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Polymer architectures in top-down (lithographically) defined channels for the bottom-up assembly of nanostructures

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Here we demonstrate the use of block copolymer self-assembly combined with photolithographically defined topographic substrate surfaces to form highly regular templates for the development of nanowire arrays. In particular, we demonstrate that the use of well-defined channelled surfaces (channels of depth around 60 nm and widths as low as 163 nm) can be used to direct nanoscale phase separation in a number of block copolymer systems. This phase separation results in periodic structures of parallel and narrow (i.e. beyond the limits of photolithography) cylinders of one polymer in a matrix of the other. Processing of films is critical as film thickness requires careful control. Initial results are presented which show how these structures might be used for deposition of nanowire arrays.

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1. Introduction

On-going miniaturization of microelectronic circuitry by continued improvements in photolithography ('top-down') will be limited by factors including resolution, availability of light sources, materials issues (masks, resists etc) and expense [1]. Alternative top down' circuit patterning techniques (e.g. e-beam lithography) are probably limited by writing speeds [2]. Many workers are pursuing chemical ('bottom-up') methods to generate surface patterns of nanostructures as an alternative to top-down patterning methods [3]. The direct self-assembly of nanoparticles or nanowires is being heavily researched [4] as well as indirect methods where a self-assembled periodic structure (template) is used to develop regular arrays of nanoentities by filling of the template [3]. We have developed supercritical fluid techniques to generate arrays of parallel nanowires in mesoporous silica and anodic alumina [5, 6].

Block copolymer systems are potentially important templates because of their tendency to phase separate into chemically distinct blocks of sizes 10 - 100 nm [7]. However, these systems show no regular arrangement but rather 'fingerprint-like' patterns in the absence of external directing forces and various alignment techniques have been tried to increase the regularity of the patterns [8]. The most successful approach to date is a hierarchical combination of 'top-down' and 'bottom-up' methods and it has been shown that block copolymer thin films can self-assemble within topographically defined substrate structures to produce parallel block copolymer microdomains [9]. To date the most elegant work in the use of block copolymers for nano-fabrication was reported by Black who used the polystyrene-polymethyl-methacrylate (PS-PMMA) system as photolithographic masks for the generation of silicon nanowires [10]. The majority of work to date in this area has been using the PS-PMMA system but the minimum feature size that can be reached is around 30 nm [11] and this offers little advantage over what might be generated using advanced photolithography. Alternative systems require exploration and careful consideration of the limitations of these methods must be probed. Below we describe how regular block copolymer structures (concentrating on the polystyrene-*block*-polyisoprene-*block*-polystyrene (PS-PI-PS) triblock copolymer system) can be generated in very small channel sizes and a strategy for how nanowire structures might be created.

2. Experimental

Film preparation: Thin films of PS-PI-PS (Sigma-Aldrich, 17 wt% PS and molecular weight = 52000 $gmol^{-1}$) and PS (46100)-PMMA(21000) (Polymer Source Inc., 30 wt% PS and molecular weight = 67100 g mol^{-1}) block copolymer were prepared by spin-coating (speed = 3200 rpm) using a Speciality Coating Systems G3P-8 spincoater, from toluene solutions (at about 0.5 to 2 wt%). Phase separation was sometimes observed at room temperature but optimum ordering was induced by annealing around the glass transition temperature. Annealing temperatures were 393 K for the PS-PI-PS system and 453 K for the PS-PMMA system. Samples were heated for periods of several hours (1 to 24 hours). **Substrates:** Samples were either flat or channel cut silicon (100) wafer substrates. The topographic substrates were processed using photolithography, mask and etch techniques. The channels were prepared at 163 nm, 282

and 433 nm width and the depth of each channel was around 60 nm. No attempt was taken to remove the native oxide of a few nm depth. In all cases the processing results in a thin crest of photoresist along the top and centre of the patterns. **Analysis:** Samples were analysed by AFM (DME DS-50 dual scope 50 µm scan area). High resolution field emission SEM (HR-SEM) images were collected with JSM-6700 FE-SEM (both JEOL, UK) operating at a voltage of 10 keV and a working distance of 55 mm. Samples were gold coated for 30 seconds at a voltage of 2.5 kV and a current of 20 mA (Bio-Rad). X-ray diffraction (XRD) data were collected on a Panalytical X'pert Pro system equipped with an X'celerator and a conventional Cu Kα anode. X–ray photoelectron spectroscopy data were collected on a Vacuum Generators ESCALAB using Al Kα radiation (25 eV pass energy and MCD detector). Samples were referenced to a silicon wafer with an evaporated gold thin film.

3. Results

Typical thin films (from 1wt% in toluene solutions) of PS-PI-PS and PS-PMMA are shown in Fig. 1. The PS-PI-PS film is of regular thickness and shows microphase separation (PS cylinders in a PI matrix) into a typical fingerprint pattern. The diameter of the cylinders is 15.8 nm and the distance apart 29.6 nm. Also shown is a Fourier transform (FT) of the image showing that the orientation of the cylinders is random. The PS-PMMA system was typified by phase separation that led to films with 'bubble-like' distributions of islands of polymer with areas between the islands almost devoid of polymer. Within the polymer islands the PS cylinders are ~25 nm in diameter and ~42 nm apart. We believe that for these systems annealing allows the polymers systems to redistribute themselves to bring areas into commensurability i.e. a thickness sufficient to support cylinders parallel to the substrate and so lower the energy. This redistribution coupled to wetting phenomena give can result in island formation observed. It should be noted that the cylinder structure arrangement (distance apart and size) of the film was found to be independent of substrate in our experiments (glass, sapphire and various thickness thermally grown oxide films on silicon) indicating that the structure is principally determined by the polymer properties and not the film-substrate interaction.

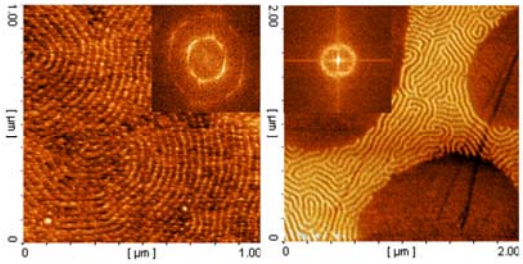

Fig. 1. AFM images of PS-PI-PS (left) and PS-PMMA (right) thin films on flat silicon substrates. The inserts in each figure are FT data from the films. In the PS-PMMA system the dark circular regions indicate areas where polymer did not coat the substrate.

Fig. 2 illustrates the completed wafers as fabricated by Intel Leixlip. It also illustrates typical data from films spun onto these topographically patterned substrates (typical cross-section shown). Care must be taken to correctly determine thickness. In these cases there are two layers of cylinders but intermediate thicknesses can lead to vertical alignment of the PS cylinders rather than parallel to the surface arrangements. This is shown in the inset to the figure where the hexagonally packed cylinders are clearly seen in the AFM image. As can be seen the channel structure confers a highly periodic arrangement of cylinders. The periodic PS-PMMA arrangements are more difficult to obtain than the corresponding PS-PI-PS system but we believe this is related to wetting of the substrates and flow into the channels [12] that leads to irregular thickness of the films within the channels. This is illustrated in the SEM data taken in Fig. 3 where the film can clearly be seen as being depressed in the centre of the channels.

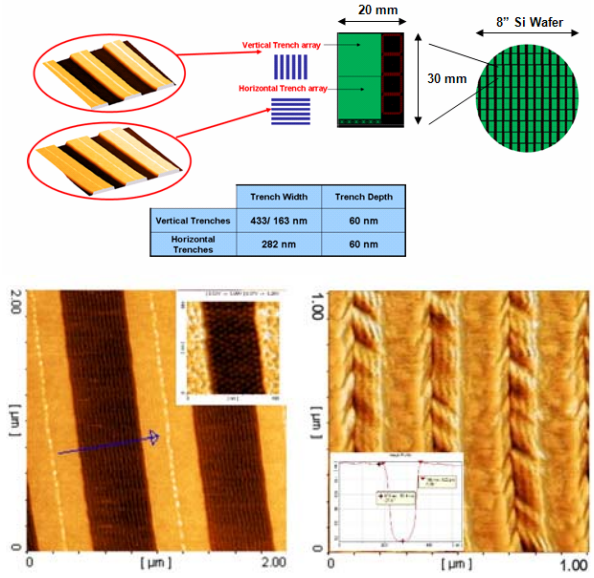

Fig. 2. Upper is a schematic showing the 8" wafer substrate processing to yield the channels in the surface. Lower are AFM images of PS-PI-PS (left) and PS-PMMA (right) thin films (spun from 0.7 and 1.0 wt% in toluene respectively) on channelled silicon substrates. The blue arrow shows the photoresist crests. The insert (left) shows an image from a film of different thickness showing a vertical alignment of the cylinders. The right insert is an AFM cross-section of the channel.

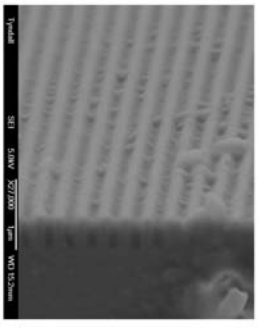

Fig. 3. SEM cross-section image of a PS-PMMA film in a series of channels.

This work reports the first investigation of channels of below 200 nm in width. Filling as function of channel size is shown explicitly in Fig. 4. In all cases there is strong parallel arrangement of the polymer (PS) cylinders. The narrow channel widths tend to show less perfect order than the wider channels. We believe this because of debris in the channels (from the processing and is difficult to remove in cleaning) that disturbs the arrangement and also partly due to problems with imaging the cylinders in the small cracks. For the larger channels the packing arrangements are close to perfect over long lengths (>10 um). There are some changes in the packing of the cylinders and the distance apart of cylinders increases as the channel size decreases. The values measured were 27.1 nm (433), 28.2 nm (282) and 33.2 nm (163 nm). The values are close to those measured on flat substrates and suggest the packing is largely determined by the polymer interactions rather the confinement within the channel. There probably is some internal strain in the channels causing some compression of the cylinder packing to below the 29.6 nm distance recorded on the flat substrate. The exception of the very narrow channels probably arises because insertion of an additional cylinder would result in too greater strain in the system.

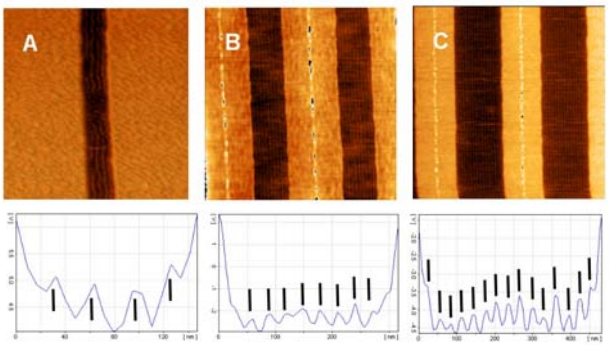

Fig. 4. Upper part of figure shows AFM images of PS-PI-PS polymer films in ~50 nm deep channels of widths 163 (A), 282 (B) and 433 nm (C). In each case the horizontal and vertical axis represent 1 µm. The lower figures show corresponding phase cprofiles across the channels and reveal the presence of cylinders.

In order to form templates, one of the blocks must be selectively removed to leave a patterned substrate. Wet and dry chemical etches can be used for this process. PS-PI-PS can be etched by ozone (room temperature, 1.4% in air for 7 minutes) and almost complete removal of PI can be achieved. PS-PMMA can be etched by a dry O_2 plasma etch resulting in complete removal of PMMA can be achieved [13]. The sample shown is an etched random arrangement of the PS-PMMA lamellar phase and details on these samples have been previously detailed [13]. Once the template is correctly formed various methods could be adopted to fill the voided polymer films to leave patterned nanoparticle or nanowire arrays.

In this work we report a simple functionalisation method to selectively deliver gold nanoparticles to the exposed silicon substrate. The etched samples were cleaned and then boiled in water to from –OH groups at the oxide passivated silicon surface. The substrates were then treated with a simple organic thiol ($HS\text{-}(CH_2)_2\text{-}Si\text{-}(O\text{-}CH_2\text{-}CH_3)_3$) to provide a thiol functionalised surface [14]. These surfaces were treated with 0.02 M $HAuCl_4$ for 6 h to develop gold nanoparticles at the exposed substrate. The presence of gold is confirmed by AFM, XRD and XPS. Data are summarised in Fig. 6. AFM reveals some bright spots at the polymer surface typical of gold nanoparticles of around 10 to 30 nm in size but these are few in number as might be expected because the polymer is inactive to the functionalisation procedure. XRD shows very sharp lines easily indexed to Au (111) and (200) reflections typical of the expected FCC structure (JCPDS 01-1172). The width of the reflections is not consistent with the particles observed by AFM which would give broad poorly resolved features and suggest that the gold present is not easily seen by AFM. Instead the XRD data suggest larger gold particles are formed at the substrate surface in the etched areas of the polymer matrix.

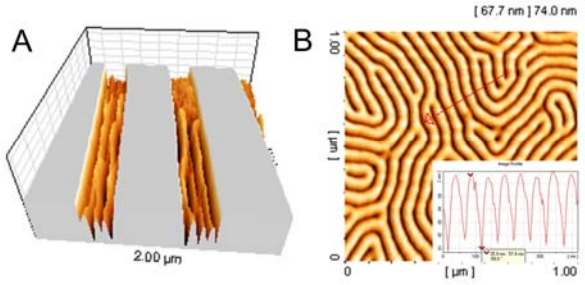

Fig. 5. AFM images showing 'etched' PS-PI-PS sample (A) and PS-PMMA sample (B).

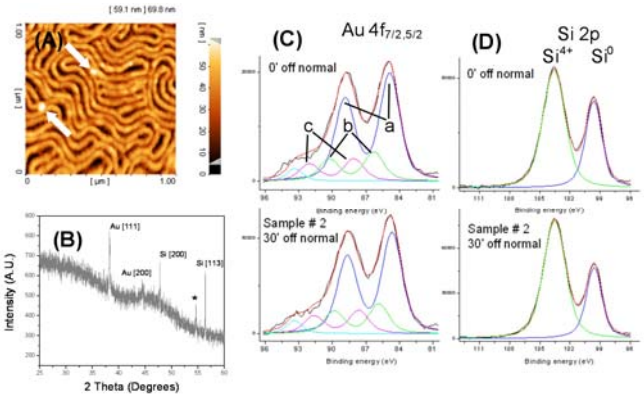

*Fig. 6. Filling of polymer templates. (A) is an AFM iamge showing the present of discrete gold nanoparticles at the polymer surface. (B) is XRD data from the surface. * is a contamination peak. (C) and (D) are Au 4f and Si 2p XPS spectra respectively. Data is shown at normal emission (top) and 70° take-off angle (to the surface plane). Features described in the text.*

XPS readily shows the presence of Au and Au 4f signals are shown in the figure. Peak-fitting reveals the presence of a triplet structure (a, b and c as shown). The

binding energies of the $4f_{7/2}$ peaks are measured at 84.7, 85.9 and 87.6 eV (a, b and c respectively). The peak at 84.7 eV can be assigned to gold in the metallic state but the binding energy is typical of alloyed gold [15] and may indicate some interaction with the substrate. A feature at 85.9 eV can be assigned to gold being present as Au_2O_3 [16]. The feature at 87.6 eV is less easily assigned but we suggest it is due to material on the top of the polymer deposit which is differentially charge shifted to higher binding energies. Si 2p spectra exhibit to peaks at 99.3 and 103.3 eV readily assigned to Si present as Si^0 and Si^{4+}. Typical XPS data are shown in Fig. 6 for 90 ° (less surface sensitive) and 60 ° (more surface sensitive) emission angles. The 2p 3/2 signal clearly shows that the Si^{4+} signal is enhanced at the lower emission angles showing this is due to oxide material at the silicon substrate. For the Au $4f_{7/2}$ data the peak area ratio of the b and c features to the a features are enhanced at lower emission angles suggesting these are closer to the surface and this is consistent with the assignment made above. On the basis of these arguments we suggest that the template has been used to allow selective delivery of gold to the substrate surface in the etched polymer film.

4. Discussion and conclusions

For bottom-up methods to rival traditional top-down volume production of processor circuitry the greatest challenge is the formation of periodic structures across large substrates with absolute accuracy in position. This is an absolute pre-requisite since subsequent processing must allow devices to be accessed through electrical contact development. It is arguable if simple self-assembly could achieve this degree of position control. These polymer systems are ideal in that the phase separation conforms to the confinement imposed by the channel by allowing small variations in the periodicity of the cylindrical domains. The arrangement can also avoids creation of high-energy dislocation defects by expanding or contracting within the accessible range as necessary. The PS-PI-PS system is probably easier to align because of the glassier nature of the PS-PMMA copolymer. We have demonstrated here that combining bottom-up and top-down methods that precisely positioned chemical patterning are achievable. Phase separation in block co-polymer systems provides simple means to deliver these nano-dimensioned patterns. The second challenge is to ensure that the size is consistent with delivering advances in photolithography and the ITRS roadmap suggests that nanoscale architectures must achieve nanowires and nanoparticles of sub-20 μm and this has also been demonstrated here.

Of course simple pattern formation is not a goal in itself. These patterns must be robust enough to function as (lithographic) masks or templates. This work demonstrates that templates can be formed by simple etch procedures to expose the substrate for development of nanowires. We have demonstrated the use of these phase-separated polymer systems to develop methods for selected deposition of gold.

It should also be recognised that these polymers are fully compatible with current semiconductor processing methods. These polymers are already used as photoresists and spincoating is a common method. Indeed, we have demonstrated that highly regular patterns can be formed over 8" wafers. However, we must stress that surface energies have to be compatible with forming films of consistent depth (surface wetting etc.) if the optimum phase separation is to be controlled and reproducible. Once formed, the templates can provide simple means to delivery of many materials including oxides, semiconductors and metals.

We believe that these methods may be used as one means to generate high density nanodevices at regular positions on a wafer and afford the opportunity to process and interrogate many devices rather than single devices as is the norm at the moment. There remain many questions to be answered including what is the minimum feature size that can be attained and at what point will strain energies within a channel prevent polymer phase separation.

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