Polyethylene Glycol (PEG) Ink

for cross-platform application

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Summary

Dip Pen Nanolithography® (DPN®) has developed as a technique for creating soft and hard materials on surfaces. Nanoscale features can be fabricated using ink materials transported through a water meniscus from a coated tip to a substrate. Often, a chemical reaction between ink and substrate makes the DPN process more favorable. For example, alkanethiol is a common ink for DPN because the gold-thiol reaction (Au-S) helps to form self assembled monolayers (SAMs) on the gold surface. Here, we demonstrate the use of PEG to generate positive (protruding) and negative (recessed) metal nanostructures, and to improve the performance of polydimethylsiloxane (PDMS) stamp.

Application Description

Recently, a PEG based ink system requiring no chemical reaction with substrate has been developed [1]. PEG is a good ink candidate, because of its easy handling and broad applications in bio-related fields. Polyethylene glycol (PEG) is the most commercially useful type of polyether. PEG is non-toxic and has been broadly used in cell-tissue engineering and drug delivery systems. In addition, a PEG coated surface can be used to prevent non-specific binding of proteins and DNA on patterned substrates. Moreover, PEG is soluble in water and most organic solvents (methanol, benzene, carbon tetrachloride, chloroform, dimethylformamide (DMF), acetonitrile, and dichloromethane). Since it physisorbs on the sample surface, PEG can be patterned on variety of substrates, including metals and plastics.

PEG ink for metal nanostructure fabrication

Alkanethiols SAMs patterned by DPN can be used as an etch resist. The SAMs protect the underlying metal layer from chemical etching when exposed to a metal etching solution [2]. Although this methodology works with many surfaces (e.g. Au, Pd, and Ag), it has a certain limitations. A positive pattern (protruding metal nanostructure) can be easily made by exposing the patterned sample to an etching solution. However, a negative pattern (recessed metal nanostructure) more difficult to fabricate, and requires electrochemical methods to desorb the DPN generated SAMs from a surface covered with thiols [3].

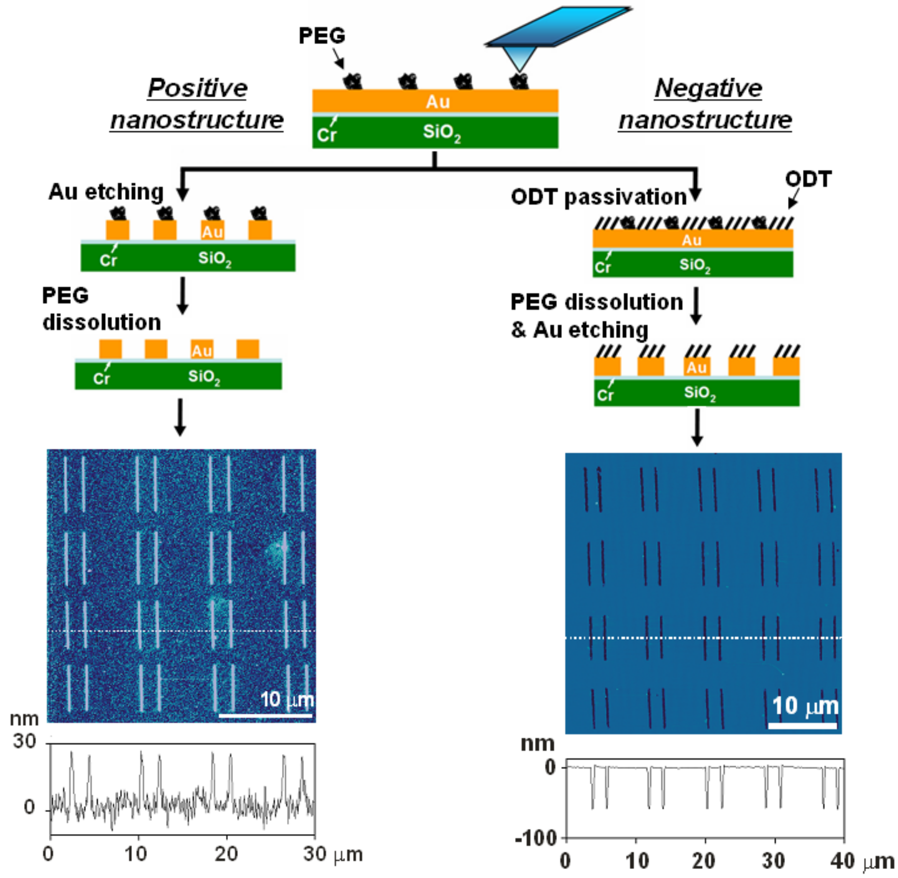

Figure 1: Scheme and AFM topography images of Au positive and negative nanostructures using polyethylene glycol (PEG). The height profiles of each line patterns clearly show the positive and negative metal nanostructures, respectively. [1]

PEG layers can be patterned directly on many metal surfaces, since physisorbtion is main mechanism of PEG DPN. In other words, PEG patterned by DPN can also be easily removed using organic solvents from metal surfaces. This is important for the purposes of generating negative features because no electrochemical set-up is needed to desorb a PEG layer from the substrate surface. Instead, the area to be protected from etching is simply covered in PEG using the tip while 1-octadecanethiol (ODT) SAM covers the other area by passivation. After PEG dissolution with sequential Au etching, negative patterns can be generated (see Figure 1, right). Moreover, positive patterns can be obtained with ease similar to that of the alkanethiol ink (Figure 1, left). Figure 1 shows AFM topographic image of positive and negative line patterns which were fabricated by PEG DPN patterning on Au substrates.

PEG DPN on soft PDMS stamp

More generally, PEG can be used to enhance other soft lithography techniques. Since the PEG DPN process does not require a chemical reaction, PEG can be on soft surface such as a polydimethylsiloxane (PDMS) stamp.[4] Figure 4 shows PEG dots patterned on PDMS stamp using DPN, which are used in conjunction with chemical processing to enhance the PDMS stamp resolution. Dots measuring less than 100 nm can be generated on the PDMS stamp by controlling tip dwell time at desired locations [4].

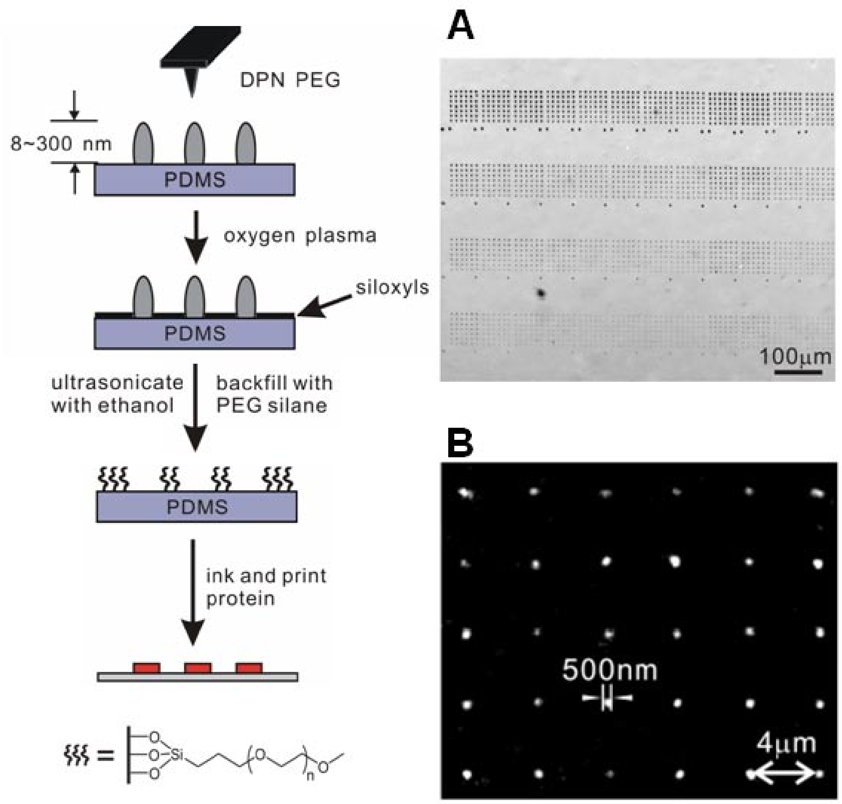

Figure 2: Fabrication scheme of flat stamps for μCP of proteins. (A) Optical microscope image of dwell time dependent PEG dot arrays on PDMS stamp. Each row was generated by same dwell time using 1-D pen array. (B) A fluorescent image of the printed TRITC conjugated anti-mouse IgG on glass substrate. [4]

DPN-generated PEG arrays on PDMS stamps can also be used as a chemical resist to reduce a micro-contact printing (μCP) feature sizes. The chemical treatment of the exposed area except PEG patterns also can be carried out (see Figure 2). Here, PEG prevents the binding of siloxyls to the surface of a PDMS stamp in regions where deposited by DPN. After the PEG is washed away, the exposed PDMS region can be coated with a second material (in this case, an IgG protein), which selectively adsorbs to the previously protected regions. The protein is then printed on another surface. This combination of PEG DPN with soft PDMS stamp, overcomes the lateral diffusion limitation of PDMS stamps. It enables the fabrication of sub 100 nm dot diameter features on various surfaces. [4]

Conclusion

Physisorbtion based ink material shows a similar DPN patterning ability as an alkanethiol ink. Because of easy washing away the structures after DPN patterning, advanced nanofabrications are available. Using PEG ink material, negative type metal structure is systemically fabricated and same methodology is applied to the improvement of PDMS micro-stamp performance. More advanced nanofabrications can be attempted with this physisorbtion based PEG ink methodology in the future.

References

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