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Electrochemical Nanofabrication Using Polyacrylamide Hydrogel as Soft Stamps

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Abstract: The fabrication resolution of electrochemical wet stamping was enhanced to several hundred nanometers from several ten micrometers by using polycarylamide gel (PAG) as soft stamps and through optimized processes. The PAG stamp was cured on a nanopatterned soft mold and soaked with 0.2 mol·L^{-1} KCl solution, then contacted with a silicon wafer with gold film and applied with electric field. And the gold nanopatterns were achieved by the selective anodic dissolving, the diameter of fabricated gold spot was around 200 nm. The parameters which affected the fabrication processes have been discussed in detail.

Key words: nanofabrication; electrochemical etching; soft stamping; polyacrylamide hydrogel

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The nanofabrication technique, that is, to modify nanoscale topographies on the solid materials surfaces, is very important in IC industry, optoelectronics and micro/nano fluidics. In recent years, considerable efforts have been and continues to be devoted to the development in new methods of surface nanostructuring, such as nanoimprint lithography[1-3] and softlithography[4-5]. By using polydimethylsiloxane (PDMS) as stamps, a serials of nanopatterning techniques were developed, such as microcontact printing[6], replica molding[7], microtransfer molding[8], solvent-assisted micromolding[9], etc. They are essentially based on printing a thin layer of molecule or solvent onto a hard material surface. However, the most of the modified layer made by softlithography are not durable during the subsequent etching. Reaction-diffusion (RD) method, developed by Grzybowski and co-workers, allows bench-top prototyping of curvilinear and/or multilevel reliefs in solid materials, which use the agarose hydrogel soaked with chemical etchant solution as the soft stamps[10-14]. Compared with chemical etching based on reaction-diffusion, electrochemical etching has higher controllability and reproducibility. Our group has developed electrochemical wet stamping (E-WETS) technique based on agarose stamps, which was applied to transfer microstructures on silicon and metal, its lateral resolution is several ten micrometers[15-18]. The main reason for the fabrication resolution of E-WETS not down to nanoscale is the structure and internal properties of agarose, which is a linear polymer hydrogel with several ten micrometers holes. Here, we reported that by using polycarylamide gel (PAG) as stamps and through optimized processes, the fabrication resolution of E-WETs could be greatly improved and down to several hundred nanometers. The aim of the study was to develop a new nanofabrication technique.

1 Experimental

As shown in Fig. 1A, nanopatterned PAG stamps were prepared by casting mixed solutions of

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monomer (acrylamide, Acr) and crosslinker (bis) on soft mold (IPS@, one kind of special polymer produced by Obducat Technologies, Sweden). The IPS mold used here was replicated from hard nickel mold with nanoimprint machine (Obducat Eitire 6, Obducat Technologies Co., Sweden). After curing, the PAG mold was peeled off from the soft IPS mold, and then soaked in 0.1 mol·L^{-1} NaCl solution overnight. Prior to use, the stamps were dried on filter paper for 10 min and under a stream of N_2 for 10 s. The substrates to be fabricated were silicon wafer with 100 nm gold /20 nm Cr film. Electrochemical etching of gold film was carried out in a designed apparatus as shown in Fig. 1B. The PAG stamp was placed in a beaker filled with 0.2 mol·L^{-1} KCl solution. The Au/Cr/Si wafer was put on the top of PAG stamp and connected to the potentialstat (CHI 1232B, Shanghai Chenhua Co., China) as the working electrode, a piece of Pt wire was immersed into the NaCl solution as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Observation of PAG stamps was carried out after freeze-dried and coated with 5 nm gold by using SEM (FESEM LEO 1530, Oberkochen, Germany). The Young's modulus of PAG stamps were obtained by fitting the approaching curve with Hertz model based on the AFM (Agilent 5500 AFM, USA) force-distance curves of the PAG stamps.

2 Results and Discussion

The material of the mold for the casting PAG stamps is IPS@ polymer, one kind of special polymer developed by the Obducat Technologies Company, which is a novel material for nanostructure transferring. As shown in Fig. 2, 20 nm width groove line

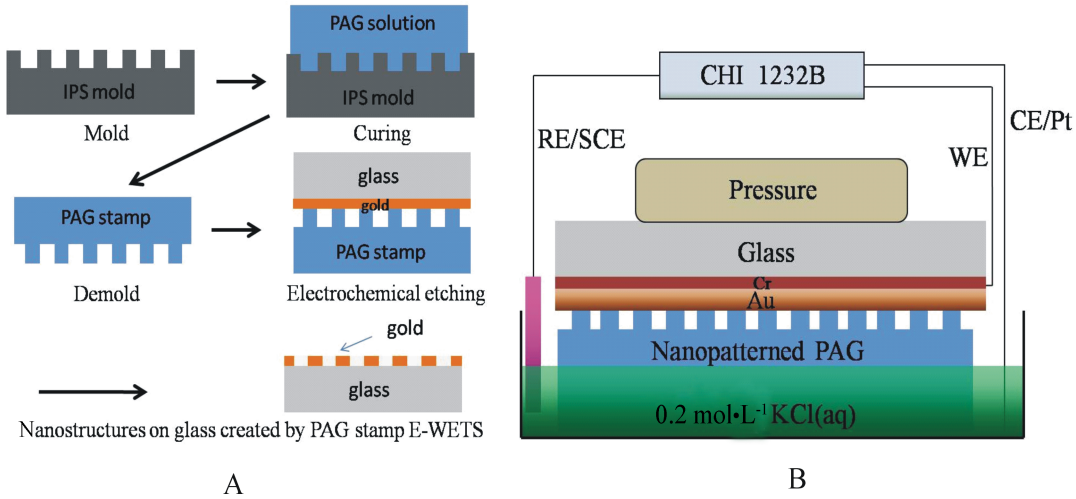

Fig. 1 Schematic illustration of the E-WETS (A) procedures and (B) apparatus used for PAG stamp electrochemical nanofabrication

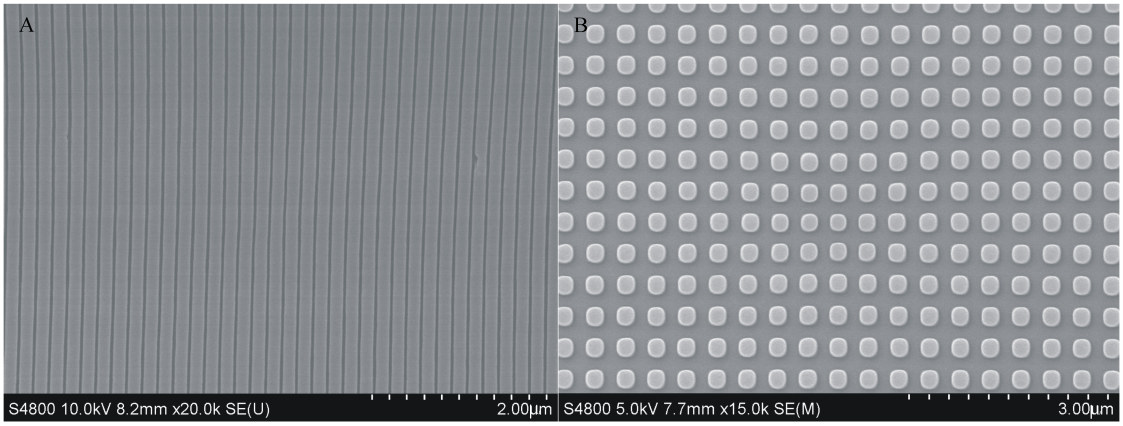

Fig. 2 SEM images of IPS molds with 20/160 nm lines (A) and 200nm/200nm spots (B)

structure was transferred onto IPS film successfully. The surface of IPS was hydrophilic, thus, the PAG solution could spread into the groove nanostructures easily. In other words, IPS is a very good material as mold for PAG stamp preparing.

The concentration of monomer (Acr) and crosslinker (bis) of PAG hydrogel is an important parameter in preparation of PAG stamps because it defines both the elastic properties (Young's modulus) and porous structure of the gel. The former is related to the deformation under press which decides the accuracy and lateral resolution; the latter affects the transport of the electrolyte and the removed gold ions. As shown in Fig. 3, the Young's modulus of PAG stamps increases with the concentration of bis and Acr. And the Young's modulus of PAG gel exponential increases with the concentration of Acr, while the concentration of bis is constant. For example, when bis is 0.6%, the Young's modulus of PAG stamps are around 15 KPa, 35 KPa and 4.5 MPa. And the Young's modulus of 1% agarose is around 10 KPa, similar to PAG with 7.5% Acr, much lower than that of PAG with 15% Acr. The material with higher Young's modulus will deform weaker. So PAG is better than agarose for nanofabrication. However, PAG with 30% Acr is not easy to be peeled off from the IPS mold for its too high Young's modulus. Therefore, we use PAG with 15% Acr and 0.6% bis as the soft stamps for nanofabrication, which gives Young's modulus around 0.35 MPa.

To observe the nanopatterns formed on the surface of PAG stamps, SEM scanning was carried out on the surface of PAG stamps after freeze-dried. As shown in Fig. 4, regular net nanostructure could be

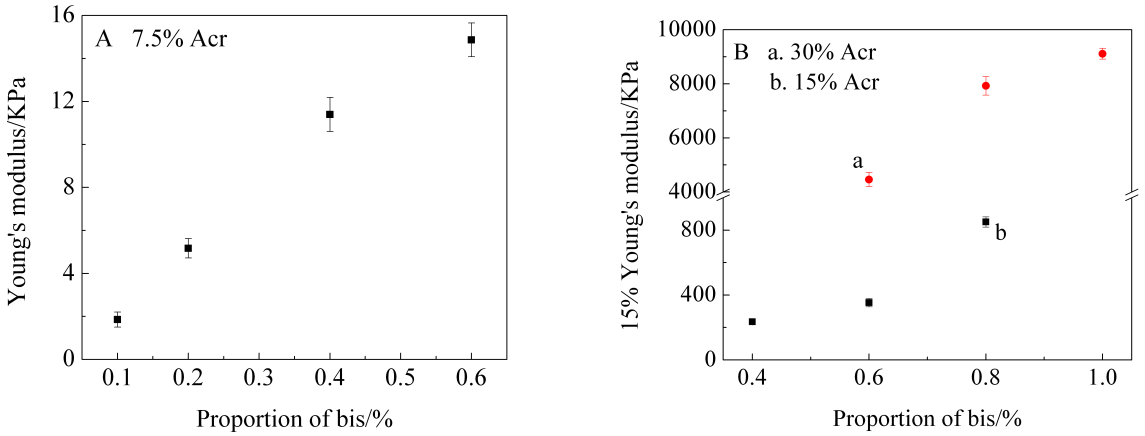

Fig. 3 The Young's modulus of PAG soft stamps

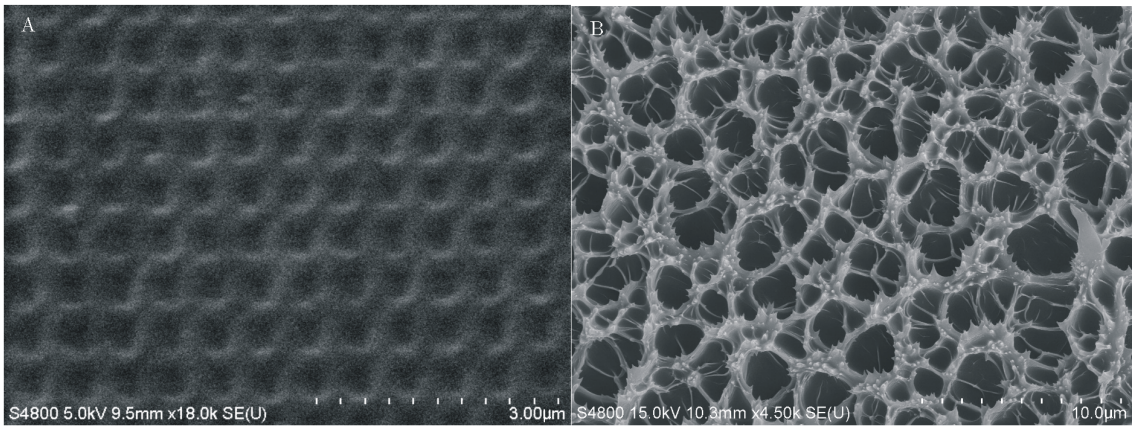

Fig. 4 SEM images of PAG stamp

A. Replica from the mold with 200/200 nm spots array; B. Intrinsic pore structure of freeze-dried PAG gel

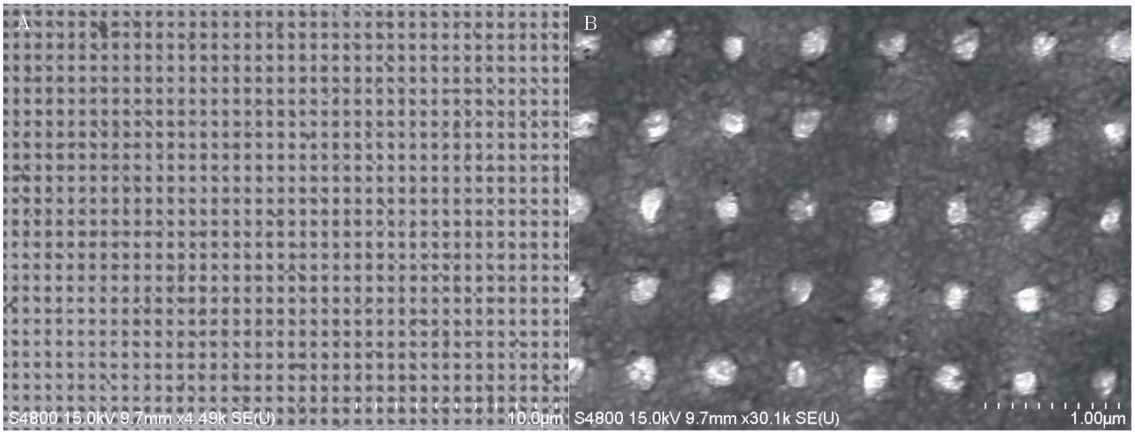

Fig. 5 SEM images of nanostructures created by PAG stamp E-WETS　A. 500/500 nm frames; B. 200 nm spots array

obtained from the IPS mold with 200/200 nm spots array, which means that the accuracy of the stamp replication is high enough for several hundred nanometer structures. And from the SEM image of cut surface of a PAG stamp, a lot of cavities with diameter around several micrometers were observed, which means that the PAG stamp is full of holes and transfers the electrolyte and gold ions quickly, favor of fastening the speed of fabrication.

After optimizing the processes and parameters, such as etching potential, pressure, time, pattern shape and the wetability of the surface of the fabricating metal, the nanoscale structures, around 200 nm, could be fabricated on the gold thin film, as shown in Fig. 5.

3 Conclusions

In summary, by choosing PAG as the stamp material and through optimizing the processes, we improved the resolution of E-WETS technique from several ten micrometers to several hundred nanometers, made it become a low-cost and high-speed nano-fabrication technique. The main reason for the promotion ascribes to the higher Young's modulus of PAG than that of agarose. Under the optimized conditions, 200 nm structures could be replicated using PAG E-WETS technique. The application of this technique could be extended to other materials, e.g., glass, by chemical or physical etching using the fabricated gold film as a sacrificial mask.

Acknowledgements

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基于聚丙烯酰胺凝胶软印章的电化学纳米加工

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摘要: 电化学刻蚀使用腐蚀性小的电解质溶液,且溶液可使用周期长,是一种环境友好的加工工艺. 本文采用聚丙烯酰胺水凝胶(PAG)作为软印章,辅以优化工艺,将电化学湿印章技术(E-WETS)的加工精度从几十微米提高到了 200 纳米. 将新配制的聚丙烯酰胺水凝胶浇注在具有纳米结构的软模板表面, 固化后脱模并保存于 0.2 mol·L^{-1} KCl 溶液中,在合适电位和压力下,对硅片表面金膜进行电化学湿法刻蚀,分别研究了聚丙烯酰胺水凝胶的聚合条件、电化学加工电位以及水凝胶表面压力对加工结果的影响. 实验表明,在最优条件下可加工出直径为 200 纳米的特征点阵结构,且该方法具有较好的可靠性和稳定性.

关键词: 微纳加工;电化学刻蚀;软印章;聚丙烯酰胺水凝胶