[1031] Structural Characterisation of ALD coated Porous Si via Beam-Exit Cross-Sectional Polishing

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1) Summary

Porous silicon (PS) samples with aspect ratios approaching 1:600 were conformally coated with Al_2O_3 using atomic layer deposition (ALD). Beam-exit cross-sectional polishing (BEXP) was used to create shallow-angled cross-sections of the ALD coated samples, facilitating the study of the internal structure of the PS via scanning probe microscopy (SPM). ALD coating was found to be conformal along much of the pore height, although pores were observed to become blocked closer to the sample surface.

2) Introduction

Conformal coatings of materials have played an important role in the development and production of a wide range of devices including insulators, conductors, diffusion barriers and adhesive layers. The application of conformal coatings in high aspect ratio (HAR) structures, such as super-capacitors, transistor channels, memory applications, catalytic membranes, biomedicine and gas sensors show great potential due to the extensive surface area compared with 2D structures [1-3]. Porous silicon (PS) is a promising candidate for a number of applications as it relatively easy to prepare and offers large surface area.

Unfortunately, the consistent coating of HAR structures presents difficulties in maintaining coverage and conformality of functional layers. ALD allows the deposition of a wide range of conducting and isolating materials with conformality and layer thickness control. The ALD coating of HAR structures requires optimisation and characterisation of coated structures can be of great benefit to the process. Scanning electron microscopy (SEM) observation of layers can be a straightforward way of checking coatings for some structures, but can encounter difficulties when imaging thin layers or material combinations that provide low contrast. Alternative techniques exist, such as exploiting the resistance of Al_2O_3 against SF_6/O_2 plasma in deep reactive ion etching (DRIE) of silicon, can involve etching away the porous frame of a HAR sample [4], allowing the subsequently revealed ALD layers to be studied.

This work presents the results of an alternative method of studying ALD coated PS. The BEXP technique allows the internal structure of a sample to be investigated using SPM techniques by producing a shallow-angled cross-section through the sample, usually 5 - 12° [5]. Crucially, this particular arrangement means that the area of interest is exposed to the Ar –ion beam-exit, rather than the beam-entry as in standard Ar-ion milling, producing cross-sections with sub-nm roughness and extremely low amounts of damage, ideal for SPM analysis.

3) Methods/Materials

Porous silicon with ALD coatings

Highly doped (10-20 mΩ.cm) silicon was etched in HF:ethanol=1:1 electrolyte to produce a 30 - 40 μm thick PS layer, with pore diameter of 50 - 80 nm. Pore diameter close to the surface was found to be much smaller (~10 nm), which necessitated the removal of the top few micrometres of PS via reactive ion etching (RIE) using SF6 plasma in order to prevent ALD growth bottlenecking. Samples were examined via cross-sectional SEM prior to coating (Figure 1).

21 nm thick Al_2O_3 ALD coating was realised using PICOFLOW™ Diffusion Enhancer in a Picosun R200 Series ALD reactor.

Sample cross-sectioning

Samples were cross-sectioned in a Leica EM-TIC020 Ar-ion beam cutter. Samples were mounted on an angled stage (3°) and aligned so that ~60μm of material was exposed to the Ar-ion beams (Figure 2). Samples were cross-sectioned with an accelerating voltage of 7 kV until beam-exit occurred and a broad (several mm wide) cross-section was formed. The accelerating voltage was lowered to 1 kV to polish the sample surface prior to SPM.

Scanning probe microscopy

Cross-sectioned PS was imaged using ultrasonic force microscopy (UFM), providing nanomechanical data and enhanced material contrast. UFM was facilitated by mounting the sample on a piezoactuator stage vibrated at a high (~4 MHz) frequency with small amplitude, and used Budget Sensors ContAl-G probes. A modified Bruker MultiMode 8 AFM was used for UFM imaging.

4) Results & Discussion

UFM images were taken at regular intervals along the height of the pores. ALD coating appears to be conformal while pores remain unblocked. As scans proceed towards the surface, sample topography indicates that pores begin to block up with ALD coating (Figure 3). UFM, previously shown to be sensitive to subsurface structure [6], potentially indicates the presence of a hollow area in the pore centre beneath the cross-section surface, meaning that pores may not be completely blocked. The majority of pores appear to remain unblocked for much of their length, with complete blockage of pores only occurring near the sample surface.

5) Conclusion

BEXP allowed SPM analysis of the internal structure of ALD coated PS, and shows that while Al_2O_3 ALD coating appears to be conformal along much of the pore height, there is a point at which the pores becomes blocked. We believe that this investigative technique can be highly useful for both optimising ALD process and for the development and fabrication of HAR structures, as it allows easy access for variant SPM methods to study material properties within the sample structure itself.

Acknowledgements

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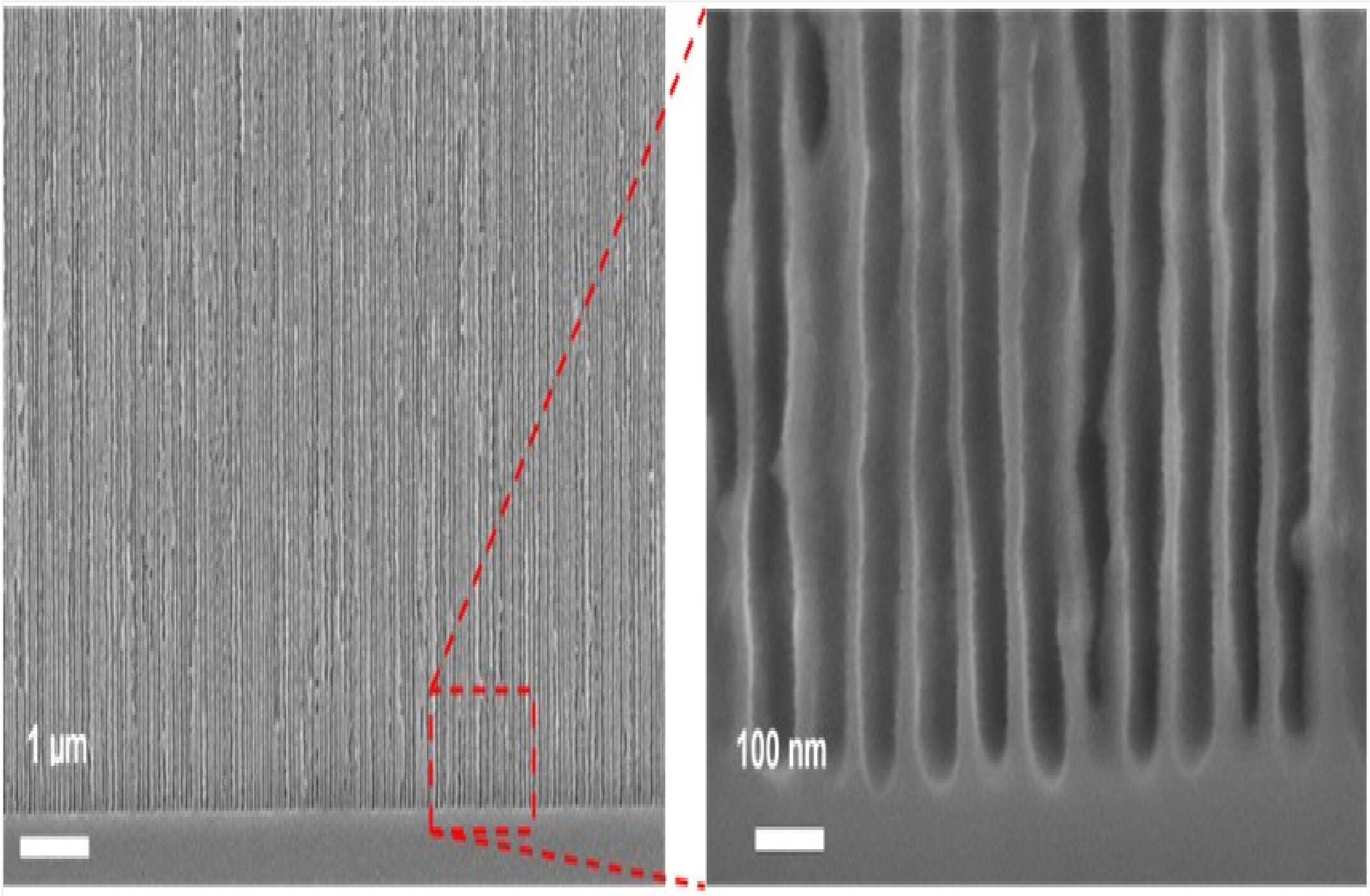

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Figure 1: Cross-section SEM picture of porous silicon layer before ALD coating. Bottom part of PS is shown at larger magnification.

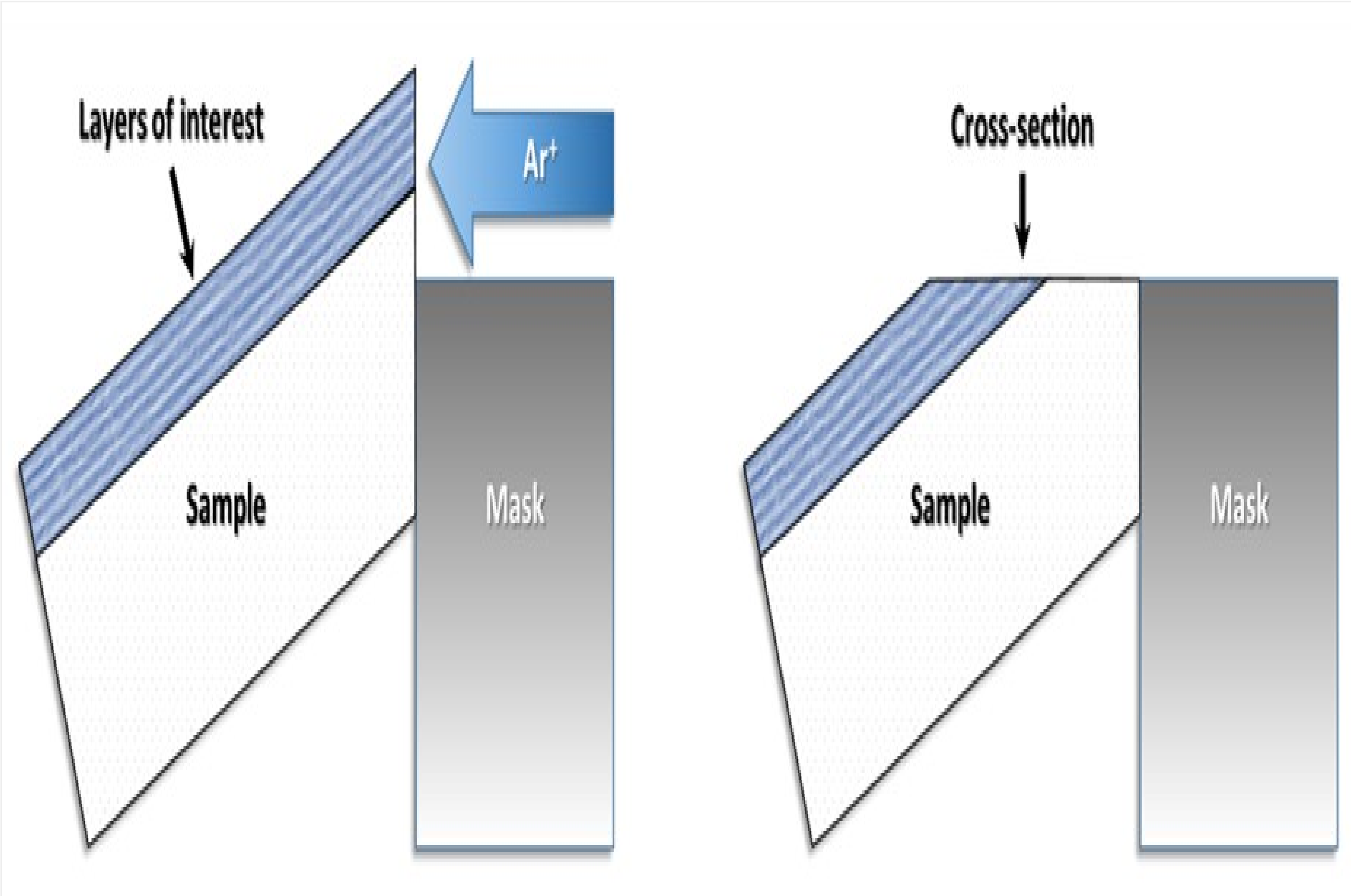

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Figure 2: Beam-exit cross-sectional polishing setup. The Ar-ion beam impinges on the side of the sample at a small angle (usually 5 – 12°), producing a cut with low damage and sub-nm roughness through the area of interest.

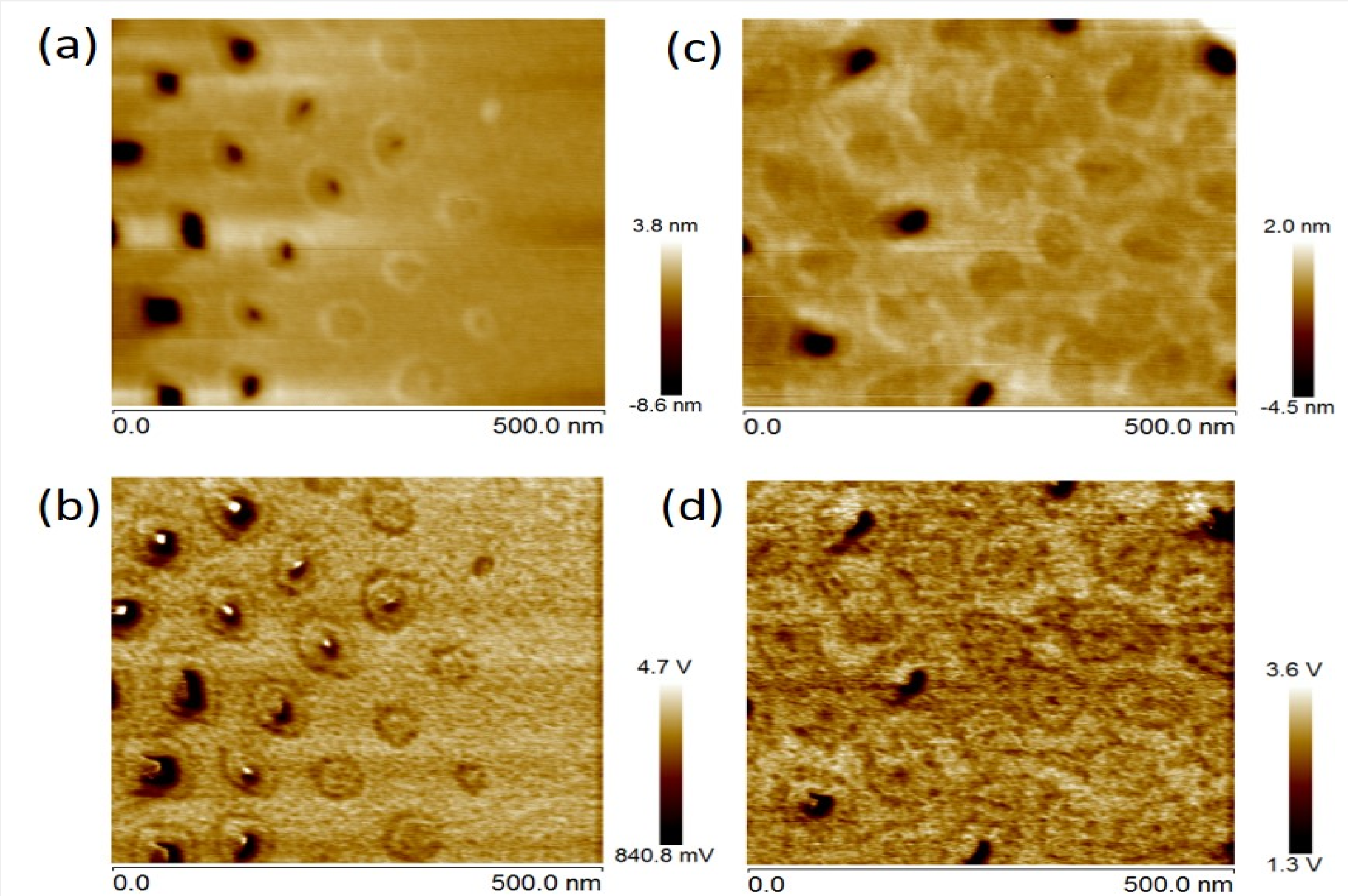

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Figure 3: Height (a, c) and UFM (b, d) images of Al2O3 coated PS. Images (a) and (b) show the bottom of the ALD coated pores. Images (c) and (d) show the pores approximately two thirds of the way up the cross – section, at which point a majority of pores appear blocked. Darker areas in UFM images correspond to areas of lower mechanical stiffness, and may indicate sub-surface structure.