparticle size but an increase in the width of the size distribution. Maicu *et al.*¹¹ utilized a hollow cathode based cluster source where the pressure was increased by adjusting the gas flow. This combined increase in both flow and pressure, increased the nanoparticle size and size distribution. Aoshima *et al.*¹² used a similar hollow cathode setup where size control of iron nanoparticles from 40 to 170 nm was possible when the pressure was increased from 130 to 1300 Pa.

Because of these differing results it is important to further study the effect of these parameters. Our approach is to vary the pressure of the system by changing the effective pumping speed. By doing so, the pressure and gas flow can be independently varied. Another benefit with the setup presented

in this work compared to cluster sources using magnetrons is that it can work in a wider pressure range. To minimize the effect of contaminants from the high vacuum system, a protective tube was constructed in which the nanoparticles could grow in an inert gas flow.

2. Experimental setup

The experiments were conducted in a high vacuum system with a base pressure in the mid 10^{-5} Pa range. The process pressure was determined and automatically regulated by a throttle valve in front of the pump. Due to the nature of high vacuum systems, increasing the pressure by restricting the pumping speed results in additional contamination due to evaporation of adsorbed species on the chamber wall and permeation through the rubber gaskets. To mitigate against this, a tube around the growth zone of the particles was constructed (“growth tube”) with an aperture with diameter of 10 mm where particles and argon gas can exit, while contaminants from the vacuum system are reduced.

Fig.1 Sketch of the experimental setup. The hollow cathode is situated atop of the chamber. On the cathode holder, a water cooled growth tube is attached with a potential of -50 V. Oxygen is injected

into the tube from underneath. There is a 10 mm hole for the nanoparticles and gas to exit through. A substrate with potential of 45 V is placed 30 mm from the opening of the tube. The gas is continuously pumped by a turbopump, and the effective pumping speed is regulated by a throttle valve that communicates with a pressure sensor to maintain a constant pressure. A differentially pumped residual gas analyzer is also connected to the chamber.

The experimental setup is described in Fig. 1, and consists of a cylindrical chamber, diameter 200 mm and height of 450 mm with a hollow cathode mounted in a water-cooled polyoxymethylene holder located on the lid of the chamber. The cathode is made of Ti with an inner diameter of 5 mm and a length of 55 mm. The growth tube consists of a grounded electrode (anode) placed between two tubes with a potential of -50 V. The anode cylinder (diameter 40 mm) was placed 68 mm below the hollow cathode. The growth region above the anode has a length of 68 mm and a width of 73 mm. A bottom narrow tube was attached so that the nanoparticles could be guided to the substrate by the gas flow. The growth tubes and anode cylinder are water cooled to prevent temperature drifts. The tubes are sealed together with rubber gaskets. It is possible to inject oxygen through the lid of the chamber to the outside of the growth tube. It is also possible to inject it through the bottom tube directly in to the growth zone.

A DC power supply (MDX 1K) connected to a homemade pulsing unit supplying square voltage pulses to the cathode was used. The DC power supply was set in current regulation mode and held at 0.52 A, the pulse width was set to 80 μ s and the frequency to 1.5 kHz. This resulted in pulses with voltages of approximately 290 V and peak discharge currents of approximately 10 A. These were the same parameters used in our previous paper³ and were found to give a stable partial pressure of oxygen during reactive sputtering. The main process gas, Ar, was fed through the hollow cathode after passing through a gas purifier (UltraPure). The gases in the chamber was analyzed with a differentially pumped residual gas analyzer (RGA) (Spectra microvision). Water vapor was the dominating residual gas, with partial pressure of an order of magnitude higher than nitrogen. Before each experimental series of 7 samples, the cathode was clean sputtered for 20 minutes or until the cathode discharge voltage reached values of 290 V or lower. The synthesized nanoparticles were collected on substrates (10 mm by 10 mm Au-coated Si), which were positively biased at 45 V to attract nanoparticles. The nanoparticles were analyzed using a scanning electron

microscope (SEM) (LEO 1550 Gemini) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford instruments). The EDS data was acquired by analyzing 5 different areas on each substrate where there was a suitable amount of particles. From these 5 measurements, the average value and standard deviation was taken. Transmission electron microscopy (TEM) was conducted using a (FEI Tecnai G² TF 20 UT). The nanoparticle size distributions were calculated from the SEM images, which were taken at random places on the substrate, by using an image analysis program written in Matlab. This image analysis program measures the visible area of the particles from the 2 dimensional images. The nanoparticles diameter is then calculated from $d = \sqrt{4area/\pi}$ for spherical particles and $d = \sqrt{area}$ for cubic particles.

Under certain process conditions, oxygen had to be added to the process in order to facilitate nucleation of nanoparticles. This oxygen flow was set to 0.05 % of the argon gas flow. The conditions where this was necessary were dependent on the base pressure.

3. Results

First contaminations from the chamber into the growth zone and subsequent reactions with the hollow cathode was investigated. Oxygen was intentionally injected into the system outside the growth tube, whilst the oxygen content of the chamber was monitored using the residual gas analyzer. The variation of voltage with oxygen flow is shown in Fig. 2. A comparison of the voltage was made with the growth tube (blue circle) and without the growth tube (red triangle). The oxygen partial pressure (black square) is shown for the run with the growth tube present. Looking at the red curve, as the gas is injected, the discharge voltage first decreases but then steadily increases with increasing gas flow. The process could only be run up to a flow of 0.45 sccm after which significant arcing occurred which could potentially damage the experimental setup. The voltage change indicated oxygen reacting with the cathode. When the growth tube was present no change in the discharge voltage could be seen, even for oxygen partial pressures of 1.25 Pa. This can be

compared to our previously published paper ³, where fully stoichiometric titanium dioxide particles were synthesized at an oxygen partial pressure of 0.04 Pa. From this result we can conclude that no contaminants outside of the growth tube were able to react with the hollow cathode and the contaminants present were those that desorbed from the growth tube walls or permeated from outside of the chamber through the cathode holder. This leads to a more stable process over time, as well as a smaller influence of the increased partial pressure of contaminants when the pumping speed is restricted.

Fig.2 Oxygen partial pressure (black square) and cathode discharge voltage (blue circle and red triangle) as a function of oxygen flow. It can be seen that with the growth tube (blue circle), the discharge voltage is constant while the partial pressure increases. Without the growth tube (red triangle), the discharge voltage first decreases, then increases when the oxygen gas flow increases

Nanoparticles synthesized with an increasing pressure at a constant gas flow (90 sccm) are first presented. These particles were studied in detail and was analyzed by TEM and EDS. After this a closer look at what happens when both the pressure and gas flow is varied independently will be taken.

No particles could be detected at pressures less than ≤ 95 Pa (at a base pressure of $6.6 \cdot 10^{-5}$ Pa) without any oxygen added to the process. For an increasing pressure there was an increase in the amount of deposited particles up to a pressure of 189 Pa, after which their number decreased.

At low pressures (109 Pa, Fig. 3a) the particles appear at low magnification close to spherical in shape. TEM reveals particles consisting of one or several grains and faceted faces in different crystallographic directions. In some rare instances cubic single crystalline particles are seen. As the pressure increases to 163 Pa the morphology is dominated by single crystal cubic particles (Fig. 3b) whose size is significantly larger than those seen at the lower pressure. Increasing the pressure to 189 Pa the particles still increase in size and retain their overall cubic shape. Interestingly the edges and surfaces of the particles do not present the almost perfect facets as seen for the lower pressure, rather they often appear fractured in appearance (Fig. 3c) and high resolution images shows that the particles still retain their single crystal structure (Fig. 3d). At the highest pressure investigated (243 Pa) several morphologies appear to co-exist. Along with the imperfect single crystal particle seen for lower pressures (Fig. 3c) there appears to be particles with a cubic core (arrow) surrounded by a matrix of significantly smaller crystalline domains giving an overall cauliflower shape (Fig. 4d). Selected area electron diffraction of several of the particles (Fig. S1 supplementary material) show that the shell is indeed polycrystalline with the same crystal structure as the cubic core.

Further analysis of the high resolution image from particles produced at 163 Pa reveals a lattice spacing close to those of cubic titanium oxide. This is a non-stoichiometric phase with a composition that ranges from $\text{TiO}_{0.7}$ to $\text{TiO}_{1.3}$.¹³

Fig.3 TEM images and size distribution of nanoparticles (as obtained from the corresponding SEM images) with different morphologies synthesized at a pressure of 109 Pa (a) 163Pa (b) 189 Pa (c),(d) and 243 Pa (e). A close up of the continued single crystal domain at the shell (d). Arrow in (e) shows the cubic core.

Fig. 4 EDS measurement (green diamond) of nanoparticle oxygen content and discharge voltage (blue circle) during synthesis at different pressures. The oxygen content in the nanoparticles and the discharge voltage increases with increasing pressure. The error bars represent the standard deviation obtained from 5 measurements on each substrate.

The oxygen content of the particles presented above were measured by EDS before they got transferred to the TEM grid. This was compared to the discharge voltage during their synthesis. The experiments were run at a base pressure of $6.6 \cdot 10^{-5}$ Pa which made nanoparticle synthesis at 93 Pa possible however at 83 Pa no particles were found. It can be seen in Fig. 4 that the oxygen content and discharge voltage increases with increasing pressure, even though no oxygen was externally supplied to the process. The most pronounced increase of the oxygen content occurs for pressures greater than 189 Pa.

Fig. 5 SEM images of typical nanoparticles synthesized at different pressures (X-axis) and flows (Y-axis). The nanoparticles inside the black border (top left) where synthesized with oxygen added to the process. At low pressure, the nanoparticles tended to be spherical. As the pressure increases, their morphology changes to cubic, and for higher pressures the morphology changes to cauliflower like.

When the gas pressure is increased, the gas velocity will decrease for a constant mass flow. Thus a hypothesis was proposed that the particles follow the gas velocity, which would influence their residence time in the plasma and thus be the dominating factor that determines the resulting size. So a second set of experiments were made in order to deconvolute the influence of pressure and

gas flow. To check this hypothesis, the gas flow and pressure were chosen so that the gas flow velocity in the growth tube will be the same if the diagonal in Fig. 5 is followed from the lower left corner to the upper right corner. However it was found that the size increases even though the gas flow velocity is the same along this diagonal. It can be seen that for the pressure of 215 Pa, the nanoparticle size increases with increasing gas velocity, contrary to the conclusions drawn by Srivastava *et al.*⁷. However at pressures of 107 to 143 Pa the size instead decreased with increased gas velocity. Three distinct particle shapes can be found and the shape is primarily dependent on the pressure. In the low pressure regime (107 to 143 Pa) the particles are mostly spherical or weakly faceted. As the pressure is increased from 143 to 177 Pa, there is a transition to larger, more cubic particles. By looking specifically at 177 Pa, 100 sccm, some particles have a hybrid structure between spheres and cubes. At 215 Pa, there is a transition to large cubical particles. Finally at 249 Pa there is a transition to cauliflower like particles.

A region where the gas flow clearly influences the particle shape is at 249 Pa. The particles start of as cubes (140 sccm). As the gas flow decreases, crystalline facets start to emerge out of the cubes (120 sccm). As gas flow is further decreased, these facets smooth out forming a cauliflower shape (100 to 80 sccm). However, at 60 sccm mostly cubical particles were found.

Experiments made for Fig. 5 was run at a base pressure of $6.1 \cdot 10^{-5}$ Pa, thus oxygen had to be added in order to synthesize nanoparticles in the region inside the black border. Oxygen was therefore intentionally introduced through the lower part of the growth tube (Fig.1) in to the growth zone and it was found that with oxygen, there was a high production of nanoparticles also in this regime. With the addition of oxygen, it was possible to synthesize particles at pressures down to 66 Pa (data not shown).

Fig.6 Nanoparticle size as function of pressure for different argon gas flows. The error bars represent the standard deviation. The black square behind the markings and dotted lines represent parameters where oxygen had to be added. The size increases with increasing pressure at a rate faster than the linear dashed line.

The nanoparticle size and the standard deviation of the size distribution (error bars) are plotted in Fig. 6. It is clear that the size increases with increasing pressure for all gas flows. The size increase is faster than linear with pressure. It can also be seen that the size distribution gets broader with increasing pressure, as shown by the increasing in the standard deviation.

Fig. 7 Nanoparticle sizes (diameter) as function of gas flow for different pressures. The black square behind the markings and dotted lines represent parameters where oxygen had to be added. At 107 Pa and 143 Pa, the nanoparticle size decreases with increasing flow. At 177 Pa, there is no clear trend in the size as a function of pressure. At 215 Pa there is a clear size increase with increasing gas flow.

The effect of gas flow on nanoparticle size and size distribution (error bars) are plotted in Fig. 7. At lower pressures of 107 and 143 Pa, a moderate decrease in particle size with increasing gas flow is found. However, as the pressure is increased, the trend stops at 177 Pa and is reversed at 215 Pa. Here, the nanoparticle size instead increases with gas flow.

4. Discussion

First the role of oxygen in the nucleation phase of the nanoparticle production will be discussed. The term “oxygen” here covers both intentionally added O₂ gas and oxygen-containing contaminants, mainly water, originating from outgassing and permeation. Other authors¹⁴ have observed the importance of oxygen for nucleation when synthesizing titanium nanoparticles. It has been attributed to a stronger binding energy between a titanium-oxygen dimer compared to a titanium-titanium dimer which leads to more stable nucleation seeds¹⁵. In addition to this, nucleation cannot occur if the number density of atoms are too low¹⁶, thus it is fair to assume that oxygen aids in forming titanium nanoparticles at lower pressures.

A compilation of experiments where nanoparticles could and could not be synthesized without adding oxygen as shown in Fig 8. Above and left of the purple dashed line, oxygen was necessary. No nanoparticles were found for combinations of high flows and low pressure without the addition of oxygen. The pressure and the flow influence each other in such a way that a higher pressure (favoring nanoparticle production) can compensate for the effect of a higher gas flow (disfavoring nanoparticle production). In addition to this, the cathode discharge voltage increases with increasing pressure which can be linked to oxidation of the cathode.

These trends are consistent with a simple model for the partial pressure of the contaminant oxygen. First the case of constant argon gas flow Q_{Ar} through the hollow cathode with a constant supply rate of contaminants Q_{ox} inside the growth tube is considered. The contaminants can likely originate from outgassing from the growth tube walls and subsequent permeation through the cathode holder. The pressure in this experiment was varied by varying the pumping speed. To a first approximation we can assume that the impurities mix into, and are carried away by, the argon gas flow. In this situation, with a constant gas flow in sccm, the total impurity level in the growth tube is proportional to the argon gas pressure p_{Ar} . If we instead consider the case where the pressure p_{Ar} is kept constant and the flow is varied, then the contaminant oxygen in the growth zone becomes diluted for higher gas speeds. The contaminants residence time in the growth tube, and therefore their density, is then inversely proportional to the flow speed. Combining the pressure and flow variations gives a partial pressure of oxygen contaminants in the growth zone with the proportionality

$$p_{ox} \propto Q_{ox} \frac{p_{Ar}}{Q_{Ar}} \quad (1)$$

where Q_{ox} is the supply of contaminants to the growth zone that is assumed to vary little during the an experiment. Based on this simple model we can draw lines of constant p_{ox} in Fig. 8, and compare them with the experimentally found limits in pressure and flow for nanoparticle production. The purple dashed line corresponds to a constant ratio p_{Ar}/Q_{Ar} which is chosen so that to the left of it nanoparticles are never produced without additional oxygen, while to the right they are always produced (at the base pressure of $5.6 \cdot 10^{-5}$ Pa). From this we can conclude that the experimentally found limit for nanoparticle production supports our model.

Fig.8 Circles represent where it was possible to produce nanoparticles without addition of oxygen. Crosses represent where oxygen had to be introduced in order to get nanoparticles. At 90 sccm, nanoparticles were sometimes produced and sometimes not (crosses and circles).

At 90 sccm and 96 to 109 Pa are borderline cases where particles were sometimes found and sometimes not. At 96 Pa, a base pressure of $6.7 \cdot 10^{-5}$ Pa was necessary to produce particles. At 109 Pa a base pressure of $4.5 \cdot 10^{-5}$ Pa did not give any particles. The limit of nanoparticle production in Fig. 8 moves towards higher pressures, and towards lower gas flows for a decreasing base pressure, as expected from Eq. (1). A similar observation has been interpreted in a different way by Clavero

*et al.*¹⁷ who were synthesizing vanadium dioxide particles in a cluster source. In their system, the pressure increased with the gas flow. They found that at and above 100 sccm the nanoparticles could grow through homogenous nucleation, due to the high inert gas pressure which allowed for the metal vapor to cool down more efficiently. However in our case, the oxygen content of the particles increased with increasing inert gas pressure and thus suggests that here, it is a chemical nucleation process.

Although a minimum oxygen density in the growth zone was found to be needed for nucleation, it seems to have only marginal influence on the final size of the nanoparticles, which was also observed in our previous paper without the growth tube.³ This finding is however different from those done by Hanu *et al.*¹⁸ who observed a size decrease and Ahadi *et al.*¹⁹ who observed a size increase. The size increase was attributed to an increased coagulation of the particles when oxygen was added to the process. It should be noted that the nanoparticles synthesized in¹⁹ had a mean size of 3.5 – 7 nm where as in this work, the size of the smallest particles had a mean size of 32 nm. Smaller particles in a plasma are more susceptible to coagulation due to stochastic charge fluctuations which can give them neutral and even positive charges.²⁰ Thus due to the larger particles in this work, coagulation will be suppressed due to repulsion between the negative charged particles.

The variations in the nanoparticle size with the pressure p_{Ar} and the gas flow Q_{Ar} are discussed next. A pressure increase results in an increase in the nanoparticle size (fig. 6). The effect of flow variations is much smaller, and has different trends for different pressure as can be seen in Fig. 7. We will therefore begin with the pressure effects.

A dashed purple line through the origin in Fig. 6 shows that the nanoparticle size increases approximately proportionally to the pressure below 170 Pa, and faster than proportional above 170 Pa.

Our approach is that the final size, r_{NP} of the nanoparticles is given by the product of their average growth rate dr_{NP}/dt of their effective radius, and their time of residence t_{res} in the growth tube,

$$r_{NP} = \langle dr_{NP}/dt \rangle \cdot t_{res} \quad (2)$$

How variations in pressure and gas flow will influence these two parameters is estimated.

Beginning with the nanoparticle growth rate $\langle dr_{NP}/dt \rangle$. The nanoparticle growth mechanism in the present experiments is dominated by the collection of ions of the sputtered material²¹, here Ti^+ ions, which makes the momentary growth rate dr_{NP}/dt proportional to the product of the ion density n_{Ti^+} and the electron temperature T_e . We here make the assumption that both T_e and the amount of Ti^+ ions which is ejected from the hollow cathode into the growth tube following each pulse is mainly determined by these pulse parameters, and only to second order influenced by the gas pressure and the gas flow. This assumption is based on COMSOL modeling of the pulse²¹ which shows that the pulse is associated with momentary flow speeds that are far in excess of the steady state feed flow, and that a main mechanism for ion extraction at the hollow cathode exit is ambipolar diffusion, driven by a steep gradient in electron pressure.

The growth material (Ti^+ ions) for our parameters is mainly lost by ambipolar diffusion to the walls, not by following the gas flow (see appendix). By calculating the ambipolar diffusion rate D_a and by knowing the radius of the growth tube r_{GT} . The ion residence time then obeys $\Delta t = r_{GT}^2/2D_a \propto p_{Ar}$, where the last step follows from $D_a \propto 1/p_{Ar}$. The ion density follows the residence time and therefore also becomes proportional to the pressure. As a consequence the average nanoparticle growth rate in Eq (2) becomes independent of the flow Q_{Ar} , and proportional to the pressure, *i. e.*,

$$\langle dr_{NP}/dt \rangle \propto p_{Ar} \quad (3)$$

If the residence time t_{res} of the nanoparticles were constant one would, by combining Eq. (2) and (3), expect the nanoparticle size to be proportional to the pressure. Fig. 6 however shows an even faster increase than this proportionality. We propose that this is due to a longer nanoparticle residence time in the growth zone at higher pressure.

The most likely scenario for this is as follows: nanoparticles are beginning to form during the initial time of fast motion of the growth material (≈ 190 m/s), and during this time they will have a much higher high speed than that of the steady gas flow speed (≈ 0.24 m/s) further down in the growth tube. With increasing distance from the hollow cathode they will be slowed down through frictional interaction with the argon gas. The friction drag force is proportional to the pressure. This means that at a higher pressure they should slow down more and have a longer residence time. The drag force and the nanoparticle residence time t_{res} should therefore to a first approximation not depend much on the flow. Due to the pressure dependence of both the growth rate dr_{NP}/dt and the

residence time t_{res} , equation 2 gives a faster than linear increase of size as function of pressure, in agreement with the trend in Fig. 6.

We note that the simple model above assumes no dependence on the particle size with the gas flow. However, the size variation with the gas flow as shown in fig. 7 show that it has to be included to make a complete explanation. There are several possible processes that could be involved here, all of which represent errors in the simplifying assumptions above.

For a given pressure the sputtered material might be more easily extracted from the hollow cathode when the gas flow is faster. This would lead to more ejected material in the growth tube, and that the particles could grow larger. It has previously been reported that an increased flow speed increases the deposition rate of platinum and silver particles, which was attributed to more ejected material at higher flows.¹¹ This mechanism is consistent with the size trends seen at 177, 215, and 249 Pa, but in contradiction with the opposite trends seen at 107 and 143 Pa. Equation (1) predicts that the partial pressure of oxygen is decreased at higher gas flows. This could also be an influencing factor for the trends in the particle size for varied gas flows. This might however lead to opposite trends. On one hand, an increased amount of oxygen would aid in the early nucleation of the particles, and give them time to grow larger. On the other hand, if the nucleation process is very efficient it could deplete the titanium in the growth zone which could lead to a smaller size of the final particles.

Finally the morphological transitions of the nanoparticles with changing pressure (as seen in Fig. 3 and Fig. 5) will be discussed. There are some striking similarities with the well-studied morphological changes of thin films when the pressure is varied. Different film growth regimes can be described by a structure zone model where the crystallinity is dependent on temperature and impurities²², and the nanoparticle growth might be explained in the same way. For higher pressures, there would be an increased cooling rate of the nanoparticles due to more frequent collisions with the surrounding gas.⁹ This would in turn decrease the adatom mobility on the surface of the nanoparticle as well as atomic diffusion on the inside, resulting in an increased polycrystallinity.

A second possibility is that the growth rate influences the morphology. According to Eq (3) the growth rate of the nanoparticles increases with the pressure. When the deposition rate of adatoms on the particle surface increases, their diffusion time before they are embedded in later-coming

depositions would decrease. This would decrease the probability of the adatom to find its lowest energy point resulting in more defects.

5. Conclusions

Nanoparticles of titanium oxide in the size range from 30 to 250 nm have been synthesized in a pulsed high power plasma where the discharge parameters have been kept constant while the inert gas pressure p_{Ar} and the flow Q_{Ar} have been varied independently. The limits for the nanoparticle nucleation process (*i.e.*, the limit between the production and the absence of nanoparticles) is found to correspond to a close to constant ratio p_{Ar}/Q_{Ar} . In the parameter range where nanoparticles are produced, their size increases when the pressure is increased. The nanoparticle morphology changes with increasing pressure giving transitions from spherical, to cubic, and finally to cauliflower shaped.

The trends with the pressure p_{Ar} and the flow Q_{Ar} of the nucleation, the final nanoparticle size, and the nanoparticle morphology are analyzed using simple considerations of how the key internal parameters in the nanoparticle growth zone are expected to vary with the pressure and the flow. These considerations are based on estimates of the different residence times in the growth zone of the impurity molecules, the sputtered growth material and the nanoparticles. The observed trends in nucleation, size and morphology are all found to be consistent with the following scaling rules that follow from the model: (1) The partial pressure of impurity oxygen is proportional to the ratio p_{Ar}/Q_{Ar} , (2) the growth material density is independent of Q_{Ar} but proportional to p_{Ar} , and (3) the nanoparticle residence time increases with p_{Ar} but probably is almost independent of Q_{Ar} .

There is also a smaller influence on the nanoparticle size when the gas flow is varied but with contradictory trends at different pressures. At 107 and 143 Pa, the size decreases with increasing gas flow. At 215 Pa, the opposite happens. These trends are not explained by the model.

In summary, the partial pressure of oxygen p_{ox} is the main parameter governing the nucleation process, while the process gas pressure p_{Ar} is identified as the most important parameter controlling both the size and shape of the nanoparticles.

Supplementary material

See supplementary material for the selected area electron diffraction of the polycrystalline shell and the cubic core.

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Ulf Helmersson and Nils Brenning holds a patent in the field of nanoparticle synthesis with this particular technique.

Appendix

We will here derive the approximate relations used for the scaling of the density of the growth material inside the growth tube with the pressure and gas flow. The key question is which process sets the time of residence of titanium ions inside the growth tube. They could either be carried out with the gas flow or be lost by diffusion to the wall. The growth material that is ejected from the hollow cathode consists of Ti atoms and Ti^+ ions. A constant injection of Ti^+ ions with each pulse independent of pressure and gas flow is assumed. The ion density n_{Ti^+} in the growth tube becomes determined by the subsequent processes of convection and diffusion. In each pulse, they are ejected from the hollow cathode in the form of a puff. The speed in such puff can reach 190 m/s initially, but the growth material cloud is then rapidly slowed down when the cloud expands by diffusion and mixes with the ambient gas.²¹ After 0.1 – 0.2 ms it has a size (radius) of about 1 cm, is located about 2 cm from the HC exit, and moves more or less with the surrounding argon gas. If the Ti^+ ions were to follow the argon gas flow, their density would be dependent on the gas flow. However, this is not a likely scenario and this is not what is observed on the resulting size of the particles. We are here interested in the Ti^+ ions which are subject to the fast process of ambipolar diffusion.²³

To be able to calculate the diffusion coefficient, the collision cross section of titanium ions σ_{Ti^+} in an argon gas has to be estimated. This was done based on measured ion mobilities in the same way as described by Pilch *et al.*²⁴ for copper ions and a value of $\sigma_{\text{Ti}^+} = 41 \cdot 10^{-20}$ was found. The

collision mean free path is thus given by $l_{coll} = k_B T_n / (p \sigma_{Ti^+})$ where k_B is the Boltzmann constant, T_n is the neutral gas temperature and p is the gas pressure.

For ions we have ambipolar diffusion with a diffusion coefficient of the order

$$D_a = \frac{v_{i,th} \cdot l_{coll}}{3} \sqrt{\frac{T_e + T_i}{T_i}} = 0.0280 \text{ m}^2/\text{s} \quad (\text{A1})$$

Where the electron temperature T_e is 0.4 eV (4640 K)²¹, The ion thermal velocity $v_{i,th} = \sqrt{8k_B T_i / (\pi m_i)}$ and ion temperature $T_i = 300\text{K}$. From the pressure dependence of l_{coll} follows that $D_a \propto 1/p$ and the total pressure is approximately the argon pressure $p \approx p_{Ar}$.

A freely expanding cloud has a Gaussian profile with a radius.²⁵

$$R_{cloud} = \sqrt{2D_a \Delta t} \quad (\text{A2})$$

We take the residence time for these Ti^+ ions to be the time when such a cloud has expanded to the radius of the growth tube 36.5 mm. This gives a residence time of ionized growth material in the growth tube that is of the order of $\Delta t = r_{GT}^2 / 2D_a = 0.0238 \text{ s}$ (again using $p = 177 \text{ Pa}$) where r_{GT} is the radius of the growth tube.

This time can be compared to the residence time of the argon gas in the growth tube, set by the value of the gas flow $Q_{Ar} = 100 \text{ sccm}$. Flow continuity requires that the total flow across all cuts in the growth tube across the flow direction is the same. In cylindrical geometry this gives the flow $Q_{SI} = p \langle v_g \rangle \pi r_{GT}^2$, from which the average gas speed is found as

$$\langle v_g \rangle = \frac{K_1}{\pi r_{GT}^2} \times \frac{Q_{Ar}}{p} = 0.239 \text{ m/s} \quad (\text{A3})$$

Where is $K_1 = 1.63 \cdot 10^{-3} \text{ Pa}$ is the conversion factor from mass flow to throughput. Dividing the length of the upper part of the growth tube l_{GT} gives the average residence time of argon

$$\langle t_{Ar} \rangle_{GT} = \frac{l_{GT}}{\langle v_g \rangle} = 0.284 \text{ s} \quad (\text{A4})$$

This is an order of magnitude slower than the time $\Delta t = 0.0238 \text{ s}$ it takes for the titanium ions to diffuse to the growth tube walls. We can conclude that the growth material is lost by diffusion to

the walls, not by following the gas flow. Therefore, its density n_{Ti^+} is independent of the argon gas flow Q_{Ar} , and proportional to the pressure:

$$n_{Ti^+} \propto p \quad (A5)$$

References

- ¹ I. Pilch, D. Söderström, M.I. Hasan, U. Helmersson, and N. Brenning, Appl. Phys. Lett. **103**, 193108 (2013).
- ² I. Pilch, D. Söderström, N. Brenning, and U. Helmersson, Appl. Phys. Lett. **102**, 033108 (2013).
- ³ R. Gunnarsson, U. Helmersson, and I. Pilch, J. Nanoparticle Res. **17**, 1 (2015).
- ⁴ B. Vermang, J. Timo, V. Fjällström, F. Rostvall, M. Edoff, R. Gunnarsson, I. Pilch, U. Helmersson, R. Kotipalli, F. Henry, and D. Flandre, Thin Solid Films **582**, 300 (2015).
- ⁵ M. Drábik, A. Choukourov, A. Artemenko, J. Kousal, O. Polonskyi, P. Solař, O. Kylián, J. Matoušek, J. Pešička, I. Matolínová, D. Slavínská, and H. Biederman, Plasma Process. Polym. **8**, 640 (2011).
- ⁶ A.I. Ayesh, H.A. Ahmed, F. Awwad, S. Abu-Eishah, and S. Mahmood, J. Mater. Res. **28**, 2622 (2013).
- ⁷ S. Srivastava, J.P. Thomas, A. Rahman, M. Abd-ellah, M. Mohapatra, D. Pradhan, N.F. Heinig, and K.T. Leung, ACS Nano **8**, 11891 (2014).
- ⁸ S. Pratontep, S.J. Carroll, C. Xirouchaki, M. Streun, R.E. Palmer, S. Pratontep, S.J. Carroll, C. Xirouchaki, M. Streun, and R.E. Palmer, Rev. Sci. Instrum. **76**, 045103 (2005).
- ⁹ S. Drache, V. Stranak, F. Berg, Z. Hubicka, M. Tichy, C. Helm, and R. Hippler, Phys. Status Solidi A **211**, 1189 (2014).
- ¹⁰ S. Yamamuro, K. Sumiyama, K. Suzuki, S. Yamamuro, K. Sumiyama, and K. Suzuki, J. Appl. Phys. **85**, (1999).
- ¹¹ M. Maicu, R. Schmittgens, D. Hecker, D. Glöß, P. Frach, G. Gerlach, D. Hecker, and G. Gerlach, J. Vac. Sci. Technol. A **32**, 02B113 (2014).
- ¹² H. Aoshima, H. Suzuki, H. Sakuma, K. Ishii, H. Aoshima, H. Suzuki, H. Sakuma, and K. Ishii, J. Appl. Phys. **105**, 07B519 (2009).
- ¹³ E. Wiberg, N. Wiberg, and A.F. Holleman, *Inorganic Chemistry*, 1st English ed (Academic Press ; De Gruyter, San Diego : Berlin ; New York, 2001).
- ¹⁴ A.M. Ahadi, V. Zaporozhchenko, T. Peter, O. Polonskyi, T. Strunskus, and F. Faupel, J. Nanoparticle Res. **15**, 2125 (2013).

- ¹⁵ P. V. Kashtanov, B.M. Smirnov, and R. Hippler, EPL (Europhysics Lett. **91**, 63001 (2010).
- ¹⁶ V.M. Smirnov, Physics-Uspekhi **37**, 646 (1994).
- ¹⁷ C. Clavero, J.L. Slack, and A. Anders, J. Phys. D. Appl. Phys. **46**, 362001 (2013).
- ¹⁸ J. Hanu, A. Choukourov, I. Melnichuk, H. Biederman, A. Serov, and D. Slavínsk, Vacuum **120**, 162 (2015).
- ¹⁹ A.M. Ahadi, O. Polonskyi, and U. Schürmann, J. Phys. D. Appl. Phys. **48**, 35501 (2015).
- ²⁰ L. Ravi and S.L. Girshick, Phys. Rev. E **79**, 026408 (2009).
- ²¹ M.I. Hasan, I. Pilch, D. Söderström, D. Lundin, U. Helmersson, and N. Brenning, Plasma Sources Sci. Technol. **22**, 035006 (2013).
- ²² P.B. Barna and M. Adamik, Thin Solid Films **317**, 27 (1998).
- ²³ F.F. Chen, *Introduction to Plasma Physics and Controlled Fusion* (Plenum Press, 1984).
- ²⁴ I. Pilch, L. Caillault, T. Minea, U. Helmersson, A.A. Tal, I. Abrikosov, E. Münger, and N. Brenning, Submitt. 2016 (2016).
- ²⁵ N. Brenning, I. Axn, J.O. Nilsson, and J.E. Eninger, IEEE Trans. Plasma Sci. **25**, 83 (1997).