We report a fast, versatile and reproducible method to make arbitrary nanoscale patterns of functional metal oxides by edge transfer printing of aqueous metal-loaded water-soluble poly(acrylic acid) (PAA) solutions on silicon. Patterns of ZnO, CuO, NiO and Fe$_2$O$_3$ with lateral dimensions below 50 nm were realized. The process uses elastomeric PDMS stamps with microscale feature sizes to fabricate nanoscale patterns, so that stamp deformation problems are minimized despite the high resolution.

The development of flexible and cost-effective nanopatterning strategies is crucial for the realization and large-scale application of many novel nanoscale device technologies in nanoelectronics, data storage and sensing, to mention just a few. Various high-end patterning methods have been demonstrated with which high quality oxide nanopatterns can be fabricated, e.g., e-beam lithography, nanoinprint lithography and photolithography. Soft lithography techniques like microcontact printing, micromolding and nanotransfer printing present low cost alternatives to such methods and are currently also receiving considerable interest, because of their technical simplicity, mild process conditions and the high flexibility regarding the choice of materials and substrates. All soft lithography techniques employ an elastomeric stamp or mould with a relief pattern that is brought into conformal contact with a substrate for replication. Polydimethylsiloxane (PDMS) is the most often used elastomer. The deformability of the elastomer makes large area patterning with resolutions below 100–200 nm complicated. Since the process requires application of pressure on the PDMS mould/stamp to make good conformal contact and avoid formation of residues between patterned features, deformation and/or buckling of patterned PDMS features can easily occur, especially when they are very small. This results in the loss of pattern fidelity. Stiffer mould materials may be employed, but in that case the conformal contact will be less so that residual layers are easily formed. Innovative techniques utilizing the edge of patterned PDMS stamps or the edge of patterned photoresist structures, such as edge transfer lithography, electrochemical edge decoration and gas phase pattern deposition, have been developed to overcome this problem. These all employ moulds and stamps with micrometre-scale patterned features to achieve patterns with much higher resolution, thereby minimizing mechanical deformation. However, the methods are limited to deposition of a few materials only.

Here we report a novel, very simple, fast and reproducible method to realize sub-50 nm scale patterns of various inorganic functional metal oxides, e.g., ZnO, CuO, NiO, Fe$_2$O$_3$, etc., by edge transfer printing of metal-loaded water-soluble poly(acrylic acid) (PAA; $M_w \approx 1800$ g mol$^{-1}$). The process uses PDMS stamps with relatively large feature sizes to fabricate patterns with much smaller lateral pattern dimensions. The process is additive, i.e., it does not require a complex fabrication scheme including resist patterning and subsequent etching steps which are common in e-beam processing, photolithography and nanoimprint lithography. The process is residual layer-free and does not need application of high pressure on the PDMS stamp.

![Fig. 1](image_url) (a) Schematic diagram of the patterning process; (b) HR-SEM image of the edge transfer-printed PAA pattern. Line width 100 nm, spacing 1 μm.

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† Electronic supplementary information (ESI) available: Experimental details, data of lap shear test and more examples of patterns fabricated. See DOI: 10.1039/c2jm31121f
A schematic diagram of the edge patterning process is shown in Fig. 1a. First, an aqueous solution of a PAA loaded with metal salt was spincoated onto an oxygen plasma-treated PDMS stamp\(^2\) to obtain a thin film on the stamp. The stamp was placed on a Si substrate to make conformal contact, and kept on a hot plate at 80 °C for 10 min. The temperature determines the drying rate of the aqueous solution. Then the substrate–stamp assembly was cooled down to room temperature and the PDMS stamp was peeled off from the substrate. Film transfer to the substrate occurred only at the edges of the protruding features of the PDMS stamp, as illustrated schematically in Fig. 1a. Experimental details can be found in the ESI†. We exploited this edge transfer mechanism of PAA thin films from the PDMS stamp to create patterns of functional materials on the scale of less than 50 to a few hundred nanometres. The size of the patterned areas was 1 × 1 cm\(^2\). Buckling or other forms of deformation are prevented since the process does not include application of pressure on the stamps (other than weight) to realize film transfer, and PDMS features are relatively large.

Fig. 1b shows an HR-SEM image of edge-transfer printed PAA line features with a line width of 100 nm and spacing of 1 μm. The PDMS stamp itself has protruding line features with a width of 1.3 μm and spacing of 1 μm between the lines. The width of the obtained features corresponds to the thickness of the dried PAA thin film that was coated on the PDMS stamp.

In Fig. 2a we show a ZnO nanoring array fabricated by edge transfer printing using a nanometre-scale PDMS stamp with arrays of circular protruding pillars of 180 nm diameter, 400 nm spacing and 350 nm height. A solution of PAA–zinc nitrate solution with a concentration of 0.5 wt% of both PAA and zinc nitrate was used to generate the ring patterns with a width of 40 nm and a height of 15 nm. In Fig. 2b we show ZnO line patterns fabricated by edge transfer printing of a PAA–zinc nitrate complex (1.5 wt% PAA + 0.75 wt% Zn(NO\(_3\))\(_2\) in water) using a PDMS stamp with a feature width of 600 nm and a spacing of 800 nm. The patterned areas of both stamps were 8 × 8 mm\(^2\). The substrates were annealed at 620 °C to convert the as-deposited patterns into ZnO. XRD analysis confirmed the polycrystalline ZnO wurtzite phase (Fig. 2c). The final ZnO line patterns in Fig. 2b had a line width of 120 nm and a height of 38 nm with a spacing of 600 nm between the lines. Fig. 2d shows the corresponding tapping mode AFM height profile. The double-peak topography of the cross-section is typically found in oxide patterns from wet-chemical solutions by soft lithography.\(^2\) Fig. 2e shows the TUNA conductivity map of the ZnO lines measured at an applied sample bias voltage of 2 V versus the conducting AFM tip.\(^2\) The results indicate uniform conductivity along the lines.

The height of the ZnO patterns can be controlled by varying the concentration of metal salt in the solution. Fig. 2f shows pattern width as a function of spin coating speed and PAA concentration. Best results were obtained when spincoating a solution of 1.5 wt% PAA with metal salts at an angular speed of 4000–5000 rpm. Fig. 2g shows the variation in pattern height versus zinc nitrate concentration in 1.5 wt% PAA solution. The pattern width can be controlled by the thickness of the PAA–metal salt layer on the PDMS stamp. Formation of higher and wider patterns required application of multiple layers of precursor solution on the PDMS stamp prior to transfer. In such cases the film was allowed to dry for 10 min at room temperature after deposition of each layer.

To elucidate the edge transfer mechanism of PAA from the PDMS stamp to the substrate, we first performed lap shear tests to obtain average values of the adhesion force between the dried PAA film and the participating surfaces, i.e. SiO\(_2\) and oxygen plasma treated PDMS. A detailed description of the lap shear test is given in the ESI†. Glass/PAA/glass and PDMS/PAA/PDMS test specimens with similar dimensions and PAA film thicknesses were investigated.

Fig. 2  ZnO line patterns created using edge transfer printing of a PAA–zinc nitrate thin film and subsequent annealing at 620 °C. (a) HR-SEM image of an ZnO nanoring array with a ring width of 40 nm. The inner diameter of the rings is 180 nm; spacing between each ring is 200 nm; (b) HR-SEM image of the ZnO line pattern with a line width of 120 nm and a spacing of 600 nm; (c) XRD diffractogram of the polycrystalline wurtzite structure; (d) tapping mode AFM height profile; (e) TUNA conductivity map of ZnO lines; (f) pattern line width versus PAA concentration and spin coating speed; (g) pattern height versus metal salt concentration. All samples were spincoated onto PDMS at 4000 rpm for 2 min.
Adhesive failure was observed during the lap shear test when using PAA between either glass slides or PDMS blocks. It is noted that the most common mode of failure in adhesive joints is adhesive failure, irrespective of the cohesive strength of the materials and adhesive used.\(^7\) The adhesion strength of the PDMS-PAA interface \(\tau_{\text{PDMS-PAA}}\) was found to be 3 times larger than the adhesion strength between SiO\(_2\) and PAA, \(\tau_{\text{SiO}_2-\text{PAA}}\). This explains why the PAA solution was not transferred to the silicon substrate in the central areas under the stamp, where the stress distribution was homogeneous and one-dimensional.

However, the force field at the edges of the stamp features is very different. Here a thin film of PAA solution covers both the contacting and vertical face of the PDMS stamp. When the stamp is retreated, the PAA film at the edge sticks to the underlying silicon surface, and is only drawn upwards by the PAA film on the side walls of the stamp. When the local cohesive strength \(\tau_{\text{PAA}}\) of the PAA film is smaller than \(\tau_{\text{SiO}_2-\text{PAA}}\), then cohesive failure will occur in the PAA film somewhere near the edges. Since the molecular weight of PAA in our experiments was rather low \((M_w \approx 1800\) g mol\(^{-1}\)), \(\tau_{\text{PAA}}\) is indeed expected to be relatively small. Cohesive failure in the PAA film is probably facilitated further by the fact that corners and edges often act as strong stress concentrators in constructs under mechanical stress. The result is that a ridge of PAA film near the edges of the stamp features remains behind upon retreat of the PDMS stamp. Hence, the edge transfer process occurs when the following two conditions are met:

\[
\tau_{\text{SiO}_2-\text{PAA}} < \tau_{\text{PDMS-PAA}} \tag{1}
\]

in the central regions under the PDMS stamp, and

\[
\tau_{\text{PAA}} < \tau_{\text{SiO}_2-\text{PAA}} \tag{2}
\]

in the edge regions of the protruding parts of the stamp.

To illustrate the versatility of the technique, stamps with different geometries and dimensions were tested. We also tested precursors with different metal salts such as nickel nitrate, copper nitrate and ferric nitrate. Fig. 3a shows ring patterns fabricated using a micro-metre scale-patterned PDMS stamp with circular pillar arrays with a diameter of 3 µm, spacing of 2.5 µm and height of 3 µm. A solution of 1.5 wt% PAA and 3 wt% zinc nitrate in water was used. The rings have a width of 300 nm and height of 150 nm measured using AFM. Fig. 3b shows CuO ring patterns fabricated using a solution of 1.5 wt% PAA and 1.5 wt% Cu(NO\(_3\))\(_2\). The samples were annealed at 600 °C for 30 min after transfer printing. The edges of the PDMS stamps used in these experiments had slight irregularities, resulting in rings with an average width of 100 nm that have some areas where a little more material is accumulated. In principle, this effect can be exploited at will to generate patterns with an inhomogeneous distribution of material along the lines. When PDMS stamps with smooth edges were employed, the ring patterns looked similar to those of ZnO in Fig. 3a and 2a. Fig. 3c shows a line array of CuO nanoparticles, fabricated using a diluted sol with a concentration of 0.2 wt% Cu(NO\(_3\))\(_2\) mixed with a solution of 0.5 wt% PAA. The nanoparticles of CuO have an average size of 15–25 nm and the lines were separated by 4 µm. Fig. 3d shows the XRD spectrum obtained from a Si-supported thin film that confirms the CuO phase. Examples of Fe\(_2\)O\(_3\) and NiO nanopatterns are provided in the ESI†.

We used the ZnO patterns described above as nucleation areas for site-selective solution phase growth of patterned ZnO nanoneedle arrays. Patterned substrates were therefore immersed in a solution containing zinc nitrate and HMTA and left for a defined period of time. Fig. 3e shows single-crystalline ZnO nanoneedles grown from such a solution on the ring patterns of Fig. 3a. Fig. 3f shows nanoneedles grown on the line patterns of Fig. 2b. Apparently, certain locations on the ZnO line patterns served as nucleation sites for growth of single-crystalline ZnO nanoneedles. The pictures clearly

![Fig. 3](image-url)
demonstrate the absence of a residual ZnO layer in the areas that were in contact with the PDMS stamp.

Conclusions

We have demonstrated a simple, inexpensive and versatile edge transfer printing technique to pattern oxide materials with resolutions from sub-50 to a few hundred nanometres using PDMS stamps with much larger pattern dimensions. Metal salt-containing PAA thin films with low molecular weight PAA were applied as ‘ink’. The technique is applicable to most metal salts that can be dissolved in aqueous PAA solutions. Further research is underway to extend the method to the fabrication of noble metal nanoparticle arrays, magnetic nanoparticle-PAA composite patterns and multi-oxide patterns on the nanometre scale with dimension and shape control.

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Notes and references

26 Veeco AFM manual, Application Modules, Nanoscope V7-B (004-1020-000).