* Manuscript

accepté pour publication dans Carbon le 29/09/2008
DOI: 10.1016/j.carbon.2008.09.051

Carbon/platinum nanotextured films produced by plasma sputtering

Hervé Rabat[1,2], Caroline Andreazza[3], Pascal Brault[1], Amaël Caillard[1,4], François Béguin[3], Christine Charles[4], Rod Boswell[4]*

[1] Groupe de Recherche sur l'Energétique des Milieux Ionisés, UMR6606 Université d'Orléans – CNRS BP6744, F-45067 Orléans Cedex 2, France

[2] MID Dreux Innovation, 4 rue Albert Caquot 28500 Vernouillet, France

[3] Centre de Recherche sur la Matière Divisée, UMR6619 Université d'Orléans- CNRS, 1b rue de la Férollerie 45071 Orléans Cedex 2, France

[4] Space Plasma, Power, and Propulsion group, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

Abstract

Platinum loaded carbon layers were synthesized by a two-step plasma sputtering process. 200 nm thick columnar (columns with an average diameter of 20 nm) carbon films having a large open porosity were formed in the first step. Using the same plasma system, the films were subsequently loaded with platinum. SEM, TEM and Rutherford backscattering spectrometry analysis show that platinum diffuses into the carbon layer and forms nano-sized particles (mean diameter ca. 3 nm) along and around the carbon nanocolumns and down to the film/support interface. Optimized catalytic layers were formed at low plasma pressure operation (<1 Pa) and had an upper platinum loading limit of about 0.1 mg.cm^{-2}.

* corresponding author: Pascal.Brault@univ-orleans.fr

1. Introduction

Heterogeneous catalysis is of primary importance in many chemical and electrochemical processes. To be efficient a solid catalyst is usually an assembly of nano-sized particles dispersed on a support with (preferably) a large surface area. Nanoporous carbons are one of the most currently used physical supports for catalysts deposition [1-9]. In the future, due to environmental concerns, both the catalyst usage conditions and catalyst preparation methods will suffer from severe international rules. The development of new and environment friendly catalyst preparation methods remains a challenging research task aimed at simplifying the industrial processes, while reducing the fabrication costs and preparation times, and increasing the catalysis efficiency and selectivity.

Plasma technologies have been involved in catalysis with some success [10-12]. Most of the studies are related to ultra-fine particles production, direct catalyst deposition on a support [13,14] and also assistance of catalytic reactions [15,16]. Although very few studies are devoted to low pressure plasma deposition of catalytic thin films, the latter is expected to be advantageous for controlling low catalyst content and location [17-23]. The present study reports on a new fabrication method using plasma sputtering for obtaining an active carbon layer loaded with platinum. The influence of the deposition parameters on the carbon layer morphology and platinum diffusion into the layer is investigated and discussed.

2. Experimental

2.1. Sputtering device Carbon and platinum were deposited by plasma sputtering and a scheme of the low pressure plasma experimental set up (MHS Equipment) is shown in Figure 1. An argon plasma is created in a 80 L cylindrical stainless steel chamber by using an external water cooled planar three turn radiofrequency antenna powered at 300 W using a 13.56 MHz Radio Frequency generator coupled to an impedance matching box. The chamber is evacuated to less than 5.10^{-5} Pa and the depositions are performed in the pressure range 0.5 Pa to 5 Pa. To sputter carbon and platinum, two

50x50 mm high purity planar targets for each material are placed at half height in the chamber and DC biased at a fixed voltage of –300 V. The targets are placed at a distance of 80mm from the substrate (100 type silicon) at an angle of 45° with respect to the grounded substrate holder axis. Silicon wafers are used as substrates because they allow a correct measurement of the thickness and composition of the carbon and Pt – carbon films. The substrate is rotated and its temperature is measured with a thermocouple.

2.2. Pt/C synthesis

The carbon films loaded by platinum catalyst are made in two consecutive steps. Initially, in order to obtain identical carbon layers, carbon is deposited onto ten silicon samples during a single one hour deposition run at 2 Pa. Catalyst is subsequently deposited onto each of these carbon layers using various pressures and deposition times to get some insight into the resulting morphology changes.

2.3. Analysis

Scanning Electron Microscopy (SEM-Hitachi S4500) and Transmission Electron Microscopy (TEM- Philips CM20) were used to characterize the film's morphology and the platinum particle size in the carbon layer. Cross sections were prepared in order to observe the in-depth profile of the deposits. The presence of platinum was detected by EDX (energy dispersive X-ray spectrometry) and the films were analyzed by RBS (Rutherford Backscattering Spectroscopy) with a Van de Graaf accelerator (CERI-CNRS, Orléans, France) using a 2 MeV $4He^{+}$ ion beam. Coupled with the SimNRA [24] software, it is a powerful method for determining the composition and depth profile. From the RBS analysis, the total number of Pt atoms per cm² (N_s) of deposited film is measured, whereas the film thickness is estimated by SEM observations of the cross-sections.

3. Results and discussion

3.1. The carbon layer

The SEM image in Figure 2 shows a typical cross-section of the carbon coating deposited by plasma sputtering on (100) type silicon. The carbon layer growth is columnar with column density

depending on plasma process parameters as a result from the so-called shadowing effect [25]. The columns stand on a 20 nm thick dense carbon interface with the silicon substrate. From bottom to top, the columns diameter increases from about 10 to 25 nm and the total film thickness is around 200 nm. Using RBS analysis, about 12 µg.cm^{-2} (560x10^{15} atoms.cm^{-2}) of carbon was found to make up this layer leading to a density of about 0.7 g.cm^{-3}. Hence this open structure exhibits an adequate morphology and can be used as a support for the catalyst.

3.2. The Pt/C layers

Platinum was deposited onto the carbon layers using different sputtering times (from 1 min to 15 min at 1 Pa) and pressures (from 0.5 Pa to 5 Pa during 10 min). Table 1 shows the quantities of deposited platinum and the morphological characteristics of the resulting Pt coated carbon thin films deduced from RBS and SEM measurements, respectively. For a given pressure (samples 2 to 4 in Table 1), the increase of the amount of deposited platinum, from 131×10^{15} atoms.cm^{-2} to 408×10^{15} atoms.cm^{-2}, leads to an increase in the height and diameter of the columns. Broadening mainly occurs at the top of the columns, but is also present at the bottom. From these results, we can deduce that platinum diffuses well inside the carbon layer.

Platinum diffuses over the whole pressure range investigated here (0.5 to 5 Pa) with the platinum deposition rate and the top and bottom diameters of the carbon columns decreasing with increasing operating pressure as shown in Table 1 (samples 6 to 8).

Figure 3a shows a TEM micrograph cross section of sample 8 (t=10min, P= 5 Pa). At the substrate interface, a dense layer, with a thickness of about 20 nm can be seen, as previously mentioned (Figure 2). Above this interface layer, nano-sized Pt particles are observed along and around all the columns (dark areas on the micrographs), from the top where the nanoparticles are more prevalent to the bottom where they are more dispersed. The nanoparticle size (1-8 nm) and density decrease from the top to the bottom of the columns and depend on the pressure and deposition time. In the HRTEM image (Figure 3c) for Pt nanosized particles well oriented to the electron beam, 0.23 nm spaced lattice fringes

corresponding to the d_{111} interplanar distance of platinum are observed . The EDX analyses confirm a decrease of the platinum amount from the surface to the interface.

Figure 4 shows the influence of the deposition time at a constant pressure of 1 Pa on platinum diffusion in the carbon layer. At the beginning of the deposition (Figure 4a corresponding to 1 min deposition time), platinum is present everywhere in the layer with a denser surface layer (10 nm thickness). Increasing the deposition time from 1 to 10 min, the thickness of this surface layer increases from 10 to 80 nm and the nanoparticle sizes increase from 1.5-5 nm for 1min deposition to 1.8-8 nm for 10 min, as shown in Table 2.

TEM analyses of two samples obtained with the same deposition time at different pressures (1 and 5 Pa, samples 4 and 8) indicate a thin and dense surface layer and smaller particle size (Table 2) at low pressure, leading to a more homogeneous distribution of the Pt nanoparticles in the carbon layer.

Figure 5 displays SEM micrographs of the cross-section of carbon layers coated by platinum for the samples 3, 5 and 6. The regions occupied by Pt atoms appear brighter than the carbon ones. Compared with sample 1 without platinum (figure 2), the micrographs clearly show that the columnar structure of the deposited film is preserved for deposition times less than 10 min at 0.5 and 1 Pa (samples 3 and 6 in Figure 5). For a deposition time of 15 min (sample 5 in Figure 5), the carbon columnar structure has collapsed and the layer thickness is considerably reduced. Interestingly, the platinum quantity deposited at 0.5 Pa for 10 min (sample 6) is similar to that of sample 5 (about 450×10^{15} atoms.cm^{-2}), although the corresponding film presents very different morphologies. The platinum diffusion into the carbon thin film is favoured at low pressure (0.5 Pa) which leads to strengthening the columnar structure and preventing the formation of a dense platinum top layer at the film surface. Otherwise, as in sample 5, a thick dense platinum layer induces stress onto the carbon column structure and it collapses [26]. The fact that platinum diffuses deeper at low pressure results from a higher kinetic energy of the sputtered platinum atoms and from ion bombardment occurring during deposition as previously reported on flat surfaces [27-30].

Hence to ensure an adequate morphology of the loaded film with a good dispersion of the catalyst, the amount of deposited platinum should be limited to 300×10^{15} atoms.cm^{-2}, e.g., 0.1 mg.cm^{-2} and the working pressure should be less than 1 Pa.

4. Conclusion

In summary, this experimental study demonstrates that plasma sputtering can be successfully applied to preparing and controlling the composition and the structure of catalyst loaded carbon layers. Low pressure (<0.5 Pa) deposition below a typical maximum limit of about 300×10^{15} atoms.cm^{-2} leads to the growth of Pt loaded porous carbon films with a good platinum dispersion. Experiments are under progress to evaluate the electrochemical performance of active layers prepared by this novel process.

Acknowledgement

This work was supported by CAdD, FSE-EU, MHS Equipment, ACI PLASMAPAC and GDR-I CNRS "Plasmas". All authors would like to thank Y. Tessier from GREMI (Orléans, France), A. Richard from CME (Orléans, France) and Thierry Sauvage from CERI (Orléans, France).

References

[1] Marie J, Berthon-Fabry S, Chatenet M, Chainet E, Pirard R, Cornet N, Achard P. J Appl Electrochem 2007; 37:147-153

[2] Marie J, Berthon-Fabry S, Achard P, Chatenet M, Chainet E, Pirard R, Cornet N. ECS Trans. 2006; 1:509-519

[3] Brault P, Caillard A, Thomann A L, Mathias J, Charles C, Boswell R W, Escribano S, Durand J, Sauvage T. J Phys D: Appl Phys 2004;37:3419-3423

[4] Wan C H, Lin M T, Zhuang Q H, Lin C H. Surf Coat Technol 2006; 201:214-222

[5] Escribano S, Blachot J F Ethève J, Morin A, Mosdale R. J. Power Sources 2006; 156:8-13

[6] Litster S, McLean G. J. Power Sources 2004:61-76

[7] Yuan F, Ryu H. Nanotechnology 2004;15:596-602

[8] Caillard A, Brault P, Mathias J, Charles C, Boswell R W, Sauvage T. Surf Coat Technol 2005; 200:391-394

[9] Caillard A, Charles C, Boswell R W, Brault P, Coutanceau C. Appl Phys Lett 2007; 90:223119

[10] Boutonnet Kizling, Jaras S G. Applied CatalysisA: General 1996;147:1-21

[11] Liu C J, Vissokov G P, Lang B W L. Catalysis Today 2002; 72:173-184

[12] Liu C J, Zu J, Yu K, Cheng D, Han Y, Zhan J, Ratanatawanate C, Lang B W L. Pure and Applied Chemistry 2006; 78:1227-1238
[13] Berthet A, Thomann A L, Cadete Santos Aires F J, Brun M, Deranlot C, Bertolini J C, Rozenbaum J P, Brault P, Andreazza P. J. Catalysis 2000;190:49-59
[14] Thomann A L, Rozenbaum J P, Brault P, Andreazza-Vignolle C, Andreazza P, Rousseau B, Estrade-Szwarkopf H, Berthet A, Bertolini J C, Cadete Santos Aires F J, Monnet F, Mirodatos C, Charles C, Boswell R., Pure and Applied Chemistry; 2002;74:471-474
[15] Khacef A, Cormier J M, Pouvesle J M, Gorce O, Jurado H, Thomas C, Djéga-Mariadassou G, Calvo S, Lendresse Y. Proceedings of the VIIIth Hakone, Pühajärve (Estonie), 21-25/07/2002.
[16] Gorce O, Jurado H, Thomas C, Djéga-Mariadassou G, Khacef A, Cormier J M, Pouvesle J M , Blanchard G, Calvo S, Lendresse Y. SAE technical paper 2001; N° 2001-01-3508,
[17]Matsumyia M, Shin W, Izu N, Murayama N. Sensors and Actuators B: Chemical 2003; 93:309-315
[18] Tiggelaar R M, Berenschot, J W, Oosterbroek R E, van Male P, de Croon M H J M, Schouten J C, van den Berg A, Elwenspoek M C. TRANSDUCERS, Solid-State Sensors, Actuators and Microsystems, 12th International Conference on, 2003; 1:746-749
[19] Randolph S J, Fowlkes J D, Melechko A V, Klein K L, Meyer H M, Simpson M L, Rack P D. Nanotechnology 2007;18:465304
[20] Ando M, Chabicovsky, Haruta M. Sensors and Actuators B: Chemical 2001:76:13-17
[21] Haruta M, CATTECH 2002;6:102-115
[22] Poelmana H, , Eufingera K, Deplaa D, Poelmana D, De Grysea R, Selsb B F Marin G B. Applied Catalysis: A 2007; 325:213-219
[23] Wilson M S, Gottesfeld S. Applied Electrochemistry 1992;22:1-7
[24] Mayer M. Tech. Report IPP 9/113, Max-Planck-Institut fur PlasmaPhysik, Garching, 1997
[25] Dumay B, Finot E, Theobald M, Legaie O, Durand J, Baclet P, Goudonnet J P. J Appl Phys 2002; 92:6572-6581
[26] Charles C, Boswell R W. J Appl Phys 1998; 84:350-354
[27] Thomann A L, Brault P, Rozenbaum J P, Andreazza-Vignolle C, Andreazza P, Estrade-Szwarckopf H, Rousseau B, Babonneau D, Blondiaux G. J Phys D: Appl Phys 1997;30:3197-3202
[28] Thomann A L, Charles C, Brault P, Laure C, Boswell R. Plasma Sources Sci Technol 1998; 7:245-251
[29] Brault P, Thomann A L, Andreazza-Vignolle C. Surface Science 1998, 406, L597-L602
[30] Thomann A L, Rozenbaum J P, Brault P, Andreazza-Vignolle C, Andreazza P. Applied Surface Science 2000; 158:172-183

Table captions:

Table 1: Pt quantities and morphological characteristics of the catalyst loaded carbon films.

Sample	Deposition time (min)	Operating Pressure (Pa)	Pt quantity (10^{15}at.cm^{-2})	Mean column height (nm)	Bottom column mean diameter (nm)	Top column Mean diameter (nm)
1	0	-	0	176	10	24
2	1	1	131	178	16	31
3	5	1	245	187	18	35
4	10	1	408	243	24	46
5	15	1	458	177	-	52<w<84
6	10	0.5	441	231	27	54
4	10	1	408	243	24	46
7	10	2	395	241	22	47
8	10	5	326	245	19	43

Table 2: Platinum particle diameter ranges.

Sample	2	3	4	8
Diameter (nm)	1.5<d<5	1.5<d<6	1.8<d<8	2.5<d<5

Figure Captions:

Figure 1: Scheme of the Transformer Coupled Plasma sputtering reactor.

Figure 2: SEM image of the cross-section of a carbon coating prepared at 2 Pa during 60 minutes.

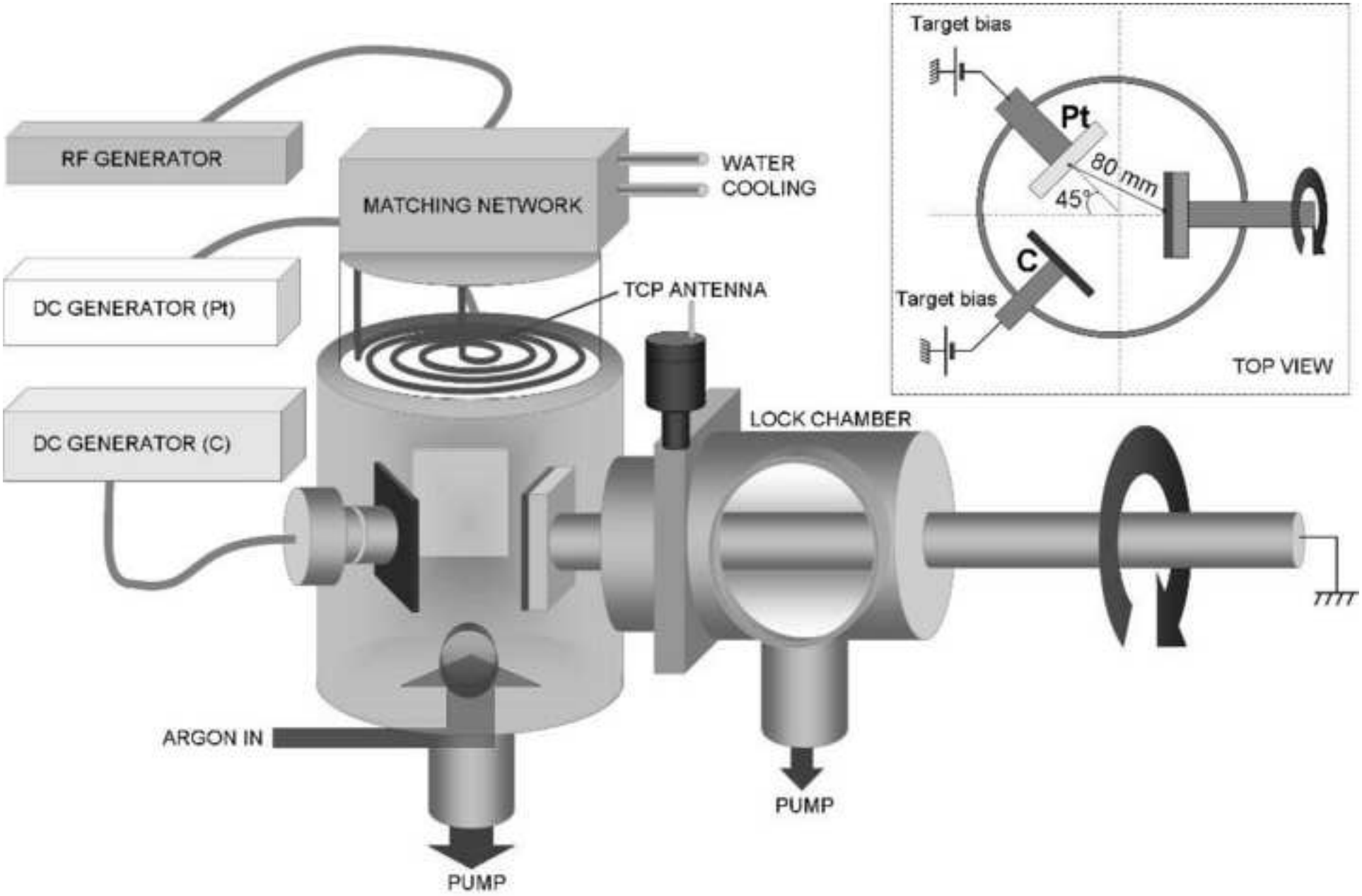
Figure 3: TEM image of loaded carbon films; Sample 8 (t=10 min, P=5 Pa). (a) cross section, (b) platinum distribution into the layer, (c) high resolution image showing the d_{111} platinum interplanar distance.

Figure 4: Influence of the platinum deposition time at 1 Pa on the surface layer thickness; (a) Sample 2 (t=1 min), (b) Sample 3 (t=5 min) and (c) Sample 4 (t=10 min).

Figure 5: SEM images of carbon films loaded with platinum at different pressures and deposition times; Sample 3 (t=5 min, P=1 Pa), Sample 5 (t=15 min, P=1 Pa), Sample 6 (t=10 min, P=0.5 Pa).

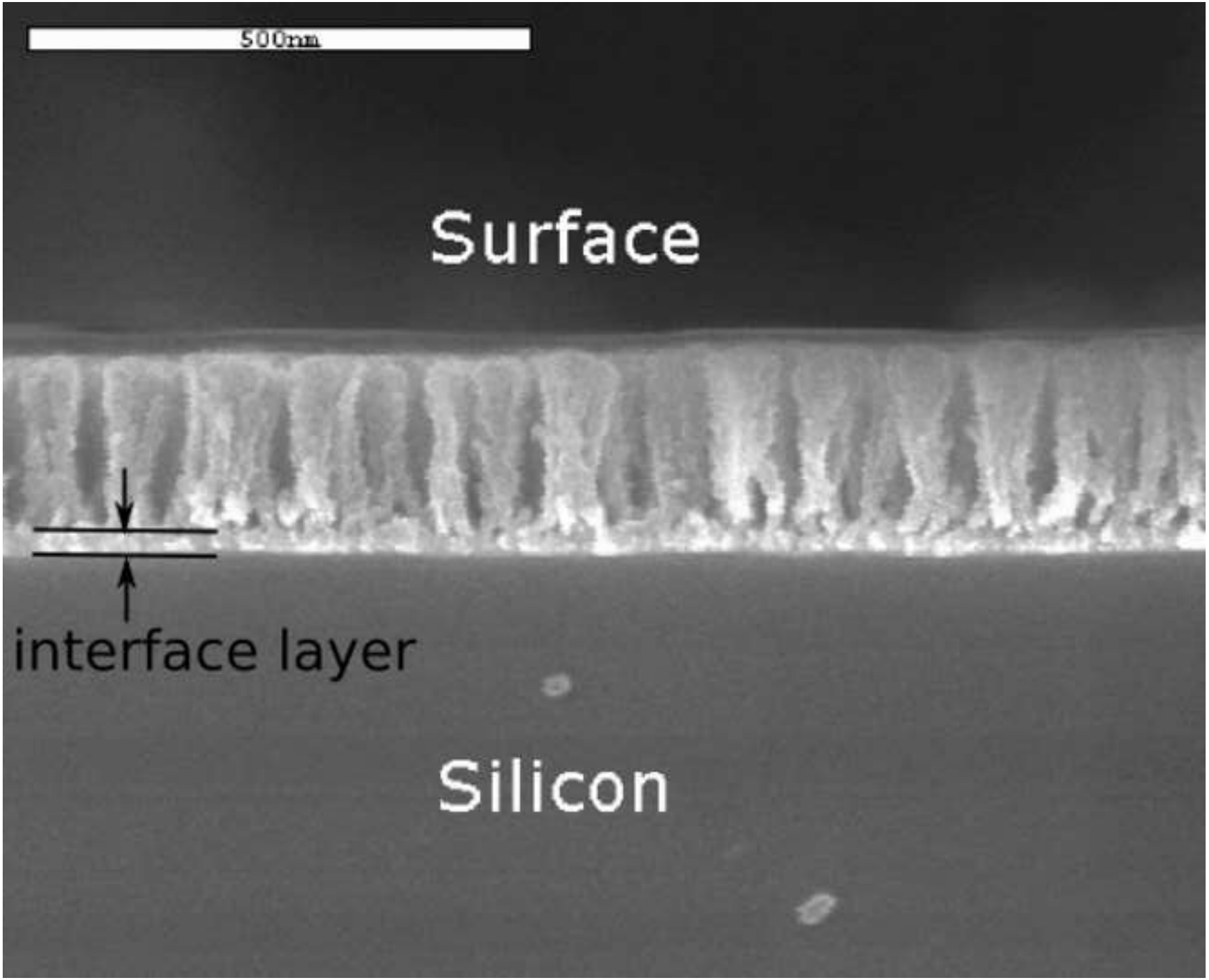
Figure(s)

Click here to download high resolution image



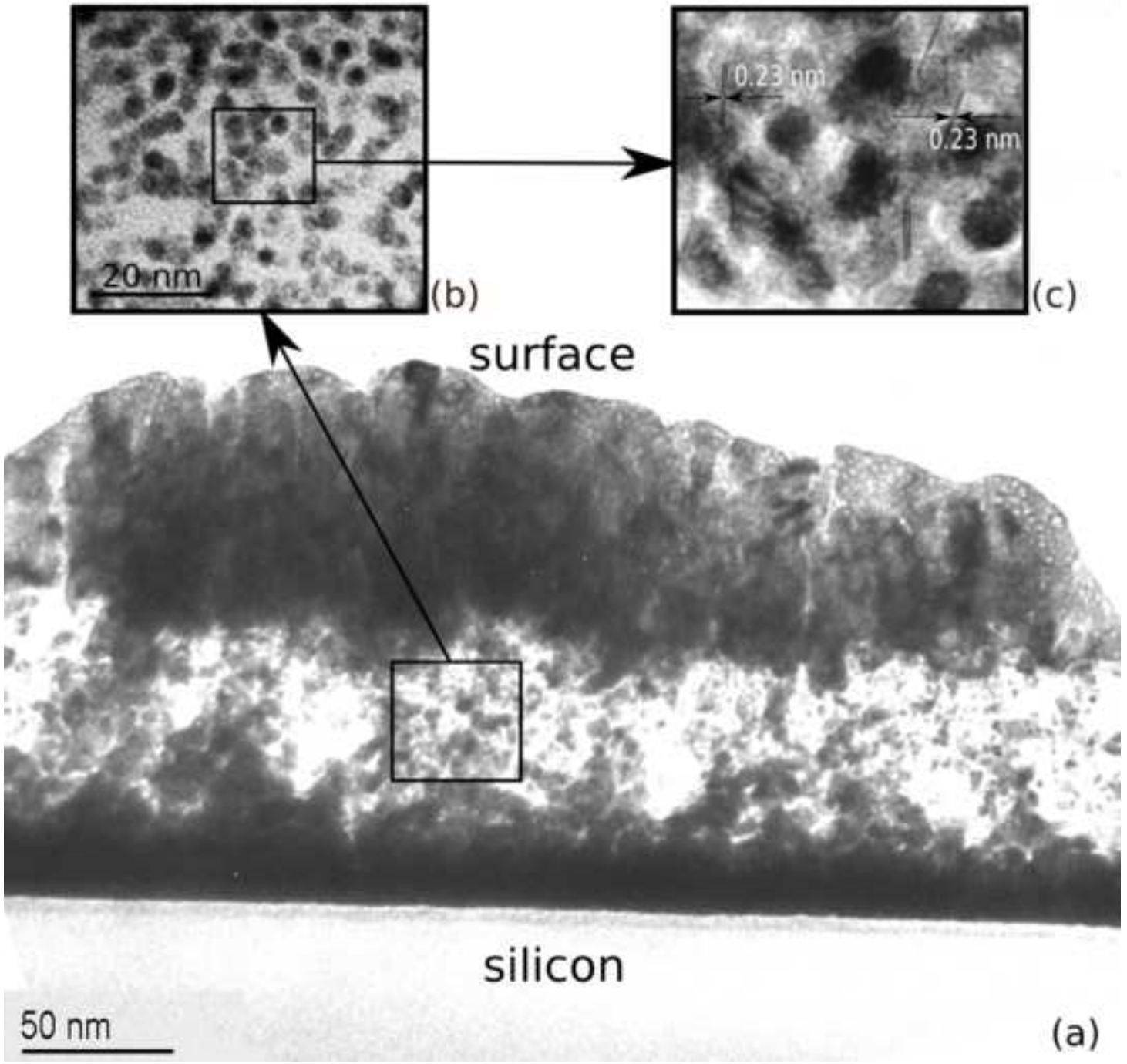
Figure(s)

Click here to download high resolution image



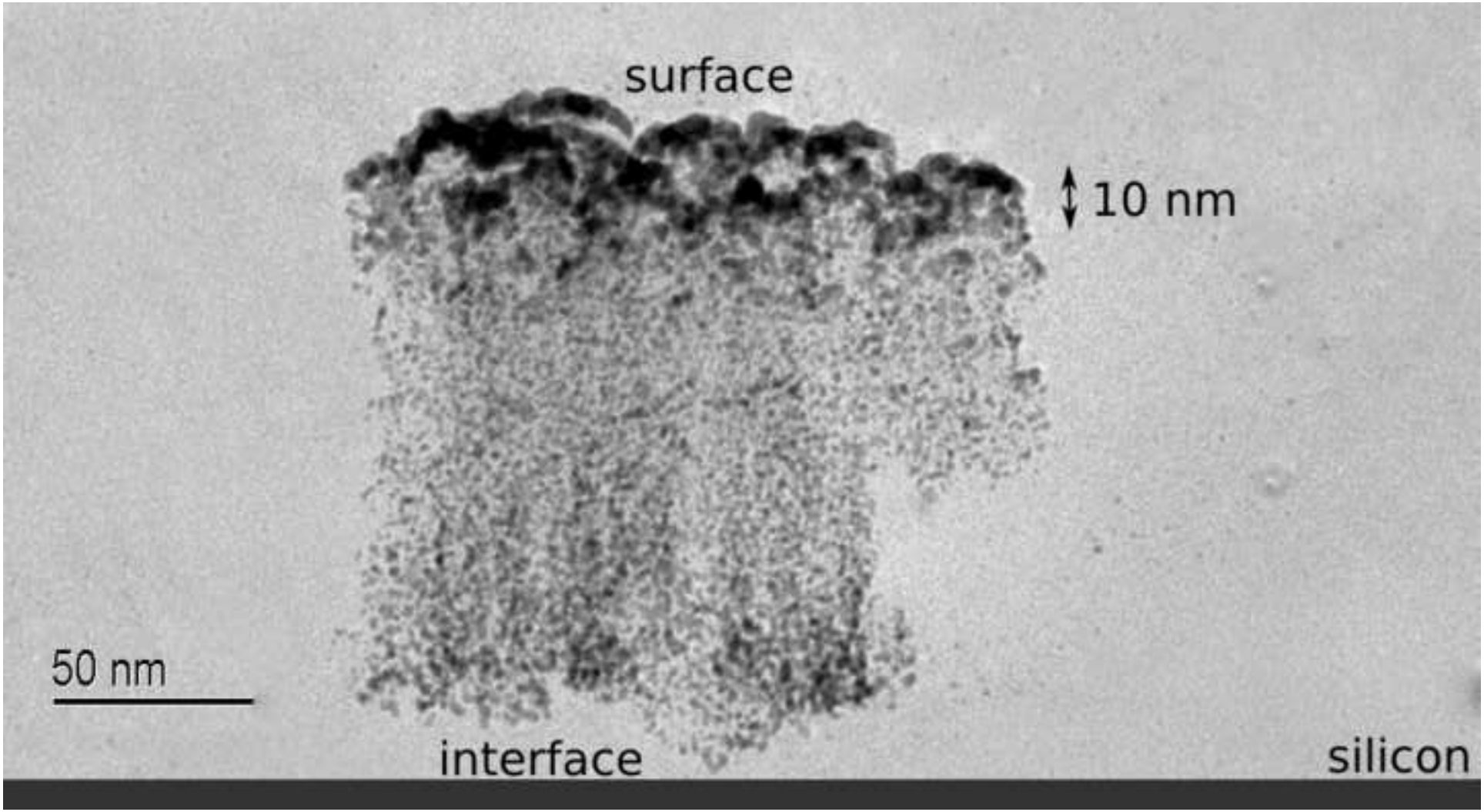
Figure(s)

Click here to download high resolution image



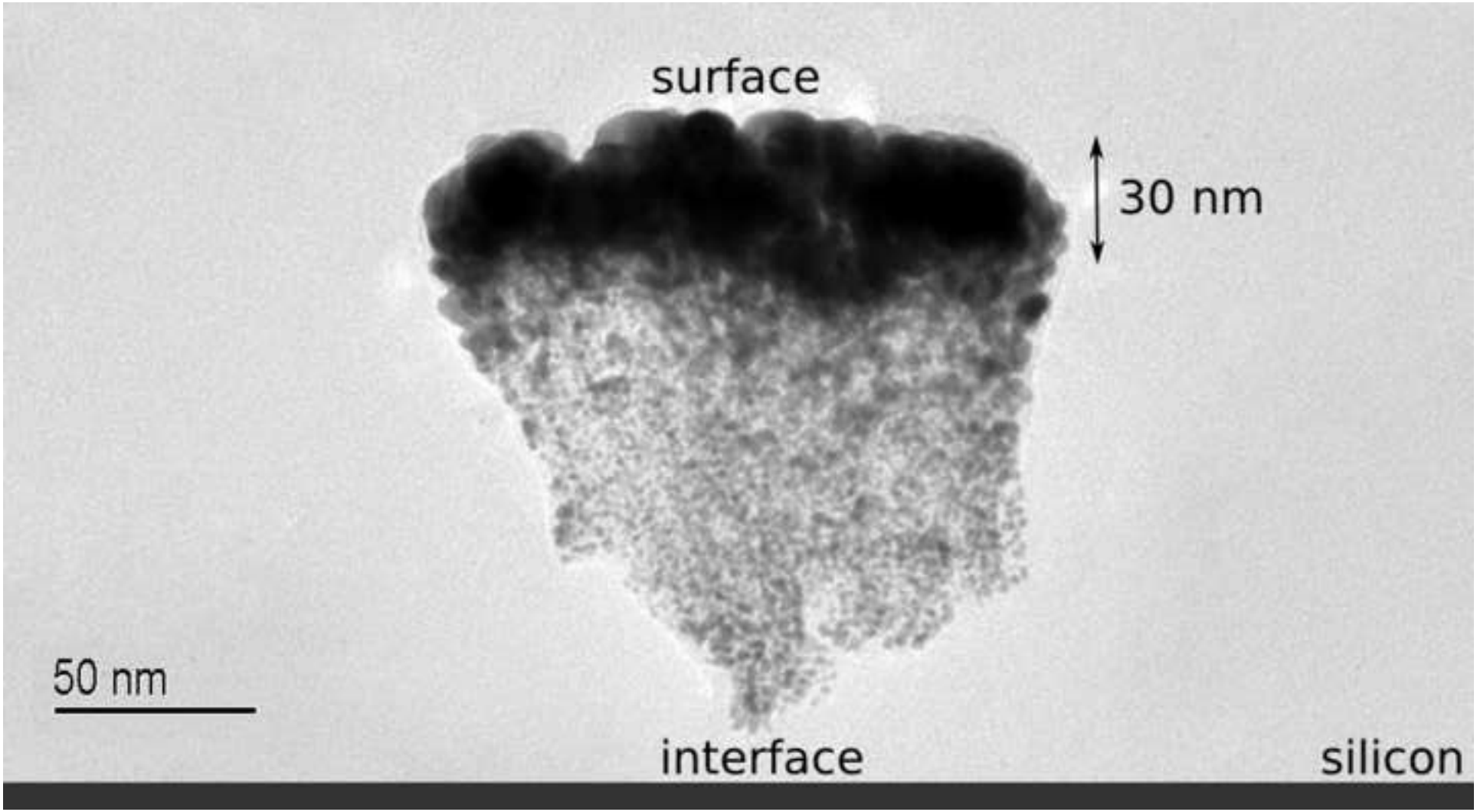
Figure(s)

Click here to download high resolution image



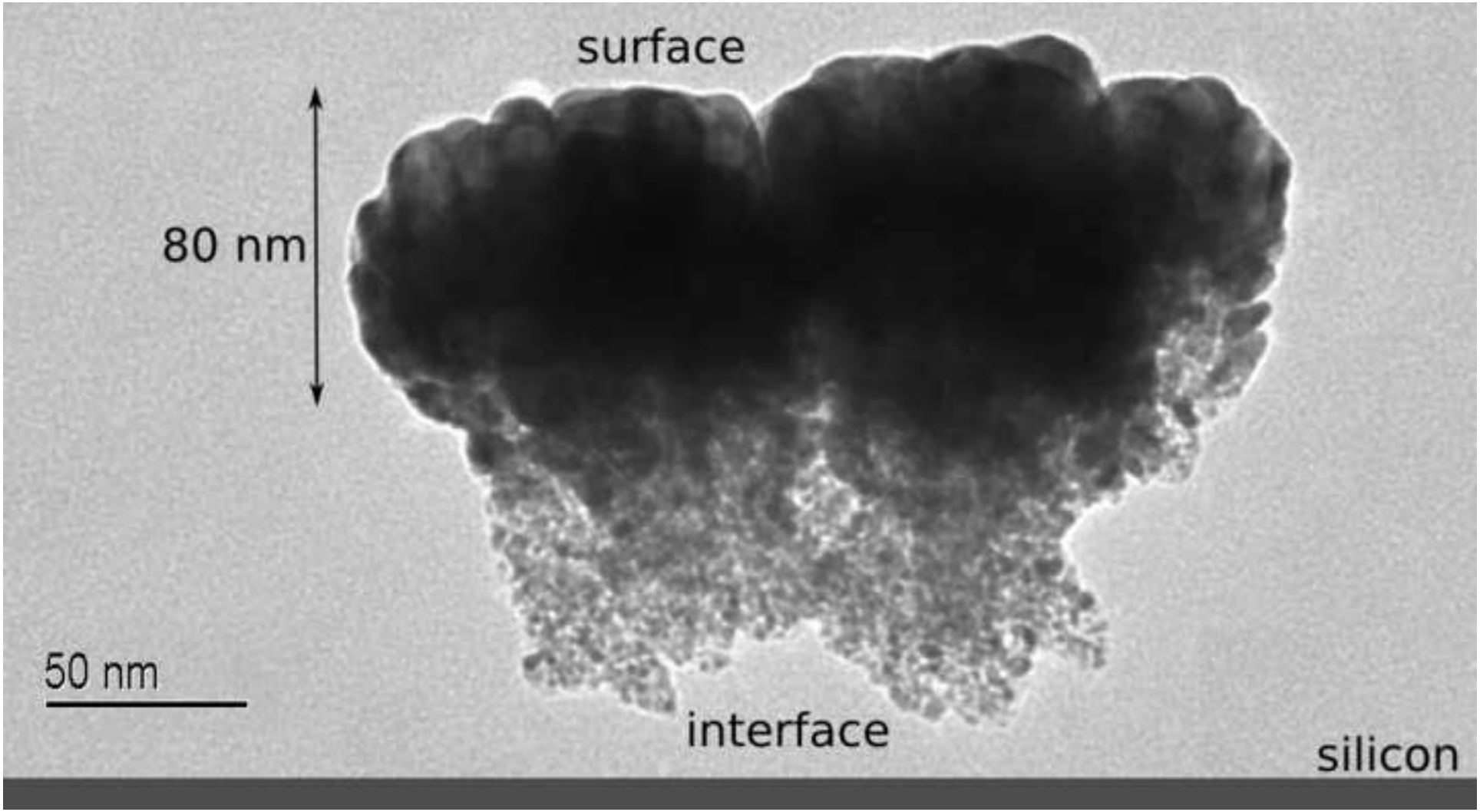
Figure(s)

Click here to download high resolution image



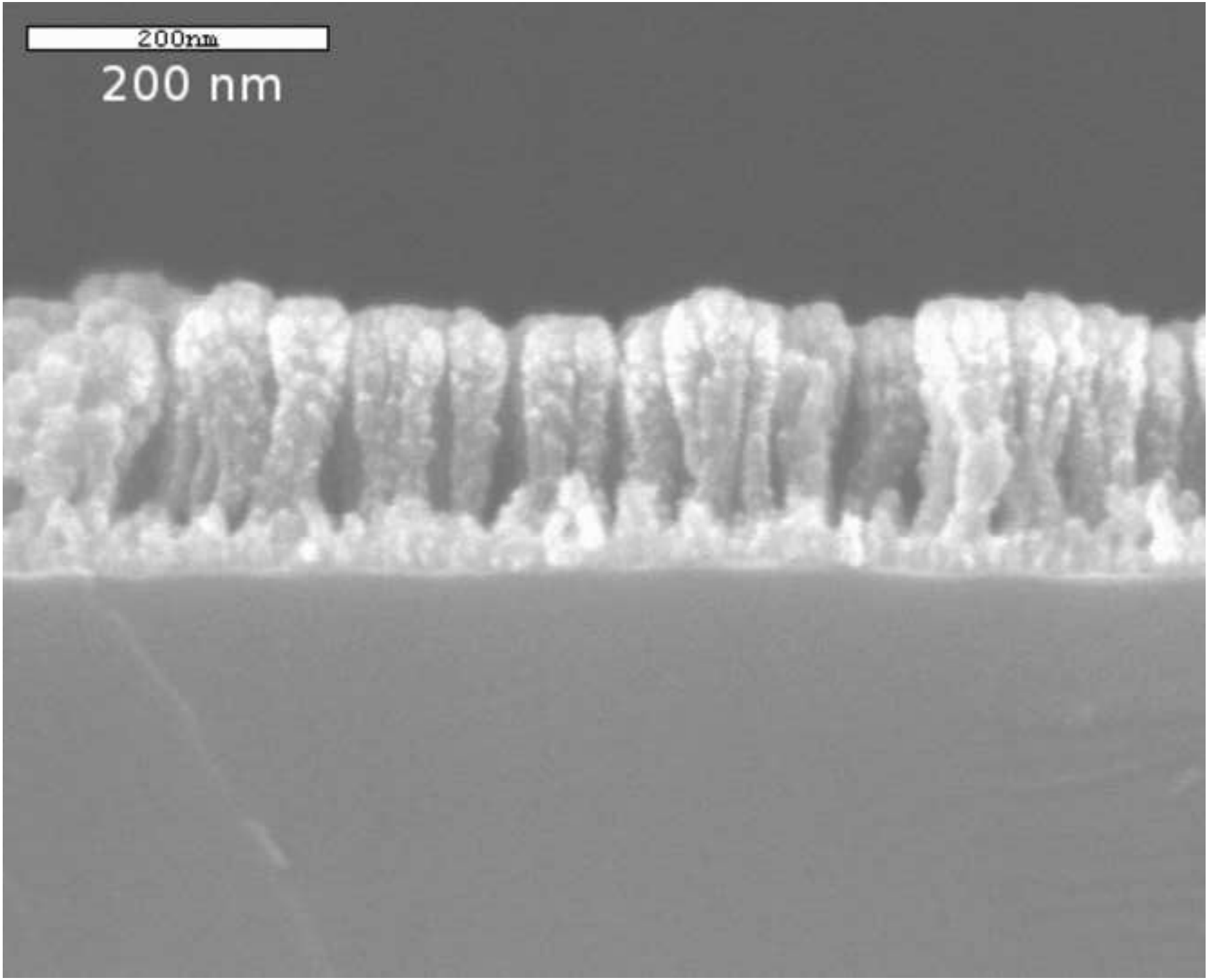
Figure(s)

Click here to download high resolution image



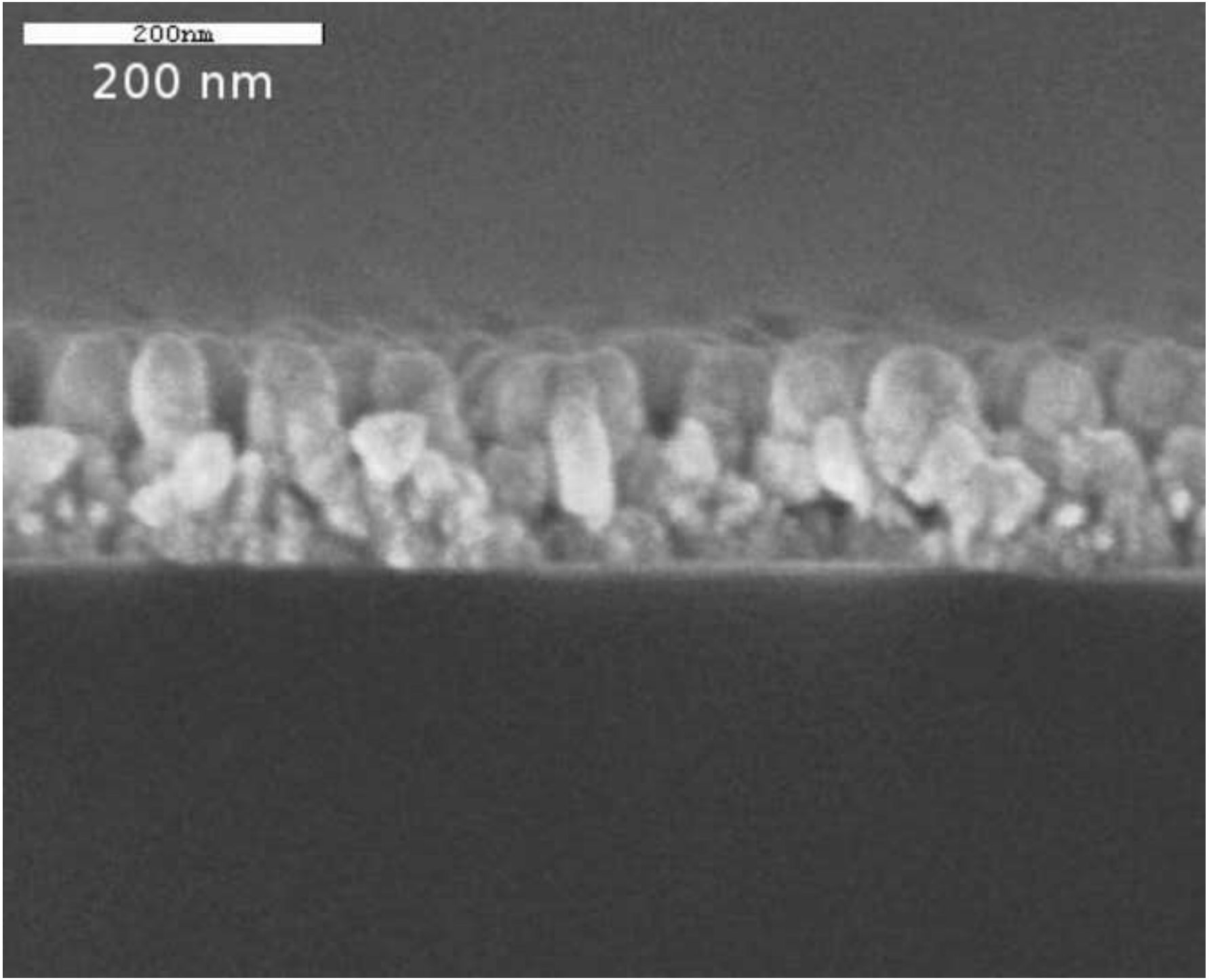
Figure(s)

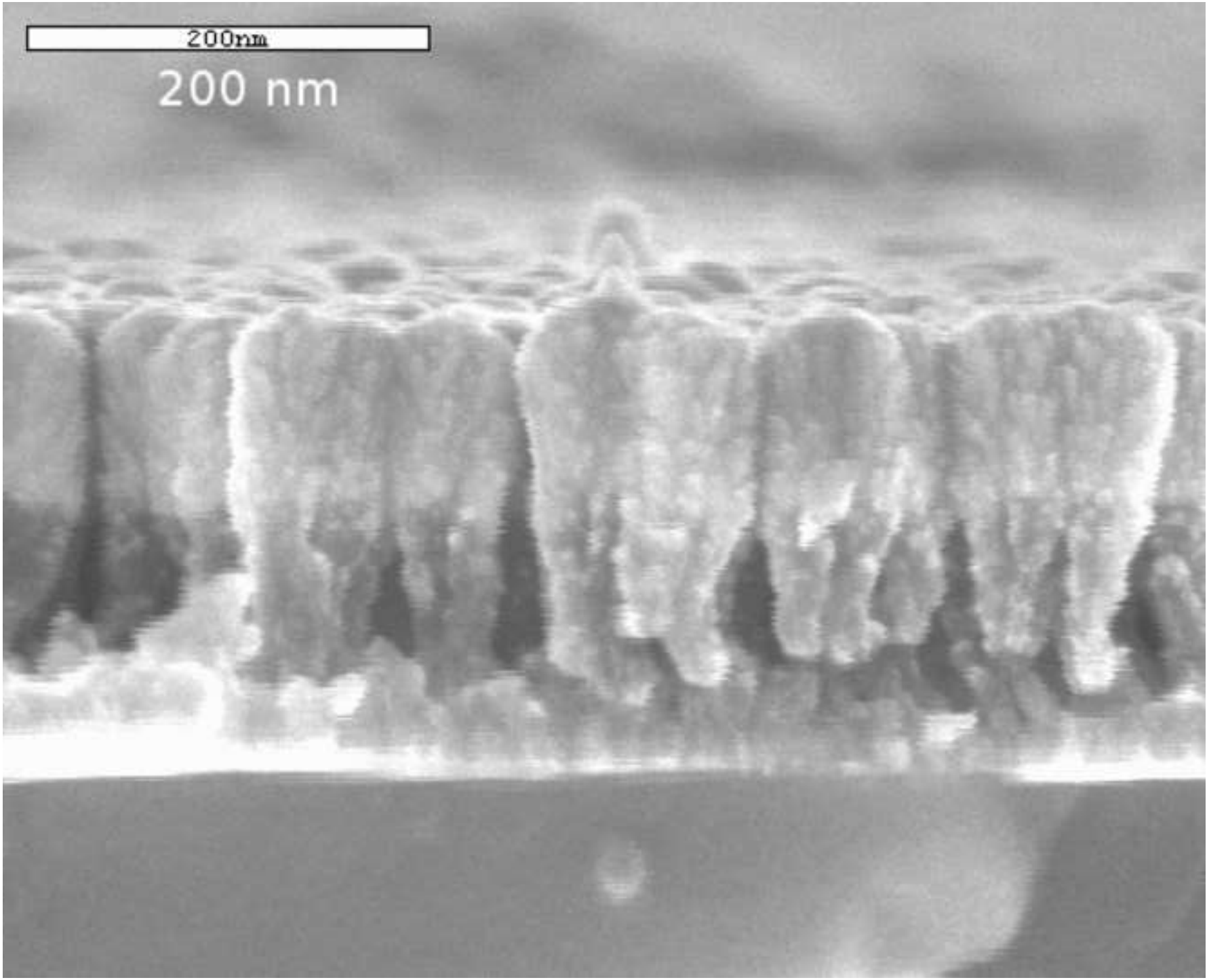
Click here to download high resolution image



Figure(s)

Click here to download high resolution image



Figure(s)

Click here to download high resolution image