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Abstract: In this work, a straightforward strategy was developed for the fabrication of cobalt thin films made of a dense array of vertically aligned nano and / or meso-crystals. Briefly, the proposed process consists in the electrodeposition of columnar cobalt thin films followed by a selective wet-etch treatment. Based on a preliminary screening of either aqueous or methanol based acid etchants, either a nitric acid or methanesulfonate methanol solution was further considered. The degree of selectivity of the etching solutions was evaluated on the basis of the observation of film surface/cross section morphology before and after etching. Contrary to water-based solutions methanol-based solutions showed definitely a degree of selectivity towards grain boundary preferential etching. In particular, with methanesulfonic acid - methanol solution, saturation of the etchant with oxygen was found to have a profound effect in improving the control of the etching process. Accordingly, an 11.2% methanol-based MSA solution was able to selectively etch the Co layer at the grain boundaries, leaving Co individual crystals separated by nanochannels.

***Highlights (for review)**

- Straightforward process of surface nanostructuring by electrodeposition and wet etching
- Effective grain boundary selective etching of columnar cobalt thin film
- Fabrication of a nanopillar array film of potential interest as a supporting scaffold structure for further deposition or surface modification

Nanopillar array film of cellular cobalt by wet etching of the grain boundaries

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Abstract

In this work, a straightforward strategy was developed for the fabrication of cobalt thin films made of a dense array of vertically aligned nano and / or meso-crystals. Briefly, the proposed process consists in the electrodeposition of columnar cobalt thin films followed by a selective wet-etch treatment. Based on a preliminary screening of either aqueous or methanol based acid etchants, either a nitric acid or methanesulfonate methanol solution was further considered. The degree of selectivity of the etching solutions was evaluated on the basis of the observation of film surface/cross section morphology before and after etching. Contrary to water-based solutions methanol-based solutions showed definitely a degree of selectivity towards grain boundary preferential etching. In particular, with methanesulfonic acid (MSA)- methanol solution, saturation of the etchant with oxygen was found to have a profound effect in improving the control of the etching process. Accordingly, an 11.2% methanol-based MSA solution was able to selectively etch the Co layer at the grain boundaries, leaving Co individual crystals separated by nanochannels.

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1. Introduction

Over the past decades nanostructured (NS) thin films have been attracting increasing interest driven by fundamental questions about material behavior at small scales and by potential applications in a variety of areas [1]. In particular, three-dimensional and two-dimensional nanostructures, such as nanoporous film, nanowire and nanoparticle arrays, have been widely explored for sensing applications, for the obvious advantage over thin films of providing significantly greater surface area, without affecting the overall device dimension. This in turn expectedly results in faster response time and increased sensitivity. Intense research activity has been in fact devoted to the development of new fabrication methods of NS thin film devices, with, understandably, a particular emphasis on device performance rather than on process viability for practical uses.

The conventional methods for obtaining NS arrays are lithographic techniques including optical lithography, X-ray lithography, electron-beam lithography and soft lithography. Although these techniques have the capability for achieving a high degree of control over the morphology of the array, high-cost of the equipment and process complexity limit their applicability. Therefore, much research effort has been focused on the development of low cost techniques, typically via wet processing, enabling a degree of control over the formation of nanostructures, though with special attention to oxide and compound thin films, e.g. [2-3].

In this paper, we propose a simple approach for the fabrication of Co nanocrystal arrays, by grain boundary selective etching of electrochemically deposited (ECD) columnar Co films [4-6]. The resulting array of nanocrystals may then be used as a supporting scaffold structure for further deposition or surface modification.

2. Experimental

Cobalt thin films with thickness in the range of 0.75±0.1 μm were deposited from 1 M cobalt methanesulfonate solutions at pH 6.2±0.1 on Ni-P10% coated brass sheets, at 30°C. Further details

on Co deposition and substrate preparation were given in ref. [7]. Acid etching solutions had the following composition: 10 ml HNO_3 (65% nitric acid, puriss. p.a., Sigma-Aldrich) and 90 ml CH_3OH (methanol, ACS, Merck); (2) 10 ml methanesulfonic acid (MSA 70%, technical, Fluka) and 90 ml CH_3OH. Etching was performed at room temperature for 30 s and 2 min, using etchant (1) and (2) respectively, the latter after bubbling with oxygen. The surface and cross section morphology of Co films was investigated by Scanning Electron Microscopy (SEM) (Zeiss EVO- 50 microscope). Surface topography was analyzed by Atomic Force Microscopy (AFM) sampling a 50 µm × 50 µm area with an NT-MDT Solver SPM apparatus operated under contact mode. Contact angle measurements were performed with a Data Physics OCA 150 instrument.

3. Results

Three-dimensional AFM imaging (Figure 1-(a)) of the surface of ECD-Co films revealed a rough surface associated with the columnar microstructure and globular morphology (Figure 1-(b)) which are typical features of [00.1] textured films –as reported in detail elsewhere [4,5]. A further peculiarity of this microstructure is the presence of inter-columnar spaces filled with cobalt hydroxide [4,6]. This is a key requirement for the in-principle viability of the proposed procedure, namely the selective etching of the non-metallic phase segregated at grain boundaries. In this respect, the wettability of the Co film turned up to be of great importance to decide the efficacy of the etching process. Notably, H_2O-based etchants were found to have low selectivity, resulting either in surface polishing –with a slight smoothing effect, as revealed by decreasing roughness, namely when the etch rate was low– or in uniform etching –with thickness reduction, though to different degree depending on the strength of the etchant.

In particular, the observation of surface smoothing, being suggestive of a comparatively fast etching rate of surface peaks, prompted the analysis of Co thin film wettability. Static contact angle measurements were performed using water or methanol as the wetting liquid (2 µL drop), in

consideration of their difference in surface tension (at room temperature: 72.8 and 22.7 dyne cm^{-1} , respectively) [8,9], as well as in view of their actual possible use as a solvent. As shown by the optical images in Figure 1-(c) and 1-(d), the contact angle was 120° and 7.6° for H_2O and CH_3OH, respectively. In agreement with the Cassie model [10], it is suggested that the Co surface in contact with water is able to form a composite interface by trapping air in the valleys of the surface topography. In this respect, it may be further surmised that a decisive factor is the characteristic bumpy topography of the surface, which is associated with the columnar microstructure and with its organization at larger scale in column aggregates [11]. Such features of the surface are clearly revealed by the AFM topography shown in Figure 1-(a) and SEM imaging of the film morphology (Figure 1-(b)). The effect of roughness on wettability is apparently nullified by the intrinsically higher spreading ability of methanol. Accordingly, methanol was preferred as the solvent in the etchant formulation. Strong acids were employed as the main component of the etchant, in particular nitric acid (NA), intended to work also as the oxidant, and methanesulphonic acid (MSA), to be used in combination with oxygen gas as the oxidizing agent.

The HNO_3 65 wt% / methanol (1 to 9 by vol.) etchant had a concentration of nitric acid of about 15.9 wt%. Etching was performed by immersion of the sample in the solution for 30 s. SEM micrographs in Figure 2 show the surface and cross section morphology of the layer before (left column) and after (right column) etching. Preferential etching at grain boundaries occurred, leaving a dense array of crystals of varying shape and size, depending on the original morphology. However, a sensible though moderate size reduction of individual columnar crystals, namely a reduction of both the height and the in-plane size of the columns, may be inferred from Figure 2. Notably, the film turned black, as a visible effect of roughening and possibly surface oxidation. Though effective, the HNO_3 based etchant was apparently too aggressive thus setting strong limits on the degree of control that could be achieved.

The MSA content in the MSA/methanol etchant was 11.2 wt%. Etching was performed at room temperature for 2 min, after bubbling for 10 to 60 min with oxygen. The effects of etching can be appreciated by comparing the SEM micrographs of Figure 3, showing the pristine surface morphology (a),(b) and the etched surface (a*),(b*), after 10 and 60 min bubbling with O_2, respectively. Obviously, grain boundary etching was effectively achieved also with the MSA/methanol etchant and interestingly the extent of etching was influenced by the O_2 bubbling time. When the latter was 60 min, larger trenches were opened between individual grains (Figure 4-(b*) vs 4-(a*)) and a slight but perceptible height reduction of the crystals is revealed by comparing the film cross-section before and after etching in Figure 4-(c) and (c*), respectively. More precisely, a shift from a preferential grain boundary etching towards a less selective attack was apparent for bubbling time in excess of 30 min.

The as-grown morphology of the layer obviously determines the specific characteristics of the crystal array, namely shape, size and size distribution of individual crystals, notwithstanding the depth of the etching process. In fact, greater control on morphology can be achieved by modifying the ECD process, as discussed in detail in [7], enabling the formation of nanopillar (NP) array of cobalt.

5. Conclusion

In the present work the fabrication of array of Co crystals is demonstrated by selective grain boundary etching of Co columnar thin film. A high degree of wetting was found to be an essential condition for the achievement of selective etching. Accordingly, methanol based solutions in the presence of an acid and an oxidant were considered a promising etching medium. In particular, an MSA/methanol solution in the presence of dissolved oxygen was found to have high selectivity towards preferential grain boundary etching. The same etchant allowed for a degree of control on the etching depth by varying the bubbling time with O_2.

NP-Co arrays produced by this method were successfully used for the fabrication of composite coating with dry lubrication capability [7]. Another field of application for the thin film matrix can be envisaged in ion sensing electrodes, either Co-based or, more generally, using the NP-Co array as the template for the deposition of the sensing material.

6. References

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Figure captions

Figure 1. Three-dimensional surface AFM imaging (a) and cross section/surface SEM micrographs (b) of cobalt thin films; water (c) and methanol (d) contact angle images on cobalt films.

Figure 2. SEM micrographs of the surface and tilted view of the fractured edge of Co layers before (left column) and after etching (right column) in 15.9 wt% HNO_3 - methanol solution, for 30 s.

Figure 3. SEM micrographs of the surface and tilted view of the fractured edge of Co layers before (left column) and after etching (right column) in 11.2 wt% MSA-methanol solution, for 2 min. O_2 bubbling time was (a*) 10 min (b*) and (c*) 1 h.

Figure 1

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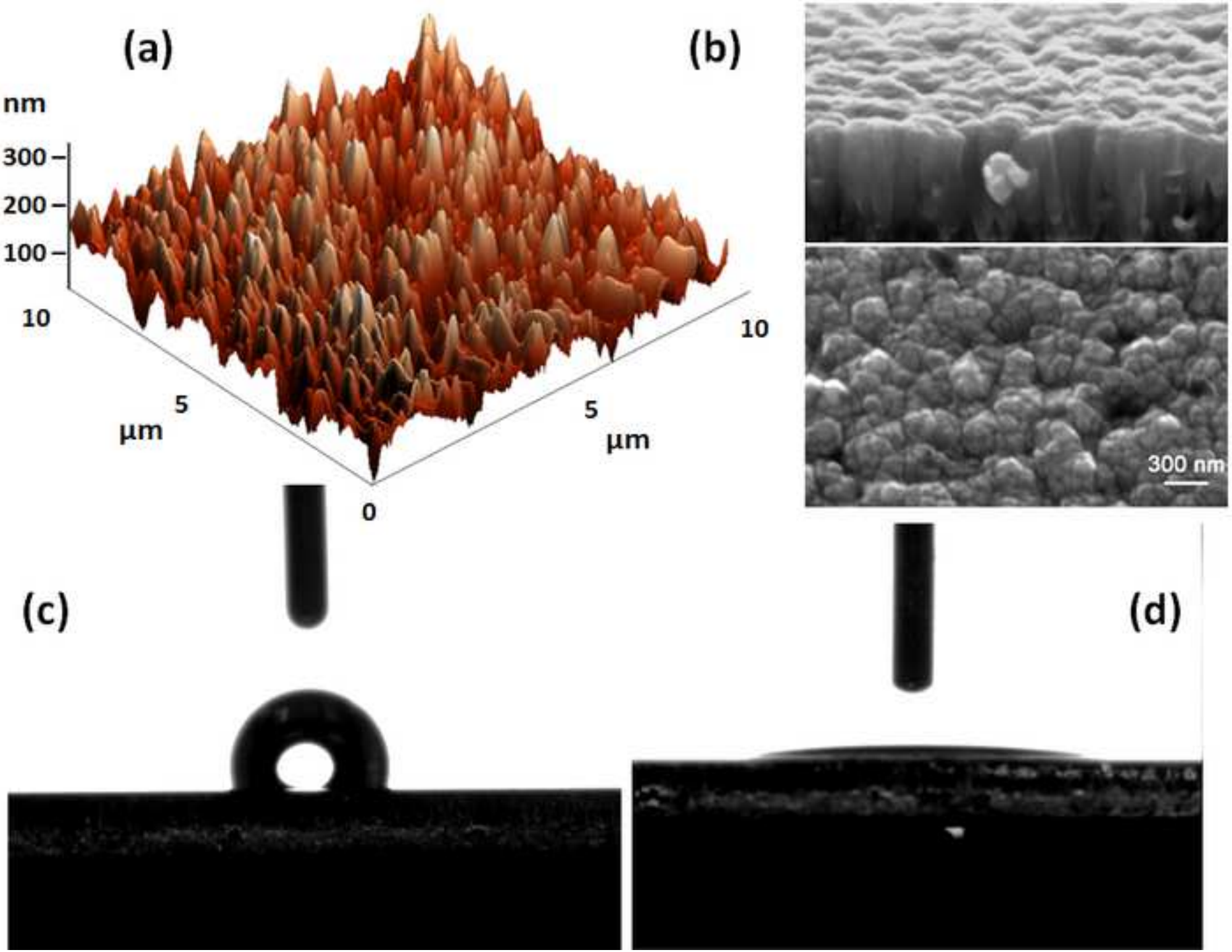

Figure 2

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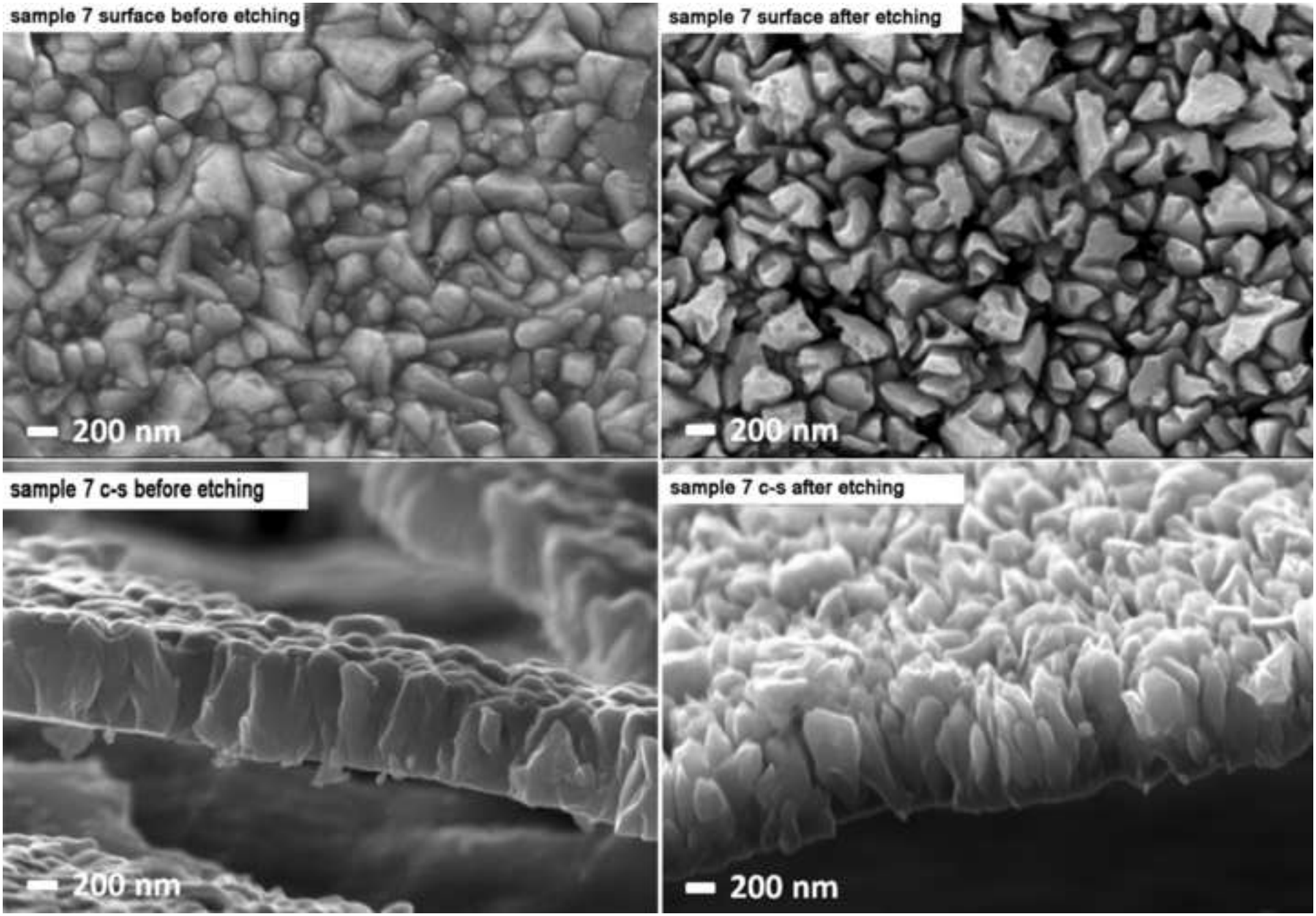

Figure 3

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