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Rapid fabrication of electrohydrodynamic micro-/nanostructures with high aspect ratio using a leaky dielectric photoresist

Guowei Lv[a], Shihu Zhang[a], Jinyou Shao[b], Guolong Wang[a], Hongmiao Tian[b], Demei Yu[a],*

[a] *Department of Chemistry, School of Science, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China*
[b] *State Key Laboratory of Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China*

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ABSTRACT

A leaky dielectric photoresist was designed and prepared for rapid fabrication of high-aspect-ratio micro-/nanostructures via electrohydrodynamic patterning (EHDP). The rheological behavior and electrical properties of the photoresists were systematically investigated, since the structure formation in EHDP essentially originates from the flow and deformation of the polymeric film actuated by an applied electric field. It is found that the photoresists exhibit the suitable rheological behavior with a low viscosity of 2.4–157.7 mPa s, controllable electrical conductivity of $5.0 \times 10^{-6} - 7.2 \times 10^{-4}$ S m^{-1}, as well as high homogeneity, minor surface tension of about 30 mN·m^{-1}, favorable wettability and film-forming property on substrate and an extremely large reduction in the contact angle (down to 1.64°) of electrowetting on dielectric (EWOD). The EHDP results have shown that a higher electrical conductivity of the photoresists can lead to a higher filling height, a smaller characteristic wavelength and a shorter patterning time, while a lower viscosity can also lead to a shorter patterning time, which is accordance with the theoretical prediction. In addition, the patterning time of the photoresists cannot be too short because the following rapid ripening and coalescence of the formed microstructure will damage the high fidelity of the final pillar arrays.

1. Introduction

Electronic systems on flexible substrates are attracting increasing attention as they show unique promising advantages such as mechanical flexibility, shape diversity, light weight [1–3]. Electrohydrodynamic patterning (EHDP) has been explored as a promising lithography for fabricating micro-/nanostructures for fundamental research as well as practical applications such as superhydrophobic surfaces, electronic devices, chemical sensors, micro-/nanofluidic systems and micro-/nanoelectromechanical systems (MEMS/NEMS) [4–11]. In EHDP, an electric voltage is applied to an electrode pair consisting of a conducting template and a conducting substrate coated with a polymeric film either in contact (i.e. electrowetting driven structure formation, EWSF) or separated by an air gap (i.e. electrically induced structure formation, EISF) to actuate the flow and deformation of the polymeric film upwards to the template, forming an EHDP structure [12–19]. EHDP, unlike some other lithography technologies such as UV imprint lithography and hot embossing, only needs a minimized external pressure to maintain proper contact or clearance of the template over the polymeric film so as to avoid poor geometrical integrity of the duplicated structure or even irreversible damage of the template and substrate, thereby promising high integrity and throughput [18].

In practice, the performance of EHDP depends upon the polymeric fluids to a certain extent, since some restrictions in achieving high-performance EHDP, such as room-temperature processing (which is strongly desirable for the electronic systems on flexible substrates), faster replication dynamics, higher aspect ratio and smaller feature size, originate from the comprehensive properties of EHDP materials. The rheological behavior of the polymeric fluid noticeably governs the length scale of EISF and remarkably affects the time scale of both EWSF and EISF as well. Sharma et al. experimentally demonstrated that the instability length scale in a viscous polymeric film is governed by a competition between electrostatic pressure and surface tension, whereas in an elastic solid film is dependent linearly on the film thickness, regardless of the field strength or elastic modulus [20]. Goldberg-Oppenheimer et al. showed that the use of low-viscosity polymers evidently reduced the completion time [21,22]. Apart from the rheological behavior, the electrical property of the polymeric fluid would influence the process of EHDP significantly. Quilliet et al. theoretically demonstrated that a larger reduction in the contact angle at a

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* Corresponding author.
E-mail address: dmyu@mail.xjtu.edu.cn (D. Yu).

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given applied voltage could be achieved in electrowetting on dielectric (EWOD) by using a leaky dielectric droplet compared to a prefect one, paving an innovative way for rapid fabrication of a higher-aspect-ratio micro-/nanostructure via EWSF [23–25]. Russel et al. theoretically and experimentally demonstrated that the characteristic wavelength λ and the characteristic time τ of EISF were shorter for a leaky dielectric or a perfect dielectric with high dielectric constant compared to a perfect dielectric with low dielectric constant, providing a novel route to fabricate a micro-/nanostructure with smaller feature size, faster growing dynamics and higher aspect ratio via EISF [26–31]. In addition, the reduction in the surface tension of the polymeric fluid is beneficial to fabricating a micro-/nanostructure with small feature size, fast replication dynamics and high aspect ratio in EISF [32–34]. For instance, Lin et al. demonstrated that the reduction in interfacial tension by substituting the air gap with another layer of polymeric fluid led to a significant reduction in the characteristic wavelength λ.

A feasible strategy to fulfill high-performance EHDP is exploring new multicomponent materials, since the beneficial property of each component can be well integrated. Along this line, a leaky dielectric photoresist is proposed as a highly potential EHDP material with all beneficial features for high-performance EHDP. However, commonly used photoresists are perfect dielectric. Available routes for transforming perfect dielectric into leaky dielectric, such as incorporating conducting fillers [35–38] or ions [39–41] into insulating matrix, have been developed extensively. However, the suitable leaky dielectric photoresists are in reality rare due to the comprehensive requirements of high-performance EHDP materials, including suitable rheological behavior (viscous fluid with low viscosity), leaky dielectric property (controllable electrical conductivity) as well as high homogeneity (especially during its flow and deformation under an applied external field), minor surface tension, favorable wettability and film-forming ability on substrate, and fast solidification rate.

In the previous study, we presented a leaky dielectric photoresist with a high dielectric constant (up to 24.5) and a high electrical conductivity (ca. $3.5 \times 10^{-3}\ \mathrm{S\,m^{-1}}$), based on which, EHDP structures with a high aspect ratio up to 5 were fabricated rapidly [42,43]. However, the rheological behavior and electrical properties of that leaky dielectric photoresist could not be systematically investigated by changing its composition due to the relatively low solubility of the soluble semiconducting polypyrrole (PMAEPy) in chloroform. As a consequence, the effect of the rheological behavior and electrical property of that leaky dielectric photoresist on its process of pattern formation in EHDP was not investigated experimentally and theoretically. In addition, the instability evolution of that leaky dielectric photoresist in EISF was not monitored because of the lighttight of the Si-substrate.

In this paper, a leaky dielectric photoresist was designed at molecular level and prepared by doping a soluble semiconducting polypyrrole (poly(2-methyl-1,3-di(1H-pyrrol-1-yl)propan-1-one, PMDPP) into an UV-curable resin (bisphenol A (4) ethoxylated dimethacrylate, BEMA) to fulfill high-performance EHDP. BEMA was also chosen as the matrix because of its extremely low viscosity, fast polymerization kinetics and excellent mechanical strength after photocuring. PMDPP was designed and prepared as new conducting filler because of its ultralow molecular weight (a number-average molecular weight of 1203 and a weight-average molecular weight of 2416), suitable electrical conductivity (ca. $9.1 \times 10^{-3}\ \mathrm{S\,m^{-1}}$) and the relatively high solubility in tetrahydrofuran (THF). The rheological behavior and electrical properties of the photoresists were systematically investigated by changing the composition. The photoresists showed high homogeneity, minor surface tension, favorable film-forming ability and an extremely large reduction in the contact angle of EWOD. Moreover, the effect of the electrical conductivity and the rheological behavior of the photoresists on the process of pattern formation in EHDP was experimentally and theoretically carried out concerning the structural aspect ratio, the structural feature size and the replication dynamics. Finally, the instability evolution of photoresists in EISF was monitored.

2. Experimental section

2.1. Materials

BEMA was purchased from Guangzhou Deco Composite Technology. The photoinitiator, 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP), was purchased from Zibo Pioneer Import & Export Co. Ltd. PMDPP was prepared according to the procedure described elsewhere [44]. Trimethoxy(1H,1H,2H,2H-heptadecafluorodecyl)silane (FAS) was purchased from SICONG chemical Reagent Co. Ltd. Reagent grade THF and isopropanol was purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. Indium tin oxide (ITO)-coated glass slide with a resistance of 8 Ω cm were used as a transparent electrode for in situ optical observations and the UV light transmittance. Polyimide (PI) films with thicknesses of 25 and 50 μm were used as electrode pair spacers.

2.2. Experimental procedures

2.2.1. Preparation of the photoresists

A finite amount of PMDPP was added into the solvent THF and was mechanically stirred for 1 h at room temperature to obtain a series of well-dissolved dilute and semidilute PMDPP solutions with different ω_{PMDPP} (the weight fraction of PMDPP). Subsequently, a finite amount of BEMA and HMPP was added into the prepared PMDPP solutions and was mechanically stirred for 12 h to obtain a series of homogeneous photoresists [38]. The components of the photoresists *A*, *B*, *C* and *D* were shown in Table S1.

2.2.2. EWOD of the photoresist droplet

The experimental schematic diagram of EWOD for a photoresist droplet was illustrated in Fig. 1. A doped n-type silicon electrode was coated by a photoresist droplet. It was worth noting that the doped n-type silicon electrode was coated with a dielectric SiO_2 film (about 500 nm) and treated by FAS. Opposing it, a Pt wire electrode with a radius of 100 μm was immersed in the photoresist droplet. Then a continuous square-wave voltage with 10 Hz supplied by a function/arbitrary-waveform generator (AGILENTER 33220A) was applied across the electrode pair. Finally, the response of the photoresist droplet was recorded. All the procedures above were carried out at ambient temperature.

2.2.3. EHDP of the photoresist film

The experimental schematic diagram of EHDP for a photoresist film was illustrated in Fig. 2. A transparent ITO-substrate electrode was coated by a photoresist film using SIYOUYEN KW-4A spin-coater. The

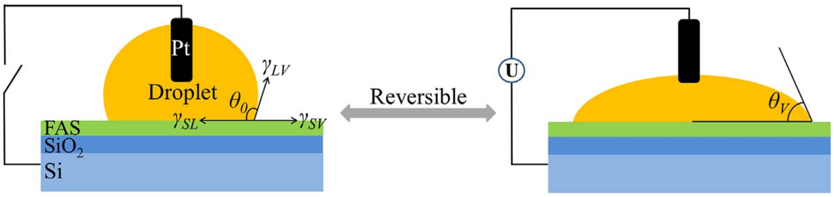

Fig. 1. Schematic illustration of EWOD for a photoresist droplet.