Supporting information

Structural, Optical and Electrical Properties of Silver Gratings Prepared by Nanoimprint Lithography of Nanoparticle Ink

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Figure S1: Bright-field optical images of grating (A-E) and planar (F-G). All samples were fabricated using AgNPI. (A) The grating pattern on a glass substrate after annealing for three hours at 130 °C. AgNPI was not fully annealed and ink was removed with PDMS mould; (B) The grating pattern on a glass substrate after annealing for three hours at 150 °C. AgNPI was not fully annealed and ink was removed with PDMS mould.; (C) The grating pattern on a glass substrate after annealing for five hours at 130 °C. AgNPI was not fully annealed and ink was removed with PDMS mould.; (D) The grating pattern on a glass substrate after annealing for five hours at 150 °C. AgNPI was not fully annealed and ink was removed with PDMS mould.; (E) The grating pattern on a glass substrate after annealing time for three hours at 180 °C, however, the weight placed on top of was only 50 g, and the grating pattern did not embedded uniformly; (F) A planar surface of AgNPI on a glass substrate left to anneal at room temperature (droplets of solvent can be seen on the surface
Supporting information

after nine days); (G) A planar AgNPI surface annealed at 180 °C for three hours, and was removed from the oven before it had come to room temperature. The sample surface has cracked due to the increase in temperature and the removal from the oven prematurely.

To determine the most appropriate temperature and time to anneal the ink fully, several different methods were assessed. Figure S1A shows the sample after an annealing temperature of 130 °C for three hours, with a weight of 50 g placed on top. These samples did not fully dry, and removal of the PDMS mould also removed the wet ink. The grating pattern was evident in this image, so initially the 50 g weight was deemed suitable. Figure S1B shows similar results were obtained when the temperature was increased to 150 °C for three hours, albeit in smaller areas. Again, the weight was maintained at 50 g. In Figure S1C, the temperature was reduced to 130 °C, but the time was increased to five hours. This yielded very similar results to Figure S1A. In Figure S1D, the temperature was increased to 150 °C, for five hours, again with the 50 g weight. Similar results to Figure S1B were obtained. Figure S1E shows the grating pattern annealed at 180 °C, for three hours, with the 50 g weight. A clear grating pattern was achieved, with no defects seen in the pattern. However, the grating pattern was not uniformly transferred across the entire sample. Therefore, additional weight was added in 50 g increments, and the pattern was checked via bright-field optical microscopy. A final weight of 1.35 kg was found to be optimal. To determine if fabrication of the grating could be achieved without annealing, a sample was left at room temperature, ~ 21 °C. However, even after nine days, droplets could be seen in bright-field optical microscopy, seen in Figure S1F, a planar surface, and the ink could be rubbed off the substrate with gloved fingers. Figure S1G shows the effects of thermal shock on the sample when it was removed from the oven before it had cooled sufficiently. Once it was determined that 180 °C for three hours was a sufficiently high temperature, long enough duration to anneal the ink and remove the solvent, and the optimum weight of 1.35 kg determined, this process was used in the fabrication of all AgNPI surfaces. Higher temperature anneals may have aided in shortening the anneal time; however, further investigation of this aspect was beyond the scope of this study.
Figure S2: Schematic of the NIL process for fabrication of gratings using PMMA and AgNPI (AgNPI/PMMA grating). PMMA is spin coated on to a cleaned glass coverslip. A ~ 60 µL drop of AgNPI is placed on top of the PMMA. The PDMS mould is placed on top of this. It is then sandwiched in between two Al plates, with extra weights added to ensure grating pattern transfer. It is subsequently annealed at 180 °C for three hours in an ambient condition oven. After the oven is turned off, the sample is allowed to cool to room temperature before being removed. The PDMS mould is peeled off revealing an Ag grating pattern.

Figure S3: Schematic of the NIL process for fabrication of gratings using PMMA and thermal evaporation of Ag (TE Ag/PMMA grating). PMMA is spin coated on to a cleaned glass coverslip. The PDMS mould is placed on top of this. It is then sandwiched in between two Al plates, with extra weights added to ensure grating pattern transfer. It is subsequently annealed at 170 °C for two and a half hours in an ambient condition oven. After the oven is turned off, the sample is allowed to cool to room temperature before being removed. The PDMS mould is peeled off revealing a PMMA grating pattern. The sample is then prepared for thermal evaporation and a layer of Ag ~ 100 nm thick is deposited onto the PMMA grating.
Supporting information

Figure S4: Schematic of the NIL process for fabrication of an AgNPI planar surface. A ~ 60 µL drop of AgNPI is placed onto a clean glass coverslip. The PDMS mould is placed on top of this. This is then sandwiched in between two Al plates, with extra weights added to ensure grating pattern transfer. It is subsequently annealed at 180 °C for three hours in an ambient condition oven. After the oven is turned off, the sample is allowed to cool to room temperature before being removed. The PDMS mould is peeled off, leaving an Ag thin film.

Figure S5: Schematic of the NIL process for fabrication of a planar surface using AgNPI and PMMA (AgNPI/PMMA planar surface). PMMA is spin coated onto a clean glass coverslip. A ~ 60 µL drop of AgNPI is placed on top. The PDMS mould is subsequently placed on top of this. This is then sandwiched in between two Al plates, with extra weights added to ensure a flat surface is achieved. It is subsequently annealed at 180 °C for three hours in an ambient condition oven. After the oven is turned off, the sample is allowed to cool to room temperature before being removed. The PDMS mould is peeled off, leaving an Ag thin film.
Supporting information

Figure S6: Schematic of the NIL process for fabrication of a planar surface using PMMA and thermal evaporation of Ag (TE Ag/PMMA planar surface). PMMA is spin coated onto a clean glass coverslip. The PDMS mould is subsequently placed on top. This is then sandwiched in between two Al plates, with extra weights added to ensure a flat surface is achieved. It is subsequently annealed at 170 °C for two and a half hours in an ambient condition oven. After the oven is turned off, the sample is allowed to cool to room temperature before being removed. The PDMS mould is peeled off, leaving a flat layer of PMMA. The sample is then prepared for thermal evaporation, where a layer ~ 100 nm thick is thermally evaporated onto the PMMA.

Figure S7: Bright-field optical microscopy images, using a 20X objective, showing: (A) AgNPI grating – method (i); (B) AgNPI/PMMA grating – method (ii); (C) TE Ag/PMMA Ag grating – method (iii); (D) AgNPI
Supporting information

planar surface; (E) AgNPI/PMMA planar surface; and (F) TE Ag/PMMA planar surface. All surfaces were fabricated on a glass substrate.

Figure S8: SEM images showing: (A) AgNPI grating – method (i); (B) AgNPI/PMMA grating – method (ii); (C) TE Ag/PMMA Ag grating – method (iii); (D) AgNPI planar surface; (E) AgNPI/PMMA planar surface; and (F) TE Ag/PMMA planar surface. All surfaces were fabricated on a glass substrate.

Figure S9: Cross-sections of gratings prepared with AgNPI (A) and AgNPI/PMMA (B). SEM image of each grating surface is shown in the bottom half of the panel, with the image of the cross section shown in the top half. The cross-section shows the AgNPI sample to have a smoother surface than that prepared with
Supporting information

AgNPI/PMMA. It also shows that the clustering of the nanoparticles has penetrated further into the sample than they have in the AgNPI sample.

Figure S10: AFM line profiles of: (A) CD; (B) PDMS mould; (C) AgNPI grating; (D) AgNPI/PMMA grating; and (E) TE Ag/PMMA grating.