

# Metallic nanostructures in a polymer matrix and substrate fabrication and structural characterization

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**Abstract** Metal nanostructures are of considerable interest in the field of plasmonics and metamaterials and could have a wider impact if they are successfully embedded in a stable, inert and flexible polymer matrix. Fabrication of such structures is challenging for a variety of reasons including thermal stability, material compatibility with processing steps and general handling of material. In this work we have demonstrated the fabrication of metal nanostructures and embedded them in a polymer. Furthermore, these structures were fabricated on a flexible polymer membrane and detached from a carrier substrate. Characterization of these structures was performed with SEM, TEM and EDS.

## 1 Introduction

Optical properties of metal nanostructures have been in the realm of current research, due to their enhanced plasmonic response and possible use in fabrication of artificial metamaterial structures [1–4]. Studies in block copolymers have looked into embedding transitional metal nanoparticles, and particles with catalytic properties, into a polymeric network [5–7]. However, a periodic structure allows a controlled study of effects of particle size, shape and separation distance, which is rarely possible in systems with random particle distributions. Fabrication of periodic nanostructures with dimensions below 100 nm remains a challenging task. We have previously looked at material selection and thin-film

processes which are important for fabrication. In our current paper we look at fabrication challenges in creating embedded metallic nanostructures in a polymer or fabricating them on a polymer membrane.

These structures have shown enhanced effects in surface-enhanced Raman spectroscopy (SERS) [8, 9], and have been proposed as waveguides [10] for optical devices and computing, as well as in biosensors [11, 12]. Embedding optically sensitive metal nanostructures have been mentioned in some studies [13] and low-temperature processes [14], but the fabrication of these structures in a polymer substrate and embedding them in a polymer matrix presents its own unique challenges. These include deposition temperature, compatibility of polymer with solvent chemistries and adhesion of thin films to these substrates. Hence, there is relatively less research and evidence of how embedding these structures in a polymer matrix would affect the aforementioned optical properties. However, there are needs where one envisions using a polymer matrix to surround these nanostructures.

A method of compensating inherent loss of metal nanostructures has been proposed by the use of photo-active dye to enhance signals [13]. In biomedical applications, stability of metal nanostructures, especially Ag, in a polymer matrix could be of added importance due to its affinity with sulfur [15]. While there have been several papers on the optical behavior [1, 4, 16, 17] obtained from these, both the periodic and the random nanostructures, surface and structural characterizing of periodic nanostructures has been limited and difficult, and presents an opportunity for further study.

In this paper we report on our efforts on fabrication of a variety of these nanostructures and on their embedment in a polymer matrix. We have successfully fabricated these structures on a relatively flexible polymer substrate.

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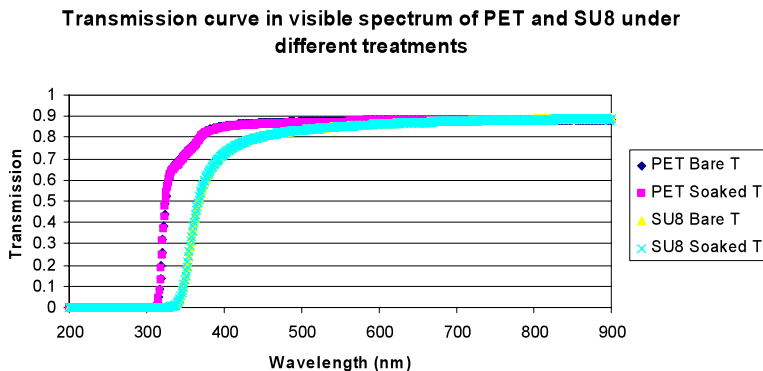
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We have worked with materials primarily identified in previously identified literature as desirable in this fabrication process. Subsequently, we performed structural characterization of these nanostructures and examined issues which may arise from the fabrication process.

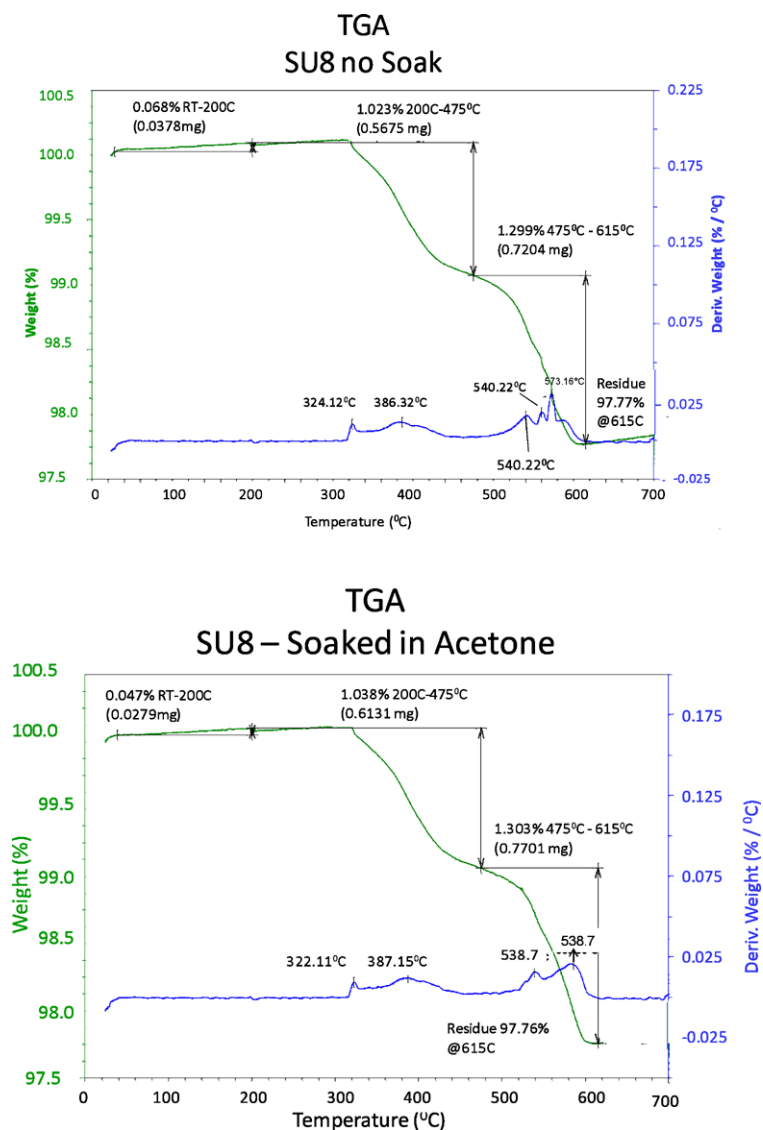
## 2 Experimental

In this section we describe our experimental and fabrication methods to envelop nanostructures we have made on glass substrates and, finally, fabrication attempts on a poly-

**Fig. 1** Optical transmission of SU8 and PET in as-obtained films as well as after soaking for 48 hours



**Fig. 2** TGA of SU8 before (top) and after (bottom) soaking in acetone



mer substrate. We discuss in more detail the latter process, as this has not been discussed in other publications and the process presents its own challenges.

## 2.1 Polymeric material selection and fabrication

The primary method used in fabricating metal nanostructures in our current work has been ion-beam etching and electron-beam lithography (EBL). Details of these two techniques and their equipment have been described in several texts [18, 19]. In this section we will describe the fabrication of the nanostructures for our devices, where we have tried to embed them in a polymer, or have fabricated them on a polymer substrate.

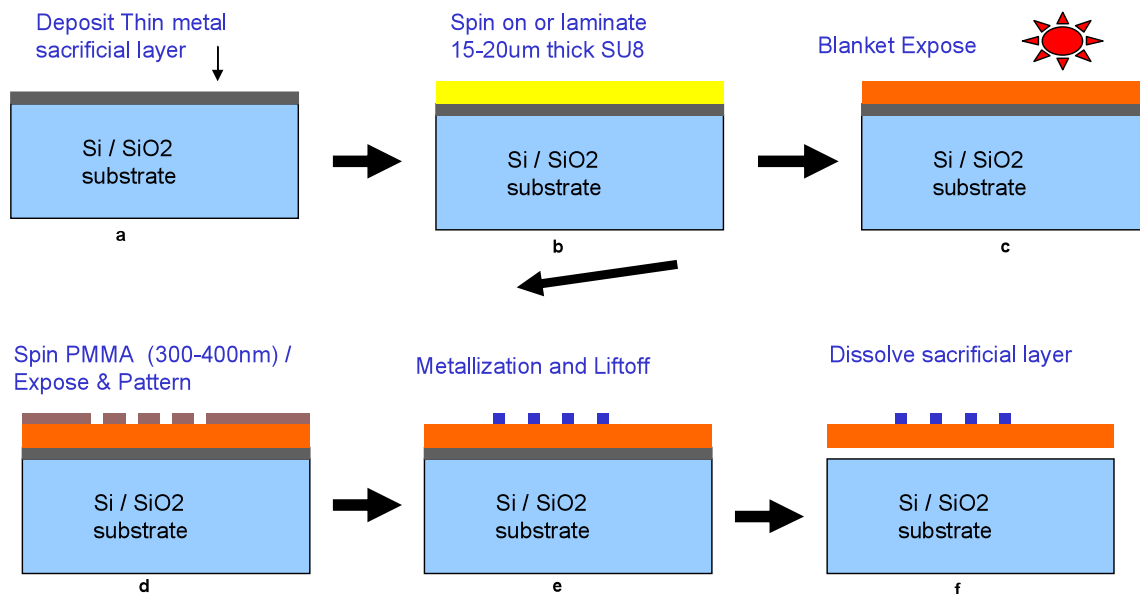
Several different approaches were taken in fabricating metal nanostructures on a polymer. The choice of polymer has been primarily dictated by its transparency in the visible spectrum, its relative inertness to processing solvents and stability at processing temperatures. Based on our research and initial screening experiments, we have selected two polymeric materials of interest—(i) SU8, an epoxy-based polymer, and (ii) polyethylene terephthalate (PET). Both of these polymers have also been considered for applications in biomedical devices due to their relative inertness. For enveloping nanostructures in a polymer, we have also considered PMMA, in addition to SU8. However, acetone is a solvent for PMMA, and hence we cannot use PMMA where acetone or a similar solvent will be used in post-processing cleans or soaks.

Transmissivity of these polymers in the visible spectrum is high (greater than 75%), as seen in Fig. 1. In addition, we soaked these PET and SU8 films in acetone over a 48-h (these times correspond to what one could possibly use in a lift-off process) period to look at the integrity of the films. No degradation was observed visually after these soaks. Subsequently, we also performed thermogravimetric analysis (TGA) on the polymers, and those curves for SU8 are shown in Fig. 2. The TGA curves shown are for a standard SU8 membrane and a PET film and then compared to those which were soaked in acetone (after the samples were rinsed and dried). None of the samples showed any weight loss over temperatures up to 200°C. Additional weight losses which can be seen at higher temperatures are consistent in both soaked and un-soaked samples, which indicate no change in sample composition or structure.

Initial metal nanostructures were fabricated and characterized on glass substrates, as described previously using ion-beam etching and EBL. Subsequently, the metallic nanostructures were spin coated with PMMA and SU8 to envelop them in a polymer. These samples were then inspected visually and subsequently imaged with transmission electron microscopy (TEM) after atomic force microscopy (AFM) indicated that we had planarized the structures.

## 2.2 Fabrication on detachable polymer layers

As described in Sect. 2.1, we chose the epoxy SU8 as one of the flexible polymer materials. One of the challenges in



•SCA used typically to enhance adhesion.

•Structures could be enveloped in another SU8 layer on top after step (e)

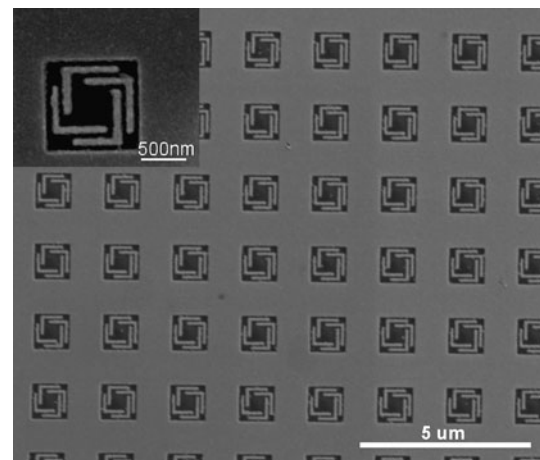
**Fig. 3** Schematic of process flow to form nanostructures on a detachable polymer membrane

processing on a flexible polymer has always been processing limitations in tools without an adequate mechanical frame or platform. Typically, the fabrication process in a polymer has involved mounting the polymer on a mechanical substrate and then performing some separation by either a delamination or a back-grinding process. In our experiments, we looked at either laminating or spin coating SU8 dry film or resist on a Si or glass wafer and processing this through different fabrication steps. The typical issue we faced was separation of the SU8 membrane from the substrate at the end of the process, without damaging the structures. In order to facilitate this process, our experiments led to putting an intermediate layer which could be etched off with relative ease at the end of the process.

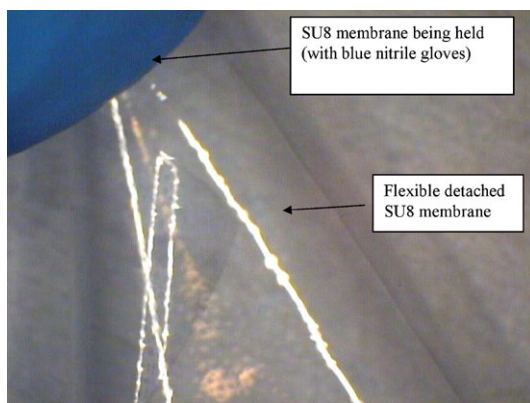
A schematic of the process flow used in fabrication of polymer embedded with metallic nanostructures is shown in Fig. 3. Glass wafers were taken, and an aluminum sacrificial layer was deposited on the surface after a brief wet-resolution cleaning. A 500-nm Al layer thickness was chosen after initial experimentation. The wafer was then treated with a silane coupling agent (SCA) to promote adhesion of the polymeric SU8 layer. A 20–40  $\mu\text{m}$  SU8 layer was then formed on this layer and soft baked to 125°C. The entire layer was then exposed at 350-nm wavelength, which allows cross linking of the SU8 structure, which is a negative resist. Cross linking allows for the structure to be more robust both chemically and mechanically. After the desired level of cross linking was obtained, a thin layer of indium tin oxide (ITO, 20 nm) was deposited on the SU8 surface. The indium tin oxide was used to facilitate patterning by e-beam lithography.

At this stage wafers were diced into 1 in square pieces to get our samples ready for PMMA spin-on and e-beam patterning. Once the processing was completed with metal evaporation and lift-off, we enveloped the structures in thin SU8 polymer using a spin-on technique. The technique is identical to spin-on resist for full wafers, except in this case we used 1 in square pieces instead of the wafer. Depending

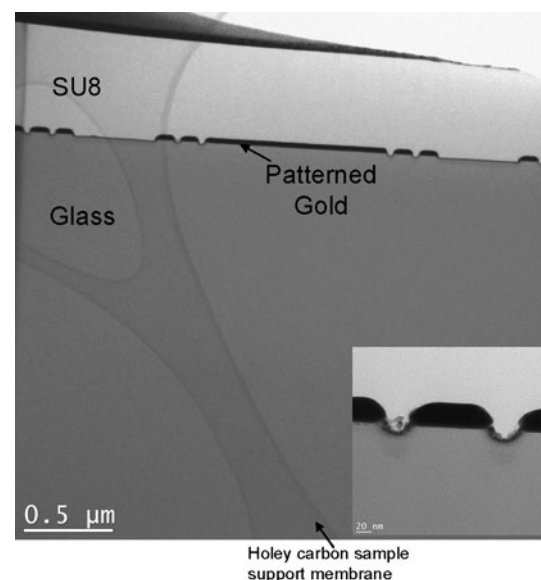
on the thickness of structures and aspect ratios, we chose a lower molecular weight SU8 for embedding the nanostructures, which are mechanically on top of the wafer. The final step in this process was separating these structures enveloped in the polymeric membrane from the glass substrate. This was accomplished by dissolving the Al in a 5% solution of TMAH in a 50°C bath. The samples are rinsed in de-ionized water and are at this stage ready for use. An optical image of our thin flexible polymeric membrane separated from the handler (glass plate) fabricated with the described method is shown in Fig. 4. The intrinsic stresses on such polymer films can be quite high (SU8 stresses 2–4 GPa), and this separation is only recommended prior to appropriate testing.



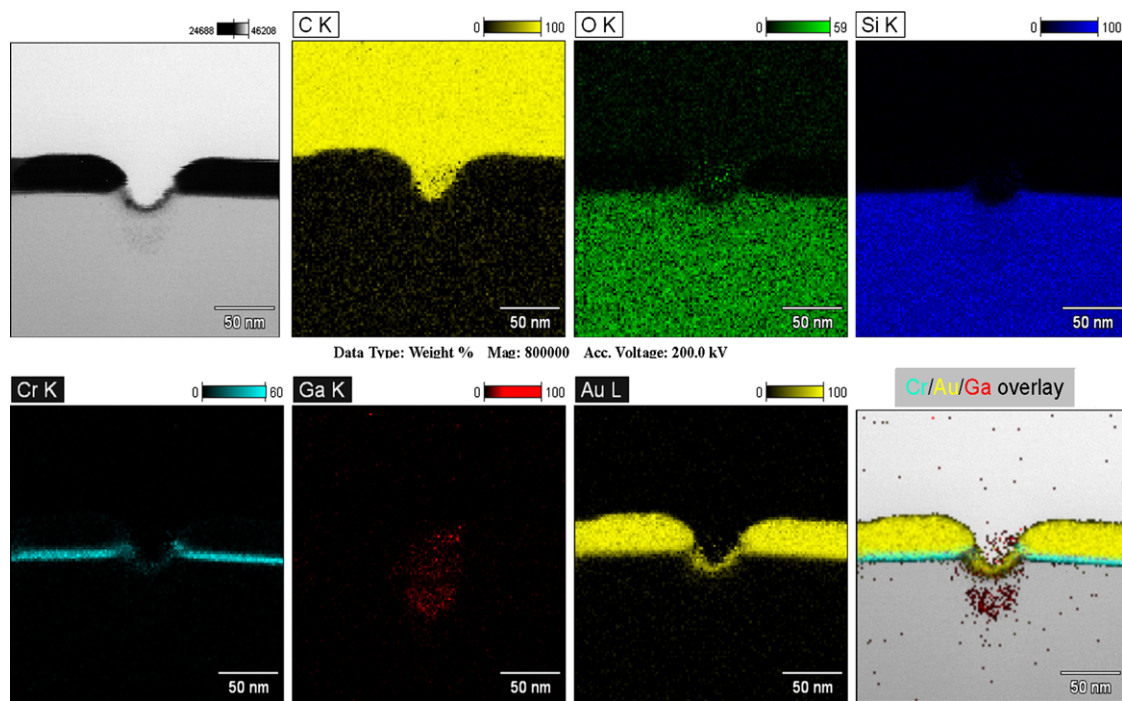
**Fig. 5** L-shaped resonators in rectangular boxes, fabricated by ion-beam milling



**Fig. 4** Optical image showing final detachable membrane



**Fig. 6** Nanostructures enveloped in a polymer SU8 thin film

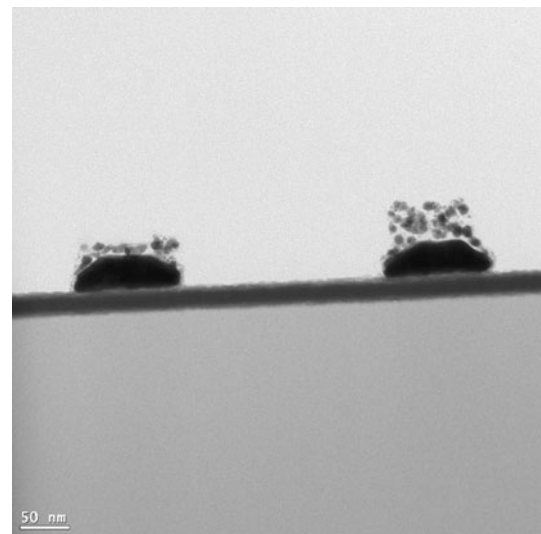


**Fig. 7** EDS spectral mapping of FIB-patterned nanostructures

Finally, we also attempted to fabricate some of the structures directly on a PET substrate. The thickness of the PET substrate was 250  $\mu\text{m}$ . Prior to any processing, the PET samples were annealed on a hot plate at 150°C to stabilize the structure. ITO was sputter deposited on this substrate while keeping the pedestal at 30°C. A fixture was fabricated to keep the sample relatively flat during spin coating of PMMA as well as while writing with the e-beam. The samples were baked for 15 min under a fume hood at 140°C on a hot plate. Different e-beam patterns as optimized in previous glass substrates were used, and a developer was used for developing PMMA. Metal deposition was accomplished by sputtering or evaporation. The deposition temperature in sputtering is again limited to 30°C by cooling the pedestal. The samples were then stripped in acetone and cleaned with IPA and dried in a fume hood.

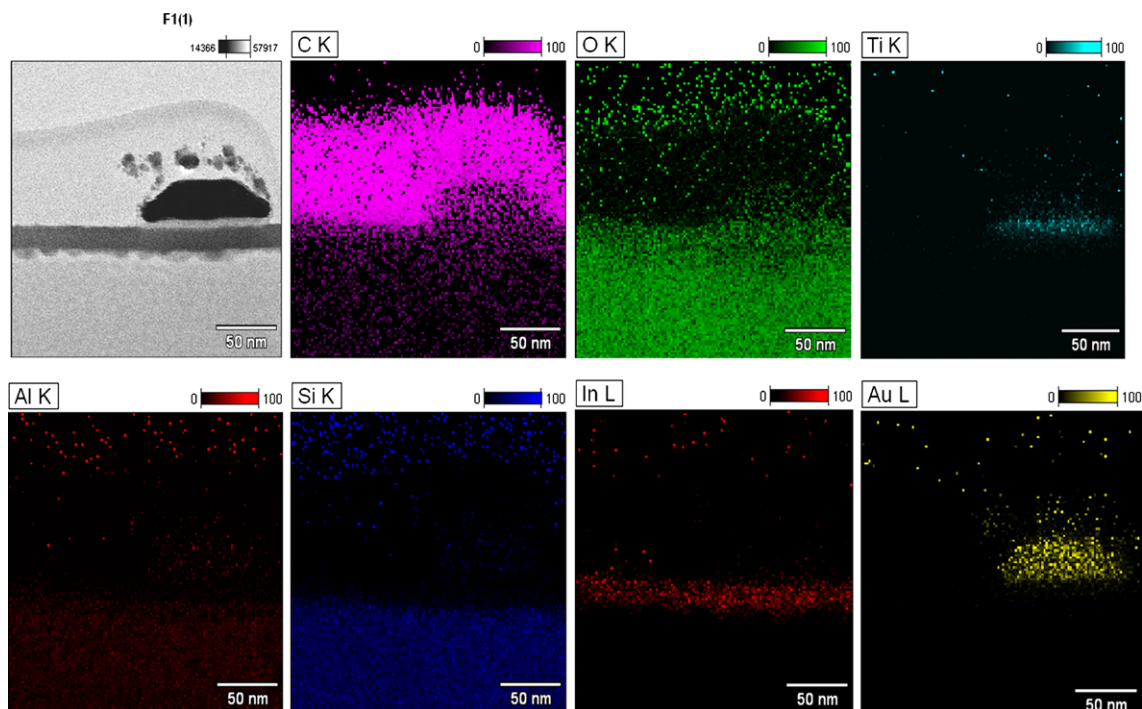
### 3 Results and discussion

Figure 5 shows the scanning electron microscopy (SEM) image of a nanostructured pattern created by ion-beam etching of a 25-nm film of Au on a glass plate. The aim of this patterning was to create L-shaped resonators inside a square box structure. Figures 6 and 7 show the TEM cross sections of these structures once they were enveloped in SU8 polymer. We were unable to create any FIB cross sections of samples coated with PMMA, as the samples have distortion from bubble formation. These defects can be due to the low



**Fig. 8** Au nanostructures formed by EBL

$T_g$  of PMMA ( $\sim 95^\circ\text{C}$ ). It is surmised that cryogenic cooling would be necessary to image that. However, using the SU8 ( $T_g \sim 185^\circ\text{C}$ ) coating we were able to coat the nanostructures without any voids. It can be seen from the images that the SU8 polymer enveloped the nanostructures and created a planarized structure. Further, energy-dispersive spectroscopy (EDS) mapping in Fig. 7 also indicated the presence of C from the SU8 polymer, Si and O from the glass substrate and Cr from the under-layer which was used as an adhesion layer. The Ga signal is from the FIB process.

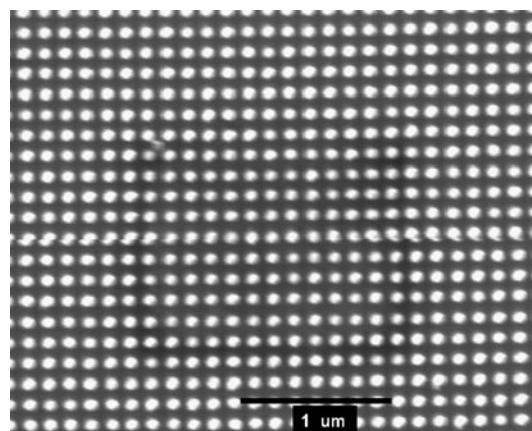


**Fig. 9** EDS elemental mapping of nanostructures formed by EBL

Furthermore, to see isolation of the discrete nanostructures, EDS was used to characterize the area in between structures. EDS showed the presence of Au in the streets where the ion beam attempted to remove the Au completely to isolate structures. It is possible that the Au atoms were either re-sputtered in the streets or diffused in  $\text{SiO}_2$  due to thermal and structural effects from the ion beam.

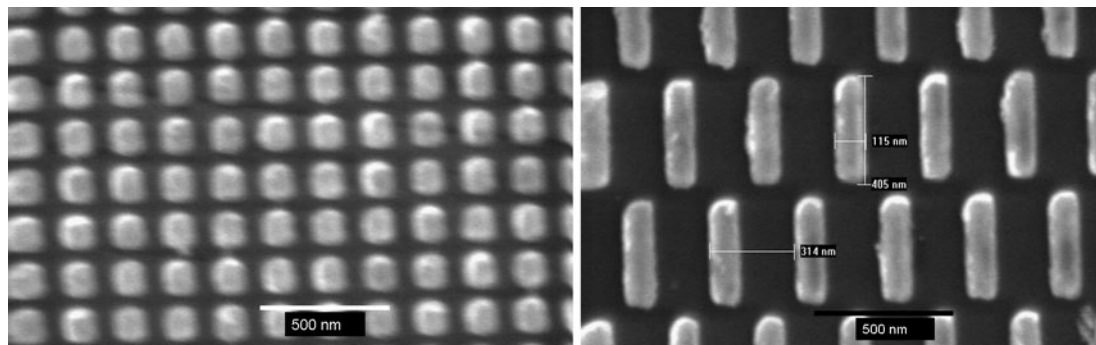
Similar nanostructures were also made by e-beam lithography using lift-off techniques. Figure 8 shows the TEM cross sections of nanostructures on a glass substrate and embedded in a layer of SU8, while Fig. 9 shows the EDS spectral analysis images from the same samples. In contrast to the nanostructures obtained by ion-beam milling, Au was not seen in the streets in these structures, indicating this to be a preferable method for fabrication of these nanostructures. Once again EDS mapping indicated the presence of C from SU8, Si and oxygen from the glass substrate and Ti as the adhesion under-layer. The In signal in the spectra can be attributed to the presence of the ITO layer which has been used in our studies to facilitate e-beam patterning.

Figure 10 shows the SEM image of nanodisc structures formed on a flexible SU8 membrane which is 20- $\mu\text{m}$  thick. A 5-nm Ti layer and a 40-nm Au layer were deposited by evaporation for these structures. The structures shown here did not have any polymer coating on top, so that we could perform SEM imaging. The processing on the SU8 membrane was accomplished by a carrier piece, as described in Fig. 3. However, patterns on PET did not develop as desired



**Fig. 10** Au nanodisc patterns on 20- $\mu\text{m}$  SU8 membrane produced by EBL and lift-off

and left very faint patterns instead. It is hypothesized that we were not getting enough back-scattered electrons in the PET sample, which in e-beam lithography plays a very critical role in exposure of PMMA resist. Larger structures, which have a lot higher exposure dose, do not have this issue. We see these structures quite clearly and hence do not think it is an adhesion issue. The Al back plate in the SU8 substrate could be allowing back-scattered electrons and thus may be able to expose the PMMA in those structures. Figure 11 shows some of the other structures which we have made successfully in a SU8 membrane using e-beam lithography and lift-off.



**Fig. 11** Au nanorods and additional patterns on SU8 membrane

#### 4 Conclusions and future direction

A wide range of structures were created using EBL and ion-beam etching. Ion-beam etching used in the conditions described has limitations in isolating structures as well as in shapes of defined structures. Structures of various shapes and morphologies were created with dimensions  $<100$  nm, with EBL. Structures were successfully embedded in a SU8 polymer without any voids in the structures. Structural characterization by TEM, SEM and EDS was also accomplished. These studies demonstrate the feasibility of processing and fabricating metal nanostructures on a flexible polymer substrate within temperature limitations of processing these materials. We further demonstrated transfer of these patterns on a thin-film SU8 layer and were able to separate these structures from a handler or carrier substrate. The nanostructures were more difficult to produce in a PET substrate, possibly due to insufficient back-scattered electrons. Additional methods could be explored where a temporary thin film could be applied to the back side during exposure. The stability and relatively inert behavior of these polymer materials make them attractive for further work with biosensors and chemical sensors. Further work will be done on these structures by examining their optical properties.

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