Brief Communications

A SEM study of nanosized metal films and metal nanoparticles obtained by magnetron sputtering*

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Magnetron sputtering was successfully used to obtain nanosized metal films and metal nanoparticles, which can be useful for development of novel methods in organic chemistry. The morphology of the nanosized (5—100 nm) objects obtained was examined by SEM. The pattern of dependence of the morphology and size of the nanosized objects on the nature of the support surface, the metal, and the sputtering conditions is described.

Key words: nanoparticles, nanofilms, magnetron sputtering, scanning electron microscopy.

In the last few decades, nanoparticles of transition metals have attracted the attention of researchers as promising and highly efficient components of drugs, diagnostic agents, transducers, sensors, new generation materials, and microelectronic devices, as well as components in some other applications.[1—4] Nanoparticles are widely used as catalysts for various chemical processes. Nanoparticles have a high surface/volume ratio; their chemical properties can be regulated by controlling their shape.[5—7] A wide range of reactions are catalyzed by transition metal nanoparticles: cross-coupling, C—H and C—C bond activation, hydrogenation, cyclization, cycloaromatization, oxidation, and some others.[5—10]

A great number of methods have been developed for the synthesis of transition metal nanoparticles. Along with chemical approaches such as the reduction of transition metal salts, direct methods for bulk metal preparation of nanoparticles are currently very common. For laboratory applications, compact and convenient magnetron sputtering systems have been designed for bulk metal preparation of nanoparticles.[11—15] The advantages of magnetron sputtering include the absence of chemical wastes (no reduction step is required), the possibility of using both pure metals and alloys, and good prospects for deposition of thin (nanosized) films onto supports of nearly all types. Possible applications of magnetron sputtering in chemical research is now under intensive study. However, the dependence of the type and structure of nanosized objects on the preparation conditions and the equipment is an obstacle in the way of development of these applications.[16]

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The scope of magnetron sputtering for the preparation of nanosized objects is of current interest for researchers. It is especially important to study how the sizes and shapes of the resulting nanoparticles depend on the sputtering conditions, the metal, and the support. The influence of the support is crucial because even a slight modification of nucleation sites (first atoms and atomic clusters of the metal appearing on the surface of the support) can alter the morphology of the nanosized object.

The study of nanoparticles and nanofilms obtained by magnetron sputtering is also of interest for improvement of experimental procedures. Deposition of a metal by magnetron sputtering onto a sample surface is used to make the SEM[17] studies of nonconducting materials more informative. Data on the shapes and sizes of metal particles allow one to estimate the influence of the sputtering on the topology of the samples under study.

Experimental

Magnetron sputtering was carried out on a High Resolution Sputter Coater Cressington 208HR instrument equipped with a sputtering thickness sensor. The structures of the samples obtained were examined by field-emission scanning electron microscopy (FE-SEM) on a Hitachi SU8000 electron microscope. SEM images were obtained in the secondary electron mode (accelerating voltage 10 kV) and processed using the UTHSCSA Image Tool v3.0 software. The particle sizes were compared against the Feret diameters. Pt/Pd and Cr targets (99.99% purity), which produce morphologically different nanoparticles, were employed as metal sputtering sources.

Aluminum foil 6 μm thick served as a conducting sample. No nanoparticles were observed on its surface within the resolution limits of the electron microscope used (1—3 nm). Silica gel on TLC plates was used as a 2D nonconducting sample. Molecular sieves (4 Å) were employed as samples with a highly developed 3D surface morphology.

The magnetron sputtering system used in the present work is schematically shown in Fig. 1. A flow of atoms of a metal to be sputtered was produced by bombardment of a target surface with glow-discharge plasma ions; the metallic targets (Pt/Pd or Cr) served as a cathode and the sample (holder), as an anode. Plasma generation was initiated by applying a potential difference of 1—2 kV to the system. A high-purity heavy inert gas (argon) at a low pressure was used as a plasma source. Neutral Ar atoms were ionized through collisions with electrons. The plasma was focused on the target by a permanent rare earth magnet placed above the target to ensure a required sputtering rate. In addition, the permanent magnet served to divert electrons from the sample. The film thickness was checked with a built-in quartz thin-film monitor. The natural frequency of the vibrations of a quartz crystal is related to the weight of substance on its surface. The frequency difference prior to and after the deposition allows one

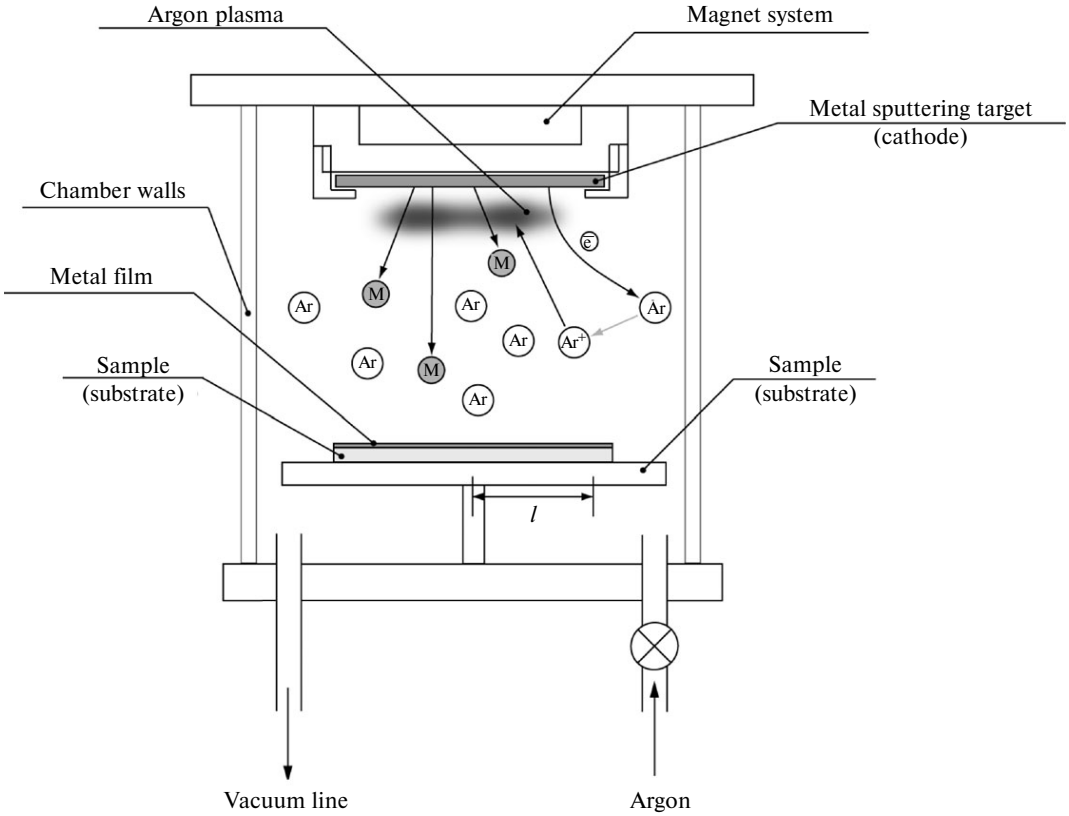

Fig. 1. Schematic representation of the magnetron sputtering system (*l* is the horizontal distance from the center of the sputtering source).

to determine the weight (and, consequently, thickness) of a film, which is converted with a standard program.[17]

Dependence of the observed morphology of nanoparticles on the distance from the center of the magnetron sputtering source. An aluminum foil strip about 10 mm wide was marked every 5 mm from its edge and fixed to the cleaned surface of a round aluminum table with double-sided carbon adhesive tape. The foil strip was placed in the chamber of the magnetron sputtering system in such a way that the zero mark on the strip coincided with the center of the chamber and the 55-mm mark, with its edge. The chamber was evacuated to ~0.005 mbar and the sample was stored at room temperature for 30 min. Then the Pt/Pd alloy (80/20) was sputtered under argon (0.02 mbar) at a current strength of 40 mA. The sputtering was continued until the film thickness reached 25 nm (measured with the sensor of the sputtering system). The sputtering was carried out without planetary rotation of the sample in the working chamber. Distances from the edge of the table were determined using the aforementioned marking and the internal coordinates of the stage in the microscope´s specimen chamber (Fig. 2).

Dependence of the observed morphology of nanoparticles on the film thickness. A piece of narrow aluminum foil was fixed with double-sided carbon adhesive tape to the cleaned surface of a round aluminum table 15 mm in diameter. Four samples prepared as described above were successively placed in the chamber of the magnetron sputtering system. In each case, the chamber was evacuated to ~0.005 mbar and the sample was stored at room temperature for 20 min. Then chromium was sputtered under argon (0.02 mbar) at a current strength of 80 mA; planetary rotation of the sample was on. The sputtering was continued until the film thickness reached 5, 10, 25, and 50 nm, respectively (measured with the sensor of the sputtering system). All the four foil samples obtained were removed from the 15-mm tables, transferred to a table 25 mm in diameter, and fixed to it with double-sided carbon adhesive tapes. The same procedure was used for sputter deposition of the Pt/Pd alloy (80/20) at a current strength of 40 mA.

Dependence of the observed morphology of nanoparticles on the sample type. A piece of aluminum foil, a piece of a TLC plate (silica gel was removed at its edges), and molecular sieves (4 Å) (shaped like a hemisphere by removing unnecessary substance with a scalpel) were fixed to the cleaned surface of a round aluminum table 25 mm in diameter with three strips of double-sided carbon adhesive tape. The resulting sample was placed in the chamber of the magnetron sputtering system. The chamber was evacuated to ~0.005 mbar and the sample was stored at room temperature for 30 min. Then the Pt/Pd alloy (80/20) was sputtered under argon (0.02 mbar) at a current strength of 40 mA; planetary rotation of the sample was on. The sputtering was continued until the film thickness reached 25 nm (measured with the sensor of the sputtering system). The same procedure was used for sputter deposition of chromium at a current strength of 80 mA.

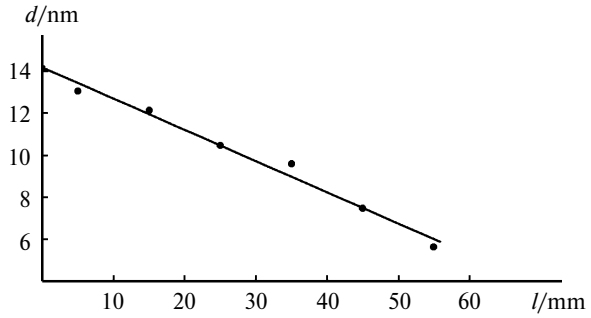

Fig. 2. Plot of the average size of metal particles (Pd/Pt on aluminum foil) *vs.* the distance *l* from the center of the sputtering source.

Deposition of bimetallic films. Layers of dissimilar metal films were deposited by sequential magnetron sputtering as described above.

Results and Discussion

To estimate the influence of the position of the sample in the chamber on the film structure, we analyzed the dependence of the film nanostructure on the distance from the center of the sputtering source (the distance *l*, see Fig. 1). Planetary rotation of the sample in the magnetron sputtering chamber was off during this experiment. On the one hand, averaging by planetary rotation makes the resulting films more uniform. On the other hand, however, the sample constantly moves in the chamber, while the thickness sensor remains immobile. Therefore, it is very important to control the accuracy of film thickness measured by the internal sensor.

In Fig. 2, the average size of the resulting metal particles is plotted versus the distance *l* from the center of the sputtering source to the sample. It can be seen that metal deposition occurs differently in different areas of the chamber, which affects the metal particle sizes and, probably, the metal film thickness. So the internal film thickness sensor provides only an approximate (qualitative) pattern of the process, its actual characteristics varying by a factor of two or more.

At the next step, we studied the homogeneity of metal films and the morphology of metal nanoparticles deposited onto aluminum foil by magnetron sputtering of the Pt/Pd alloy and Cr under the conditions of "homogeneous" deposition provided by planetary rotation of samples. A SEM study revealed a long 2D structure (film) formed by deposited Pt/Pd particles (average size 5—9 nm) at film thicknesses of 5, 10, and 25 nm. Intermediate structural elements are "islands" consisting of several tens of united particles. A similar structure was observed for a film thickness of 50 nm but the average size of metal particles was ~17 nm. The field-emission SEM (FE-SEM) images of aluminum foil samples coated with 25- and 50-nm layers of the Pt/Pd alloy are shown as examples in Fig. 3.

Three-dimensional metal films with characteristic nanostructures were obtained on samples with 2D and 3D structures such as silica gel and molecular sieves (Fig. 4). For a film thickness of 25 nm, the average size of metal particles was ~7—8 nm.

A different pattern was observed in the case of chromium deposition. At film thicknesses of 5 and 10 nm, indi-

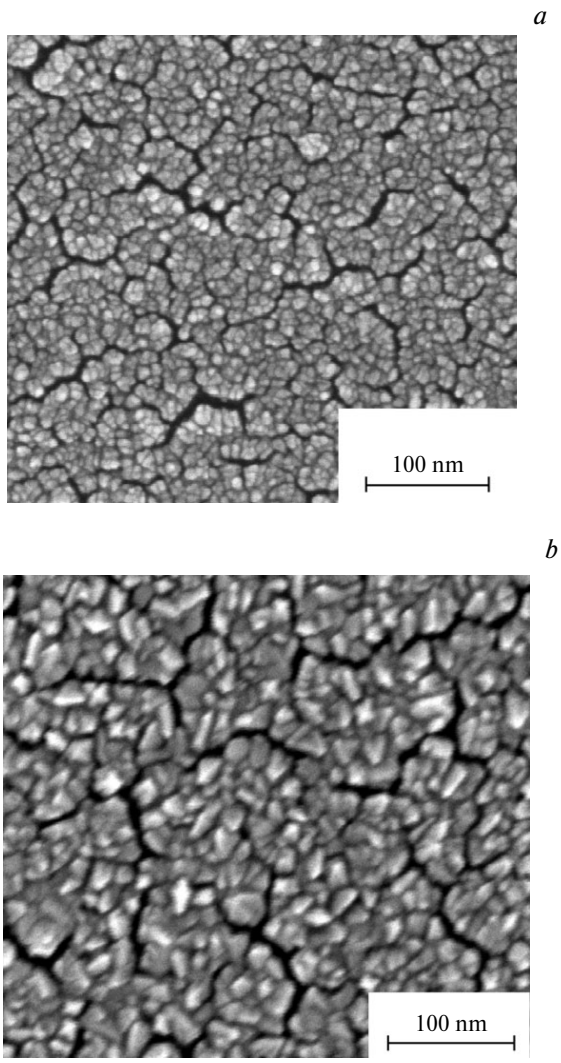

Fig. 3. FE-SEM images of aluminum foil samples coated with 25- (*a*) and 50-nm layers (*b*) of the Pt/Pd alloy (200 000x magnification).

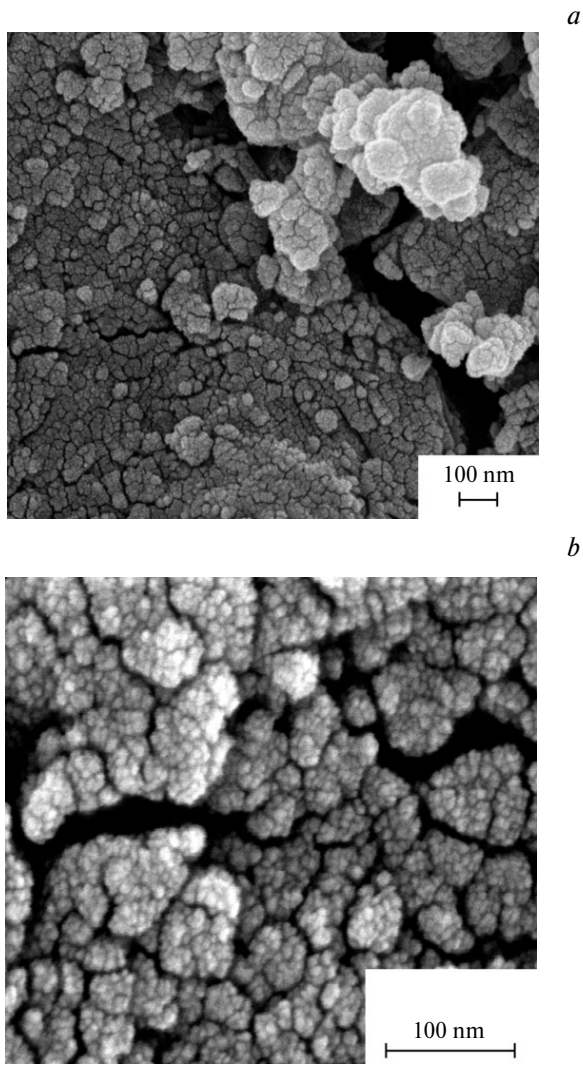

Fig. 4. FE-SEM images of the surfaces of molecular sieves coated with a 25-nm layer of the Pt/Pd alloy (50 000x (*a*) and 200 000x magnification (*b*)).

vidual metal particles are indiscernible. For 25- and 50-nm-thick films, the resulting metal layer on aluminum foil is made up of tetrahedral particles (average sizes 10 and 17 nm, respectively) united into a long 2D structure without any superstructures (Fig. 5). For low-thickness chromium films deposited onto molecular sieves and silica gel, the SEM images were of unacceptable quality because of a strong "charging" effect of the samples.

Finally, we examined mixed coatings. One piece of aluminum foil was successively coated with a 25-nm layer of Cr and a 25-nm layer of the Pt/Pd alloy and another piece of it was coated with the same metals in the reverse order, the layer thicknesses being the same. The SEM images of the samples obtained are shown in Fig. 6.

In both cases, there are considerable modifications in the nanostructure of the film compared to that of the individual films on aluminum foil. Each mixed film shows the morphology with differently contoured "islands" corresponding to the Pt/Pd layer. The average particle sizes in the former and latter mixed films were 11 и 22 nm, respectively. Some increase above the average particle size in the individual films can be explained by the fact that the particles in the lower layer serve as a substrate containing nucleation sites for the upper layer. Our experiments showed that pretreatment of a substrate has a substantial effect on the morphology of the metal film obtained by magnetron sputtering.

Thus, deposition of the Pt/Pd alloy does not produce homogeneous films in a thickness range of 5—50 nm because of the formation of "islands" separated by cracks (see Fig. 3).

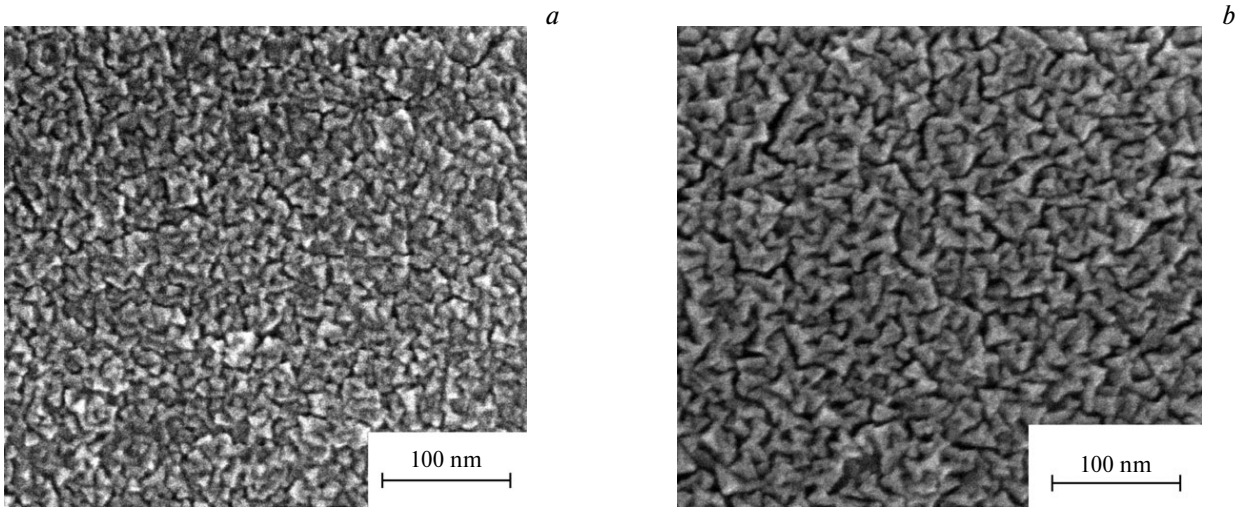

Fig. 5. FE-SEM images of aluminum foil samples coated with 25- (*a*) and 50-nm chromium layers (*b*) (200 000x magnification).

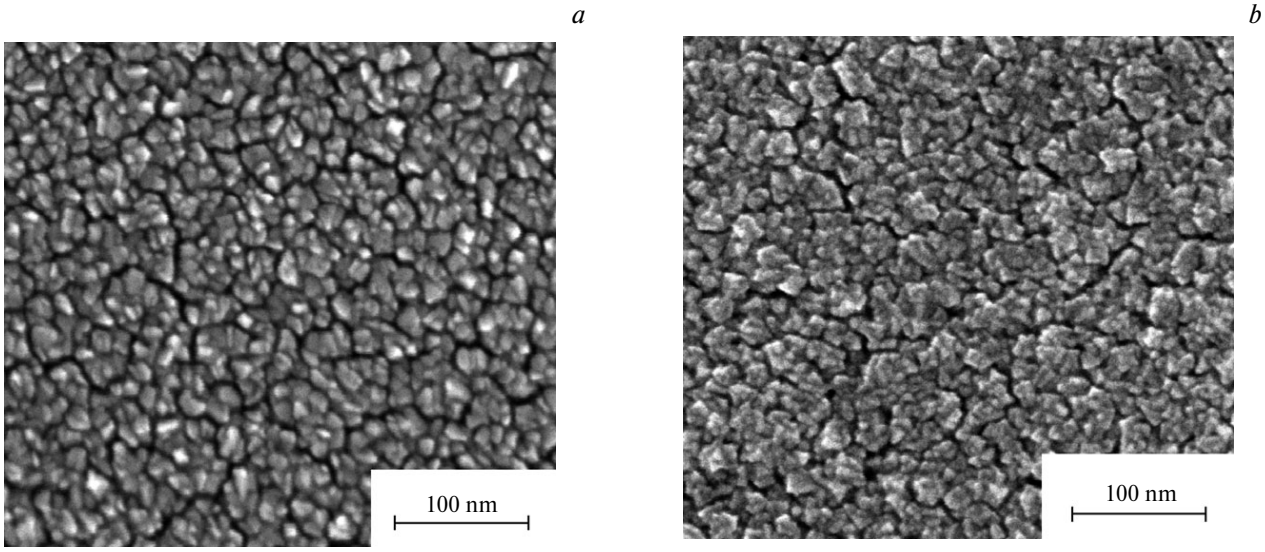

Fig. 6. FE-SEM images of aluminum foil samples coated with Cr + Pt/Pd (*a*) and Pt/Pd + Cr (*b*) (200 000x magnification).

However, this effect can be substantially alleviated by using preliminary deposition of chromium (see Fig. 6, *a*).

In contrast to the Pt/Pd alloy, the deposition of a Cr layer by magnetron sputtering allows the formation of more homogeneous films (see Fig. 5). Our study revealed the characteristic structure patterns for both cases, which makes it possible to identify the films by examining their morphology with SEM. According to the results obtained, magnetron sputtering can be used to obtain metal nanoparticles with characteristic sizes of 5—17 nm for the film thickness varying from 5 to 50 nm.

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References

1. H.-E. Schaefer, *Nanoscience: The Science of the Small in Physics, Engineering, Chemistry, Biology, and Medicine*, Springer, Heidelberg, 2010.
2. G. A. Ozin, A. Arsenault, L. Cademartiri, *Nanochemistry: A Chemical Approach to Nanomaterials*, Royal Society of Chemistry, 2008.
3. H. S. Nalwa, *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publishers, 2004.
4. T. K. Sau, A. L. Rogach, *Adv. Mater.*, 2010, **22**, 1781.
5. A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.*, 2002, **102**, 3757.
6. R. Narayanan, C. Tabor, M. A. El-Sayed, *Top. Catal.*, 2008, **48**, 60.

7. J. P. Wilcoxon, B. L. Abrams, *Chem. Soc. Rev.*, 2006, **35**, 1162.
8. J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, *ChemSusChem*, 2009, **2**, 18.
9. B. Wu, Y. Kuang, X. Zhang, J. Chen, *Nano Today*, 2011, **6**, 75.
10. K. Mori, H. Yamashita, *J. Jpn Petrol. Inst.*, 2011, **54**, 1.
11. P. J. Kelly, R. D. Arnell, *Vacuum*, 2000, **56**, 159.
12. I. Safi, *Surf. Coat. Technol.*, 2000, **127**, 203.
13. R. M. Nielsen, S. Murphy, C. Strebel, M. Johansson, I. Chorkendorff, J. H. Nielsen, *J. Nanopart. Res.*, 2010, **12**, 1249.
14. E. Quesnel, E. Pauliac-Vaujour, V. Muffato, *J. Appl. Phys.*, 2010, **107**, 054309.
15. B.-X. Chung, C.-P. Liu, *Mater. Lett.*, 2004, **58**, 1437.
16. I. Stokroos, D. Kalicharan, J. J. L. van der Want, W. L. Jongebloed, *J. Microsc.*, 1998, **189**, 79.
17. P. Echlin, *Handbook of Sample Preparation for Scanning Electron Microscopy and X-Ray Microanalysis*, Springer Science + Business Media, LLC, 2009.

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