Surface & Coatings Technology 205 (2011) S577–S581

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Carbon nanoparticles synthesized by sputtering and gas condensation inside a nanocluster source of fixed dimension

Virginie Bouchat [a,g,*], Olivier Feron [b], Bernard Gallez [c], Bernard Masereel [d,g], Carine Michiels [e,g], Thierry Vander Borght [f,g], Stéphane Lucas [a,g]

[a] University of Namur (FUNDP), Research center for the Physics of Matter and Radiation (PMR), Namur, Belgium
[b] Université Catholique de Louvain-FATH, Brussels, Belgium
[c] Université Catholique de Louvain-CMFA, Brussels, Belgium
[d] University of Namur (FUNDP)-DP, Namur, Belgium
[e] University of Namur (FUNDP)-URBC, Namur, Belgium
[f] Université Catholique de Louvain-IMRE, Yvoir, Belgium
[g] NARILIS — NAmur Research Institute for LIfe Sciences, Namur, Belgium

ARTICLE INFO

Available online 24 March 2011

Keywords:
Carbon nanoparticle
Cold plasma
Magnetron sputtering
Cluster source
Transmission electron microscopy
PVD

ABSTRACT

This paper presents the results of the production of carbon nanoparticles by magnetron sputtering inside a gas aggregation tube of fixed dimension, placed vertically in a high vacuum chamber. The nanoparticles are negatively charged, and their morphology was studied according to the positive biasing of a substrate holder. The carbon nanostructures were deposited on formvar grids to be analyzed by transmission electron microscopy. For positive bias voltages larger than 30 V, results showed spherical and randomly dispersed nanoparticles with a mean diameter, which varied from about 10 nm to 20 nm depending on the choice of plasma parameters. By contrast, if the bias voltage was grounded or was lower than or equal to 30 V, only nanoribbon-like structures mixed with compact or fractal groups of nanoparticles were observed on TEM grids. Results are discussed in terms of a 3-step process inside the aggregation tube: nucleation, coalescence and agglomeration of negatively charged nanoparticles.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Carbon particles can exist in different shapes and structures due to their ability to form single, double or triple bonds by hybridization of s and p orbitals [1]. Among these carbonaceous structures, spherical carbon nanoparticles (CNPs) have been the subject of numerous studies. Their biocompatibility, their high surface area and their unusual chemical or physical properties can be very useful for industrial and biomedical applications. In general, spherical CNPs are produced by arc-discharge in the gaseous or liquid phase, (pulsed) laser ablation, and various chemical vapor deposition processes [2]. However, most of these methods lead to the synthesis of nanoparticle agglomerates [3–5], the formation of spherical particles with various diameters [4,5], or the production of nanoparticles mixed with nanofibers and nanotubes [3,6]. It is commonly recognized that any modification in size or shape can radically alter the intrinsic properties of these nanoparticles, and that the production of isolated identical particles still remains an important challenge in research [7].

In this paper, another synthesis technique is proposed, in which CNPs are generated in an aggregation tube by the condensation of free carbon atoms that result from the magnetron sputtering of a graphite cathode. This method is mainly used to produce non-agglomerated metallic nanoparticles with a narrow size distribution [8–13] and, to the best of our knowledge, the synthesis of isolated CNPs had never been tested until now. The technique was proposed for the first time by Tikana et al. in 1972 to produce high quality films by ionized cluster beam (ICB) deposition [14]. Their idea was to generate a cluster beam formed by inert gas condensation (IGC) [9] after evaporation of film materials. A few years later, Haberland et al. decided to vaporize the film material by magnetron sputtering rather than by evaporation [15]. This modification allows the target to be maintained at high pressure and at room temperature, thereby favoring the condensation process [1,8,10,11]. Moreover, magnetron sputtering has the advantage of being able to produce an atomic vapor from a wide variety of solid materials or composites, which is not always possible with evaporation [16]. This technique, which combines magnetron sputtering and IGC can form high-purity nanoparticles at room temperature. Furthermore, in contrast to the island formation by Stranski–Krastanow [17] or Volmer–Weber growth mode [18], this method is ideal for controlling the dispersion as well as the size of these nanoparticles onto any desired substrate [7,19].

* Corresponding author at: University of Namur (FUNDP), Research center for the Physics of Matter and Radiation (PMR), Namur, Belgium. Tel.: +32 81725479; fax: +32 81725474.
E-mail address: vbouchat@fundp.ac.be (V. Bouchat).

0257-8972/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2011.03.055

2. Experimental setup

The nanostructures are synthesized by direct current (DC) magnetron sputtering in a gas-aggregation tube. Fig. 1 presents a schematic of the experimental device used to generate the carbon deposition. A gas aggregation tube with an inner diameter of 5 cm and a length of 25.5 cm was introduced vertically in a high vacuum (HV) chamber. Carbon atoms were generated by sputtering a graphite cathode of 2.54 cm (1 in.) in diameter and 1 mm thickness placed inside the aggregation tube. The pulverization gas, typically argon or helium, was injected directly into the aggregation tube in order to maintain a high pressure around the cathode. The carbon atoms in supersaturation near the cathode condensed after successive collisions and gave rise to small clusters (~2 nm in diameter) which grew by aggregation [1,20,21]. Condensation and cluster growth are encouraged by cooling down, at room temperature, the graphite target as well as the aggregation tube with chilled water [1,7,8,11].

The nanostructures are then ejected into the HV deposition chamber through an orifice with a constant diameter of 5 mm located on the top of the aggregation tube. Low pressure is maintained in the HV deposition chamber by a turbomolecular pump TMH/U 261/262. The base pressure inside the HV deposition chamber reaches $\sim 10^{-7}$ mTorr. During the deposition, the pressure inside the aggregation tube can be estimated by applying the formula of molecular conductance through an orifice:

$$P_0 = \frac{S}{S_0} P \quad \text{with} \quad S_0 = 3.64 \sqrt{\frac{T}{M}}\, \pi \frac{D^3}{L} \tag{1}$$

where P and P_0 are the pressure inside the HV deposition chamber and inside the aggregation tube, respectively. S is the pumping speed of the vacuum system, which varies following the pressure and the type of gas. For P = 0.7 Pa, pumping speeds reach a value of 170 l/s for He gas and 180 l/s for Ar gas. For a greater pressure of 5.3 Pa, pumping speeds decrease until they reach values of 85 and 75 l/s for helium and argon gasses, respectively. S_0 is the molecular conductance through the aperture. The aggregation tube is maintained at room temperature T (300 K). M is the atomic mass of the inert gas used for the magnetron sputtering. D and L are the diameter and the thickness of the orifice (0.5 cm × 0.5 cm). The flow of He or/and Ar gas guides and accelerates the growing cluster particles through the aperture of the tube. Following formula (1), the molecular conductance for He (S_0 ~ 27.6 l/s) is about 3 times more than for Ar (S_0 ~ 8.7 l/s), which means that residence time of nanoparticles inside the tube can be decreased by increasing the flow of helium gas [11] and, at the same time, reducing their mean diameter. Under these conditions, the value of P_0 reaches about 14 Pa when the argon pressure outside the tube is maintained at 0.7 Pa and decreases to 4 Pa if argon is replaced by helium. At a pressure of 5.3 Pa, on the other hand, P_0 increases from 14 Pa to about 46 Pa when Ar gas is used for magnetron sputtering and from 4 Pa to approximately 16.7 Pa when helium rather than argon is applied as the inert gas. The nanoparticles or other nanostructures produced inside the aggregation tube can be collected on a substrate holder in the HV deposition chamber. Moreover, due to the high pressure maintained in the aggregation chamber, the kinetic energy of small clusters formed in the tube is reduced by successive collisions with atoms of inert gas, which ensures a soft landing of the clusters onto the substrates [9–11]. This soft landing allows the structural and morphological properties of the nanoparticles to be retained. The graphite cathode is located at a fixed distance of 5 cm below the aperture inside the aggregation tube, whereas the height between the aperture and the substrate holder outside the aggregation tube can vary from 5 to 10 cm. So, a better control of size and distance between the nanoclusters is possible by decreasing or increasing the height separating the orifice of the aggregation tube and the substrate holder. Different positive and negative bias voltages can be applied to the substrate holder.

Standard Cu grids (300 mesh) coated with a thin formvar film were placed onto the substrate holder of the HV deposition chamber and exposed to the cluster beam during deposition. These grids were then analyzed by a Philips TECNAI-10 transmission electron microscopy (TEM) with accelerating voltage of 100 keV in order to study the morphology and to quantify the size distribution of the nanoparticles extracted from the aggregation tube. Densities and nanoparticle size distributions were determined from TEM images by using ImageJ software.

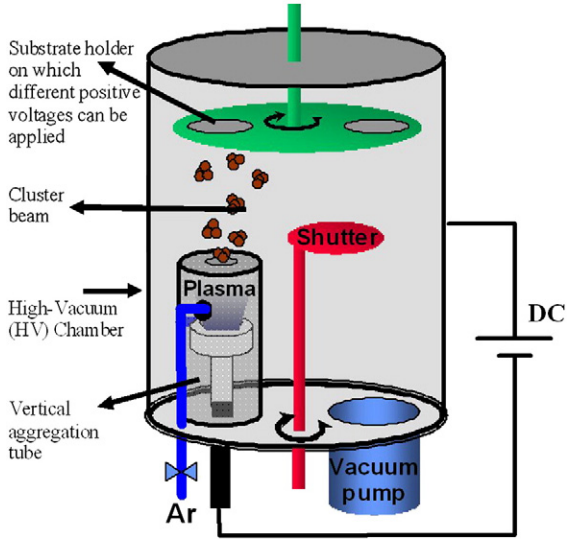

Fig. 1. Schematic diagram of physical vapor deposition system. Plasma is generated inside the aggregation tube by direct current (DC) magnetron sputtering.

3. Results and discussion

When negative bias voltages are applied on the substrate holder, no carbon nanoparticle is visible on the TEM grids. Inversely, different structures and sizes of CNPs are observed after application of positive bias voltages ranging from 0 V, corresponding to the ground, to 60 V. In this section, we will see that the structures observed on the TEM grids vary dramatically, depending upon the positive bias voltages applied to the substrate holder.

3.1. Agglomerated nanoparticles

It is generally accepted that nucleation and coalescence comprise the early stages of nanoparticle formation inside an aggregation tube [9,20]. The size of the particles depends on various factors, such as the power applied to the target, the choice of inert gas for the sputtering, and the pressure and the length of the aggregation tube [9,10,12,18]. It is well known that the nanoparticles leaving the tube are larger when the length of aggregation increases. In fact, the latter determines the residence time of carbon particles inside the plasma; during this time, numerous collisions among C atoms and clusters occur [9,21].

For our first experiments, the pressure inside the HV deposition chamber was set to 0.7 Pa, the argon gas flow was fixed at 10 sccm and the power supply was set to 45 W. Under these conditions, the pressure inside the aggregation tube is estimated at about 14 Pa by formula (1). After a deposition time of 40 min, TEM images, presented in Fig. 2, do not show isolated nanoclusters, but instead reveal the presence of rare agglomerations of numerous spherical nanoparticles whose diameters vary from 10 to 20 nm. The absence of isolated nanoparticles around these structures implies that the agglomerations are synthesized in the gas phase inside the aggregation tube and not by diffusion or superposition of nanoclusters when they reach the sample on the substrate holder. Consequently, the process of particle growth inside the aggregation tube would take place in 3 different

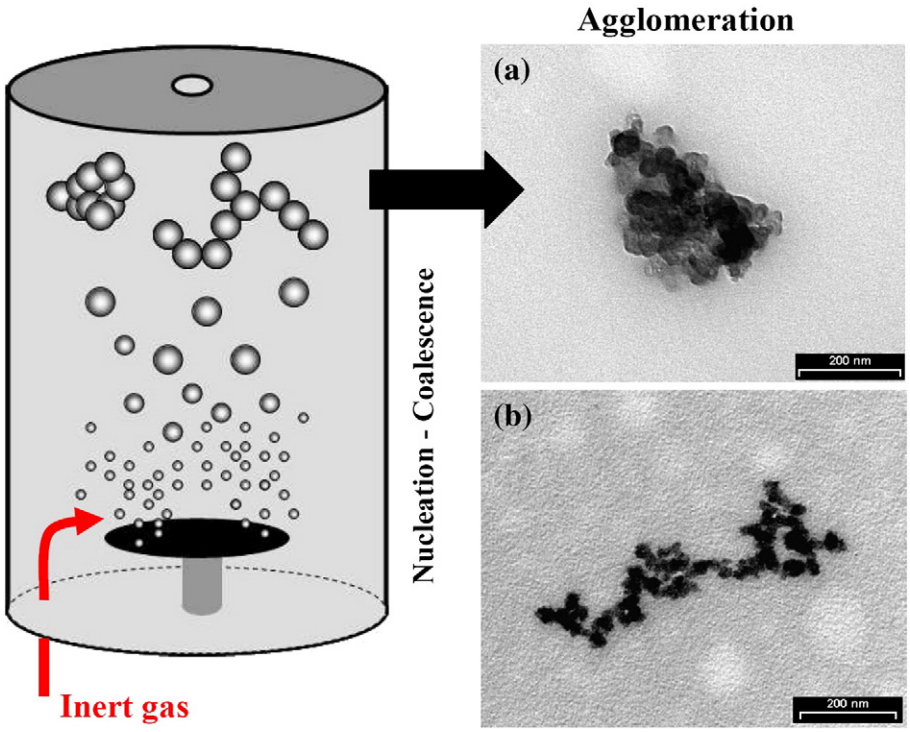

Fig. 2. Schema of particle growth process inside the aggregation tube. Positions of the different phases in the figure are random and depend on sputtered materials and plasma parameters. Images of graphitic agglomerations, compact (a) or fractal (b), generated by magnetron sputtering inside an aggregation tube.

steps as represented in Fig. 2: nucleation, coalescence, and agglomeration of negatively charged CNPs. Indeed, when the carbon atoms or clusters are immersed in the discharge, they collide with one another but also become charged by collecting plasma ions and electrons [1,16,22–24]. So, after a long residence time inside the discharge, the carbon nanoparticles can acquire an important negative charge, which is often explained by a much higher mobility and temperature of the free electrons in the plasma than the mobility and temperature of positive ions [8,15,19,20,22–24]. The most negatively charged particles are probably trapped in the plasma whereas the less charged ones continue their ascent toward the tube aperture [25]. The latter can then agglomerate to form spherical or filamentary particles. The difference between fractal and compact shapes can be easily explained by the kinetic energy and Coulomb repulsion of nanoclusters before agglomeration [20,25]. Indeed, the pile-up of nanoparticles in a compact and more spherical form is facilitated if they have small charges and high velocities. Inversely, when the charge is higher and the velocity is weaker, the incoming particle prefers to stick to the end of a chain to avoid strong Coulomb repulsion. In this last case, the nanoparticles can agglomerate into filamentary or fractal shapes.

3.2. Non-agglomerated nanoparticles

We have proposed that the formation of agglomerated nanoparticles proceeds in three steps. The first one is the formation of small nuclei by condensation of the carbon atoms. This phase is followed by the coalescence of these small nuclei, leading to larger spherical nanoparticles. The last stage is the agglomeration of independent and negatively charged particles. If this theory is correct, the growth by agglomeration can be avoided by decreasing the length of the aggregation tube or increasing the electrostatic force directed towards the aperture at the top of the tube. The latter is possible by applying a positive bias voltage on the substrate holder that is capable of extracting the negatively charged nanoparticles from the coalescence phase. Inversely, no nanoparticle should be visible if a negative bias voltage is applied on the substrate holder. Fig. 3 shows non-agglomerated nanoparticles

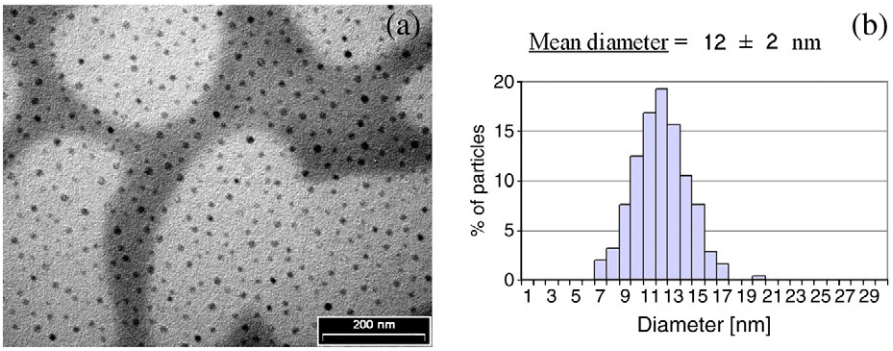

Fig. 3. (a) Image of CNPs deposited for 70 min on a formvar grid if 40 V is applied on the sample located at 6 cm from the aperture of the aggregation tube. The pressure inside the HV deposition chamber, the pure argon mass flow and the power applied on the cathode are respectively 5 mTorr, 10 sccm and 45 W. The density of nanoparticles is approximately 7×10^{10} cm^{-2}. Figure (b) shows the frequency distribution of sizes. The mean diameter is 11.9 ± 2.2 nm.

obtained with a DC power of 45 W, a pure argon flow of 10 sccm, a pressure of 0.7 Pa inside the HV deposition chamber and a calculated pressure of 14 Pa inside the aggregation tube. The clusters were deposited on a TEM grid substrate which was kept at a distance of 6 cm from the orifice of the aggregation tube. A positive voltage of 40 V was applied to the substrate holder. The deposition time was 70 min. Under such conditions, the nanoparticles are well separated and all of them have a spherical shape. The plot beside Fig. 3 presents the frequency distribution of the sizes, as measured from more than 200 nanoparticles. The mean diameter is 12 nm with a standard deviation of 2 nm. Under these experimental conditions, the density of particles deposited on the grid is about 7×10^{10} cm^{-2}. This density increases or decreases according to the deposition time, but the mean diameter of CNPs remains unchanged. Notice that the positive bias voltage attracts only negatively charged nanoparticles and provokes a slight heating of the sample, thus favoring the diffusion on the substrate. Fortunately, the nanoparticles are randomly dispersed due to the unipolar charge, which reduces the agglomeration of the nanoparticles on the substrate [8], and the grid shows only isolated nanoparticles, in spite of the fact that they are relatively close to each other.

Depositions were made at different bias voltages larger than 15 V to verify their influences on the mean radius of non-agglomerated nanoparticles collected on the substrate holder. For all samples, the nanoparticles were deposited over a period of 60 min and were produced under the same plasma conditions, i.e. an HV deposition chamber pressure of 0.7 Pa, a DC power of 45 W, a pure argon flow of 10 sccm for the magnetron sputtering of graphite cathode, and a distance of 6 cm between the tube aperture and the sample. Positive biasing less than or equal to 30 V only shows compact and fractal agglomerates. The first isolated nanoparticles appear at 35 V. Table 1 presents the calculated mean diameter for isolated CNPs when bias voltages varying from 35 V to 60 V are applied on the substrate holder. For bias voltages between 35 and 55 V, the mean diameter remains constant, with a value ranging from 11 to 13 nm. A larger mean diameter seems to appear for depositions at 60 V. As the number density of about $2\cdot10^{10}$ cm^{-2} remains identical for all depositions, augmentation of the CNP size is probably due to an increase in their kinetic energy and a flattening of the nanoparticles when they reach the substrate. Similar experiments were performed with a negative bias voltage and TEM grids do not present any CNPs.

An analysis of current intensity on the sample when positive voltages are applied on the substrate holder during deposition has been performed at different pressures inside the HV deposition chamber: 0.7, 1.3, 2.7 and 5.3 Pa. Other parameters remain identical to previous experiments, with a DC power of 45 W, a pure argon flow of 10 sccm and a distance between the orifice and the sample of 6 cm. This current intensity is probably caused by the presence of CNPs and electrons escaping from the magnetron plasma. All curves in Fig. 4 begin to increase from 15 V, and present a maximum plate at 35 V, which induces a current intensity of about 90 mA. This plate indicates that the density of isolated CNPs (which are observed for the first time at 35 V) remains constant even if the bias voltage applied on the substrate holder increases. Moreover, the current for 0.7 and 1.3 Pa presents a step between 20 and 25 V. An explanation for these steps must still be found.

Table 1
Evolution of the NP mean diameter observed on TEM grids with positive biasing.

Volts	Mean diam (nm)	Dev (nm)
35	11	3
40	12	2
45	12	3
50	11	3
55	13	3
60	15	3

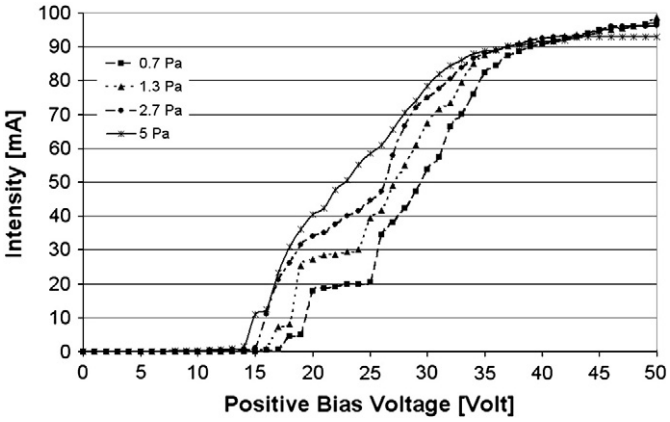

Fig. 4. Electric current on the sample as a function of biased voltage.

It is interesting to see what happens when the plasma conditions are modified while the positive bias voltage is preserved at the same value. New depositions were performed by increasing the pressure inside the HV chamber to 2.7 and 8 Pa, which means that the pressure inside the aggregation reached values of about 35.3 and 55.3 Pa, respectively. For these experiments, TEM grids were exposed for 35 min in a pure argon flow at 10 sccm. A DC power of 45 W was applied to the cathode for sputtering while the substrate holder, located at 6 cm from the orifice of the tube, was maintained at $+35$ V in order to extract the negatively charged particles from the coalescence phase. The mean diameters for 2.6 and 8 Pa correspond to 16 ± 3 nm and 20 ± 4 nm. So, results indicate an increase of the mean diameter with an increase in pressure. That can be easily explained by the fact that more primary nuclei are formed due to more collisions between sputtered atoms and inert gas [7,9,26]. A last series of experiments was performed with identical experimental data to those in Fig. 3, except that the inert gas used to sputter the graphite carbon is a mixture of 3 sccm Ar gas with 7 sccm He gas, which produces a total pressure of 0.7 Pa inside the HV chamber. As the molecular conductance through an orifice of helium is higher than that of argon, the CNPs are more quickly ejected from the aggregation tube and the number density on TEM grids has already reached a value of about 1×10^{10} cm^{-2} after a deposition time of 10 min. Usually, nanoparticle sizes should also decrease when argon gas is partially replaced by helium gas. However, the mean diameter obtained for these CNPs increased from 12 ± 2 nm to 18 ± 4 nm. Such a result can be easily explained by the fact that He gas decreases the pressure inside the aggregation tube. This decrease causes an acceleration of the CNPs when they are ejected from the orifice of the aggregation tube and a flattening of these nanoparticles when they reach the substrate. All these experiments strongly confirm that any change in plasma parameters can lead to a modification of nanoparticle sizes, even if a positive bias voltage is used to extract the negatively charged particles.

4. Conclusion

In conclusion, we have added an aggregation tube in a high vacuum deposition chamber to produce carbon nanoclusters after pulverization of a graphic cathode. If no substrate biasing is applied, the density of nanostructures remains very low even after a deposition time of 1 h, and we observe only compact or fractal agglomerations of nanoclusters. The agglomeration of spherical particles can appear as a third step after nucleation and coalescence phases in the particle growth process inside the aggregation tube. During their ascent towards the aperture of the aggregation tube, the nanoparticles acquire a negative charge. So, it is possible to extract these negatively charged nanoparticles by applying a positive bias voltage larger than 30 V to the substrate. In this case only non-agglomerated nanoparticles with spherical shapes are

visible. Moreover, this voltage has a weak influence on the mean radius which means that this method is ideal to produce isolated CNPs with a narrow size distribution. The density and the distances between the CNPs can also be controlled by changing the deposition time or the height between the substrate holder and the aperture of the aggregation tube. Another advantage is that no reactive gasses are used and the purity of these NPs remains very high. Finally, production of CNPs with this method is very slow but the use of a mixture of argon and helium flow allows us to decrease the deposition time significantly to obtain approximately the same mean diameter. Further studies are necessary to control the nanoparticle sizes better, but the addition of a positive bias voltage induces an electrical force that can be considered as a useful means of extracting only negatively charged particles and of controlling their structure in agglomeration in the same way.

Acknowledgments

This research (Targan Project) was supported by the Walloon Region (Belgium). Olivier Feron is a senior research associate at FNRS (Fonds National de la Recherche Scientifique, Belgium).

References

[1] C. Arnas, C. Dorninique, P. Roubin, C. Martin, C. Brosset, B. Pegourie, J. Nucl. Mater. 353 (2006) 80.
[2] A. Huczko, Appl. Phys. A Mater. Sci. Process. 74 (2002) 617.
[3] S. Kuroda, K. Hosoi, Chem. Lett. 37 (2008) 54.
[4] D. Roy, M. Chhowalla, H. Wang, N. Sano, I. Alexandrou, T.W. Clyne, G.A.J. Amaratunga, Chem. Phys. Lett. 373 (2003) 52.
[5] M. Zhao, H.H. Song, X.H. Chen, W.T. Lian, Acta Mater. 55 (2007) 6144.
[6] V.V. Chuprasov, M.S. Tret'yak, V.V. Toropov, S.A. Chizhik, A.P. Solntsev, J. Eng. Phys. Thermophys. 77 (2004) 647.
[7] P. Ayyub, R. Chandra, P. Taneja, A.K. Sharma, R. Pinto, Appl. Phys. A 73 (2001) 67.
[8] A. Bapat, C. Anderson, C.R. Perrey, C.B. Carter, S.A. Campbell, U. Kortshagen, Plasma Phys. Control. Fusion 46 (2004) B97.
[9] E. Perez-Tijerina, M.G. Pinilla, S. Mejia-Rosales, U. Ortiz-Mendez, A. Torres, M. Jose-Yacaman, Faraday Discuss. 138 (2008) 353.
[10] Y. Qiang, J. Antony, A. Sharma, J. Nutting, D. Sikes, D. Meyer, J. Nanopart. Res. 8 (2006) 489.
[11] G. Schultes, M. Schmidt, M. Truar, D. Goettel, O. Freitag-Weber, U. Werner, Thin Solid Films 515 (2007) 7790.
[12] I. Shyjumon, M. Gopinadhan, O. Ivanova, M. Quaasz, H. Wulff, C.A. Helm, R. Hippler, Eur. Phys. J. D 37 (2006) 409.
[13] N. Moreau, C. Michiels, B. Masereel, O. Feron, T.V. Gallez, S. Borght, S. Lucas, Plasma Processes Polym. 6 (2009) S888–S892.
[14] T. Takagi, Pure Appl. Chem. 60 (1988) 781.
[15] H. Haberland, M. Mall, M. Moseler, Y. Qian, T. Reiners, Y. Thurner, J. Vac. Sci. Technol. A 12 (1994) 2925.
[16] G. Praburam, J. Goree, J. Aerosol Sci. 27 (1996) 1257.
[17] W. Seifert, N. Carlsson, M. Miller, M.E. Pistol, L. Samuelson, L.R. Wallenberg, Prog. Cryst. Growth Charact. Mater. 33 (1996) 423.
[18] M. Volmer, A. Weber, Z. Phys. Chem. 119 (1926) 277.
[19] C.M. Wang, D.R. Baer, J.E. Amonette, M.H. Engelhard, Y. Qiang, J. Antony, Nanotechnology 18 (2007) 255603.
[20] A. Bouchoule, L. Boufendi, Plasma Sources Sci. Technol. 2 (1993) 204.
[21] D. Samsonov, J. Goree, J. Vac. Sci. Technol. A 17 (1999) 2835.
[22] J. Berndt, E. Kovacevic, V. Selenin, I. Stefanovic, J. Winter, Plasma Sources Sci. Technol. 15 (2006) 18.
[23] X. Bonnin, G. Lombardi, K. Hassouni, A. Michau, F. Benedic, C. Arnas, J. Nucl. Mater. 363 (2007) 1190.
[24] A.A. Samarian, O.S. Vaulina, A.P. Nefedov, V.E. Fortov, B.W. James, O.F. Petrov, Phys. Rev. E 64 (2001) 056407.
[25] V. De Vriendt, F. Maseri, A. Nonet, S. Lucas, Plasma Process. Polym. 6 (2009) S6.
[26] P.R.I. Cabarrocas, A.F.I. Morral, S. Lebib, Y. Poissant, Pure Appl. Chem. 74 (2002) 359.