

## **XTEM characterization of modulated ion implantation through self-organized anodic aluminium oxide (AAO) membranes**

Wei Guan<sup>1</sup>, Jay Ghatak<sup>1</sup>, Nianhua Peng<sup>2</sup>, Yong Peng<sup>1</sup>, Chris Jeynes<sup>2</sup>, Beverley Inkson<sup>1</sup> and Günter Möbus<sup>1</sup>

<sup>1</sup>NanoLAB Centre, Dept. Materials Science & Eng., University of Sheffield, S1 3JD, UK

<sup>2</sup> University of Surrey Ion Beam Centre, Guildford, GU2 7XH, UK

**This paper was published as:** Guan W, Ghatak J, Peng Y, Möbus G, Peng N, Jeynes C, *Materials Research Society Symposium Proceedings* **1411**:49-54 2011;  
<http://dx.doi.org/10.1557/opl.2012.757>

### **ABSTRACT**

Penetration of a nanochannel mask by 190keV Co<sup>+</sup> ions is tested for the purpose of achieving laterally modulated ion implantation into a SiO<sub>2</sub> thin film on a Si substrate. A 2D-nanoporous membrane of anodic aluminum oxide (AAO) is chosen as the mask. Criteria and challenges for designing the mask are presented. Implantation experiments through a mask with pore diameter of 125 nm and inter-pore distance of 240 nm are carried out. Cross-sectional TEM (XTEM) is shown as an ideal tool to assess depth distribution and lateral distribution of implanted ions at the same time, complemented by Rutherford backscattering spectroscopy. Using energy dispersive x-ray spectroscopy linescans, a Co distribution with lateral modulation is found at 120 nm below the oxide surface. First experiments in converting the atomic distribution of Co to discrete nanoparticles by in-situ TEM annealing are presented.

### **INTRODUCTION**

Patterned media on the nanoscale are a promising class of nanostructured materials with perspective applications in magnetic data storage, sensors, nanooptics and plasmonics, as well as in semiconductor electronics. Of the many patterning processes, such as growth or deposition from gas phase on the one hand, or sputtering and materials removal on the other hand, few have the ability to combine flexible choice of chemical elements, large substrate area, tunable patterning depth inside the substrate, and compatibility with established industrial processes such as doping of semiconductors. Ion implantation fulfills all these criteria, but normally lacks the ability to achieve lateral patterning modulation to the required nanoscale resolution. While focused ion beam systems (FIB) provide resolution, they do not allow element choice and do not reach energies high enough for actual implantation. The combination of accelerator based ion implantation with periodic nanochannel masks to achieve patterned implantation has therefore recently attracted great attention by a small number of research groups [ , ]. In this work we introduce a particular mask-on-substrate growth and irradiation setup and demonstrate the importance of cross-sectional analytical TEM to confirm the achieved chemical microstructure by means of Z-contrast imaging and energy dispersive X-ray line-scan spectroscopy.

## EXPERIMENT

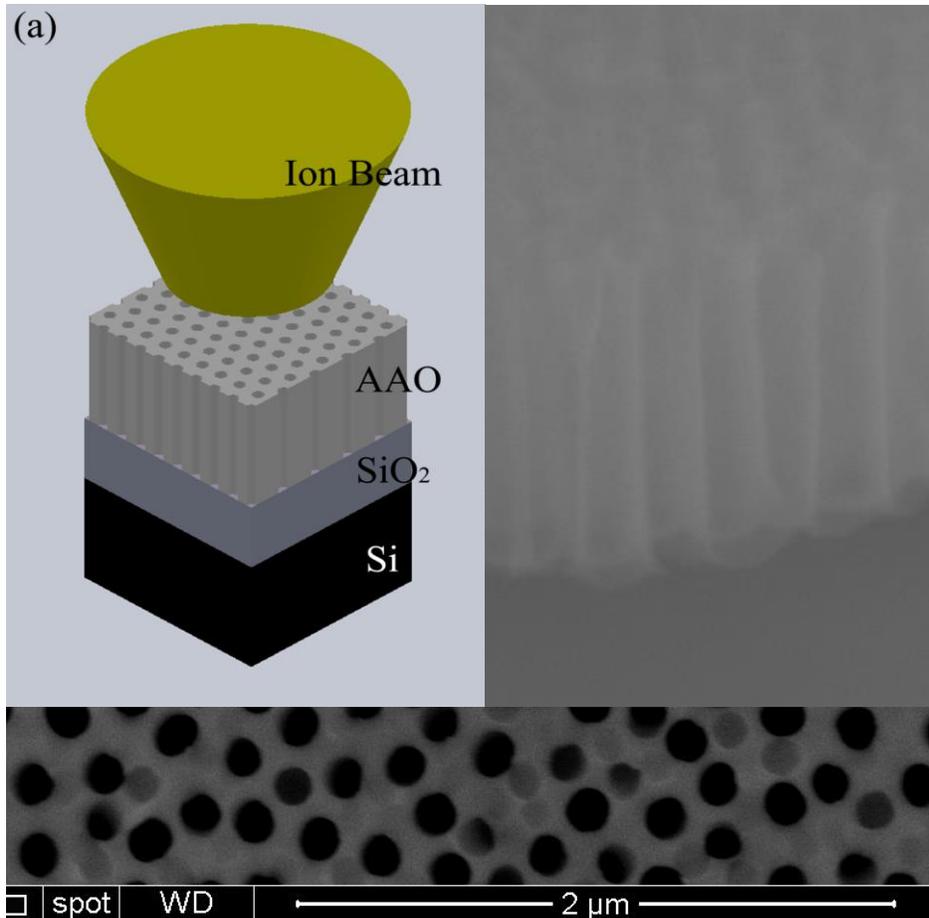
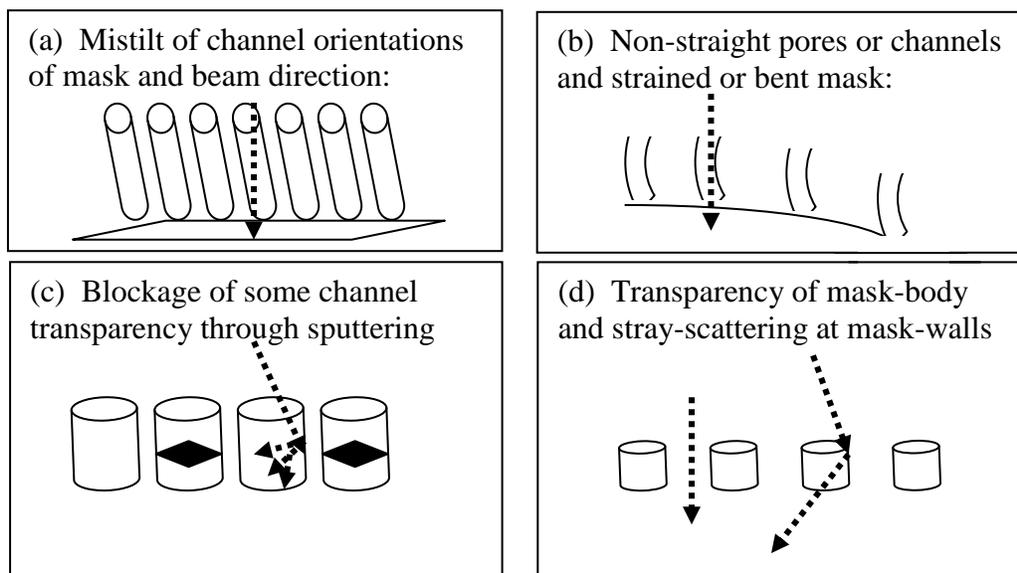


Figure 1. (a) A schematic drawing of the whole structure used for patterned ion implantation. It consists of 550nm AAO and 300nm SiO<sub>2</sub> on Si substrate. (b) FEG-SEM secondary electron image of the AAO membrane in diagonal view: above: top surface of pores, middle: side view of pores, bottom: substrate surface. (c) plan view SEM image of the top AAO surface.

The principle setup of the experiment is characterized by the neat-less connectivity of porous membrane and substrate surface (Fig 1). To achieve this, a thin film of 550 nm of aluminum was thermally evaporated on an oxidized n-type Si wafer, and anodized while connected to the substrate. Alternatively, a porous AAO-mask could be grown in the standard way from a free-standing aluminium thin film, and transferred to the substrate and attached via glue/wax or (if thin and light enough) relying on van-der-Waals bonding. The latter method has the advantage of greater flexibility, exploring several mask morphologies on one substrate. However, the main disadvantage is that masks are subject to fracture, can bend or delaminate during ion irradiation and below 1 micron thickness can hardly be mechanically handled, and require float processes. The anodisation of Al directly grown on the substrate, as applied here, has the advantage that

mask and substrate do not move and separate during any specimen preparation and irradiation steps.

While details of the growth process will be given in [ ], we summarise the main steps involved as follows: The Si wafer was converted at its surface to silica by a wet thermal oxidation process at 1000 °C for 58 min. to grow about 300 nm of SiO<sub>2</sub> layer. **500 nm Al was deposited on this SiO<sub>2</sub>/Si by thermal evaporation in vacuum.** A piece of Al/SiO<sub>2</sub>/Si was anodized in 0.05 M phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) at 100 V. Removal of a continuous barrier layer at the bottom and assurance of the pores being open required further anodisation in negative potential and finally in 0.5 M H<sub>3</sub>PO<sub>4</sub> to minimise the barrier layer and open the pores further. A very thin carbon-coating preceding the ion implantation to prevent charging with possible risk of mask-ablation completes the preparation.



**Figure 2:** Challenges for the concept of ion implantation through a patterning mask

The difficulties in achieving ion implantation through a nanoscale porous mask can be grouped into (i) misalignment problems and (ii) stability/damage problems, and a fine sub-classification into challenges is drawn up in Fig 2. At first, misalignment can either be due to a mis-orientation during specimen mounting in the accelerator between the ion beam direction and the pore direction (Fig 2a). The tolerance is given by the pore aspect ratio, as previously described by Rehn et al. [Rehn]. Secondly, misalignment can be intrinsic to the membrane, which could be curved, allowing penetration only in some lateral zones, or more commonly, the pores are not straight (Fig 2b). It is an intrinsic feature of the AAO anodisation process that order and straightness develops deeper into the specimen, while nearer to the top surface pores can be inclined or even merging/di-merging from each other. Within the group of stability problems, we have to distinguish ablation and redeposition by ions hitting the walls of the pores, which can eventually lead to particle nucleation and closure of the pores (Fig 2c). Thermal disintegration and sputtering from the top surface can totally ruin the mask after extensive high-dose implantations. If membranes are too thin, such as to minimize misorientation problems, ions

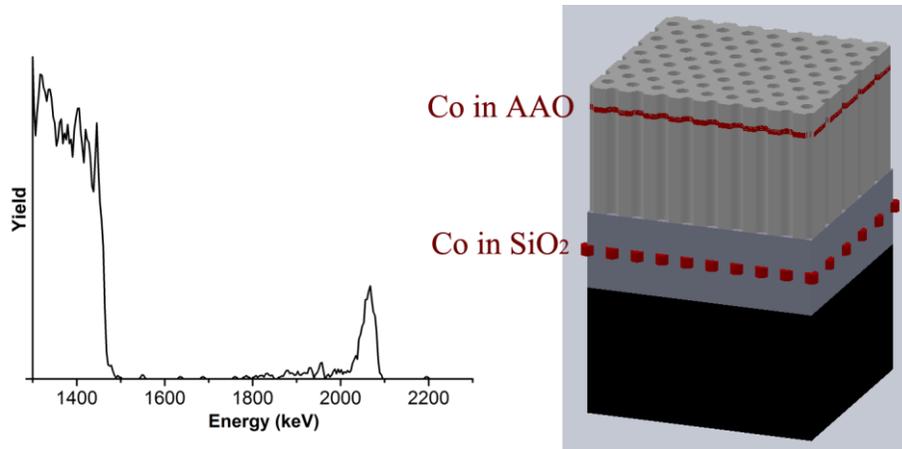
might penetrate through the solid mask, or ions scattered by the wall might laterally spread into the substrate and blur the attempted patterning effect by filling areas between pores (Fig 2d).

Field-emission scanning electron microscopy (FE-SEM, InspectF, FEI) was used to analyze the quality of the AAO membrane and address the challenges. Figure 1 (b) shows clearly the fully opened bottom side of the AAO membrane allowing transparency to ions, and confirms enough pore straightness for the chosen aspect ratio. With the thickness of AAO and SiO<sub>2</sub> layer being about 550 and 300 nm respectively and an average pore distance of ~260 nm and pore diameter of ~125 nm (Fig 1c), we arrive at a pore aspect ratio of 125/550 ~ 1 : 5.

The implantation process was carried out with 190 keV <sup>59</sup>Co<sup>+</sup> with a fluence of 3 × 10<sup>16</sup> ions/cm<sup>2</sup> and an average scanning ion beam flux of about 3 × 10<sup>12</sup> ions/cm<sup>2</sup>s. The sample was kept at room temperature and was mounted normally with respect to the beam with any residual misalignment error estimated to less than 1°.

## RESULTS AND DISCUSSION

The depth profiling was carried out by Rutherford backscattering spectrometry (RBS) at normal incidence with a 3.046 MeV <sup>4</sup>He<sup>+</sup> beam. Unmasked implantation would result in a normal **Gaussian** depth profile with centre at about 120nm below the substrate surface, and a **symmetric Gaussian** peak in the RBS spectrum **around 2050 keV**. During the implantation **with AAO mask**, only a fraction of ions through the mask can reach the SiO<sub>2</sub> layer and others would be stopped inside the AAO pore walls at a variety of depths below the AAO surface. Considering the fact that the backscattering ion detector is at an angle with the normal incident ion beam, those backscattered ions from the collision with Co in SiO<sub>2</sub> would lose more energy through both SiO<sub>2</sub> and AAO mask, while those backscattered ions from Co in AAO mask would only lose energy through AAO mask. The **asymmetric** tail to the left of the **Co** peak in the RBS spectrum is evidence of existence of **Co in both AAO mask and SiO<sub>2</sub> matrix**.

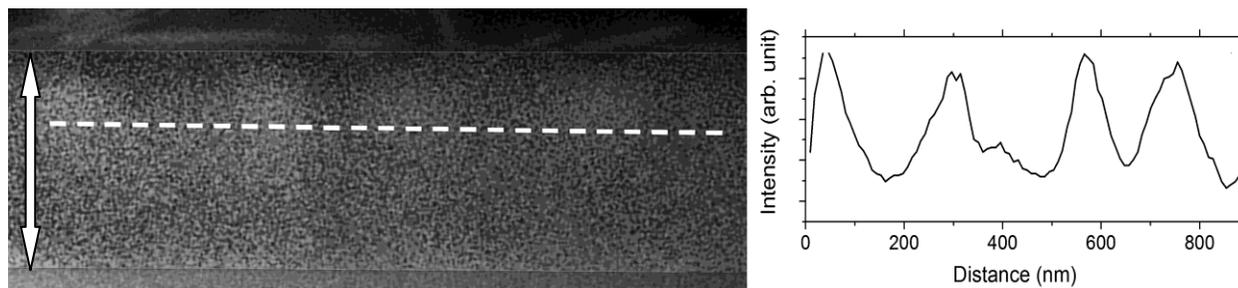


**Figure 3:** The RBS spectrum of the Co implantation zones and the schematic idealised distribution of implanted Co inside AAO and SiO<sub>2</sub>.

In order to prepare the implanted samples for TEM investigation, the AAO mask was etched off by 1 M NaOH followed by cross-sectional TEM (XTEM) sample preparation. The

XTEM preparation involved standard mechanical thinning and dimple grinding followed by argon ion milling with 3.5 keV energy. While full details of the TEM characterization will be presented elsewhere [ ], we concentrate on annular dark field (ADF) STEM imaging and energy-dispersive X-ray spectroscopy (EDX) techniques with a JEOL 2010F TEM operating at 200 keV.

While the implantation zone shows poor contrast in TEM, indicating lack of any crystalline precipitates, the Z-contrast mechanism of ADF-STEM leads to bright contrast in the Co enriched zones against the low-Z background of Si and O. In the field of view selected for Fig 4, four high contrast regions are laterally and periodically distributed inside the top half of the SiO<sub>2</sub> layer at about 120 nm below the surface. As our TRIM simulations predict a mean implantation depth of 148 nm, we suggest that thermal out-diffusion of Co atoms towards the surface happens during the implantation. An EDX line scan conducted across the Co rich region of Fig 4 (dashed line) is used to confirm the elemental identity as Co. The width and center-to-center distance of the Co regions are about 125 nm and 260 nm respectively, which is compatible with pore diameter and inter pore distances of the AAO mask displayed in Fig 1 (c).



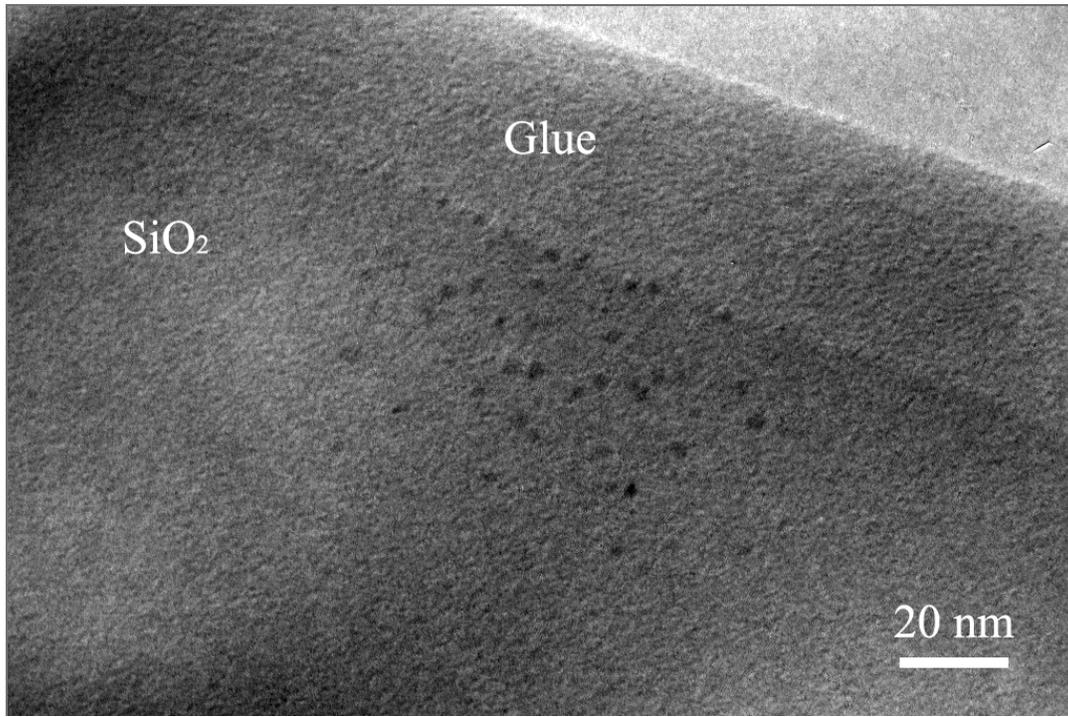
**Figure 4:** Left: ADF-STEM image of the implantation zone in the SiO<sub>2</sub> layer (arrowed, 300nm). The periodic high contrast regions, indicating high atomic number (Z-contrast), are confirmed as modulated Co concentration in silica by an EDX line scan (right, Co-K-peak spectrum) along the dashed line of the STEM image (JEM 2010F and Oxford Instruments ISIS).

Preliminary annealing tests were also carried out to study the formation of Co particles. The XTEM specimen was annealed at 500 °C for 60 minutes. Instead of all Co atoms merging into a single Co particle, many tiny Co particles with diameter about 2 nm were formed inside one implanted zone. During the annealing, the Co atoms diffused towards the SiO<sub>2</sub>/glue interface of the XTEM sample, but were still restrained inside their own implanted zone without lateral straggling into adjacent zones. One of the implanted zones after annealing and Co particle formation is shown in figure 5.

## CONCLUSIONS

Successful patterned implantation of Co into a SiO<sub>2</sub> thin film on a Si substrate was achieved via an ultrathin 2D-nanoporous membrane of AAO directly grown on the substrate. The modulation of the Co implantation was revealed by cross-sectional TEM/STEM which can map simultaneously the depth distribution and lateral distribution of sub-surface chemistry by a combination of Z-contrast and X-ray mapping. The proven transfer of the modulation of the AAO membrane into the substrate allows the consideration of this technique as a promising

wide-area nanopatterning tool to generate embedded nanoparticle arrays for any kind of chemical element. The application of a self-organised periodic mask and a particle beam for pattern transfer is an interesting combination of top-down and bottom-up structuring.



**Figure 5:** In-situ XTEM of Co implantation zone in silica layer: Upon annealing at 500 °C for 60 minutes in a TEM heating holder a cluster of small Co particles is formed within one implantation mesh zone (JEOL JEM 3010 at 300kV).

#### **ACKNOWLEDGMENTS**

This work was funded by EPSRC, UK, under grant number EP/F062710/1.

#### **REFERENCES**

We only need a few references, not all about nanoparticle generation.  
We can include the MRS papers from 2007.