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Electrohydrodynamic patterning in a curable resin over a wide range of fabrication parameters

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ABSTRACT

This work reports the first use of a room-temperature curing epoxy resin to produce microscopic arrays of ordered 2-D structures via electrohydrodynamic instability (EHD) patterning. The measured spacing of these structures, and the formation of novel 'starburst' shapes, support a leaky dielectric theoretical model over perfect dielectric ones. The existence of the starbursts implies that traces of ionic residues in the uncured epoxy should be taken into account in any model of the patterning process, and their formation implies that mobile surface charges arising from trace ionic impurities must be considered when seeking to achieve smaller length-scale structures in epoxy by EHD using flat electrodes. Samples patterned in the μm range showed mid-infrared spectral features with wavelength maxima that broadly scaled with the pillar spacings in the films.

1. Introduction

Patterning polymers at the micro- and sub-micrometre scale has applications in a large and diverse range of fields from diffraction gratings and optical lenses, to tissue culture, sensing devices and even the treatment of surfaces to prevent the build-up of ice crystals [1–3].

Surface structures at these scales are generally produced by techniques such as photolithography and nano-imprint lithography. Typically, a photo-mask pattern is transferred to a photoresist material in order to protect areas of a silicon wafer prior to etching and the production of devices or moulds. These kinds of technologies are capable of achieving high resolution and reproducibility, but can sometimes be expensive and equipment-heavy, and many studies are being conducted into ways of fabricating micro- and nano-structured surfaces by simpler and cheaper technologies.

The technique of using an electric field to destabilise the interface between two fluid layers has been broadly understood for many decades, but in recent years there have been developments in its use as a micro- and nanoscale fabrication method called electrohydrodynamic (EHD) instability patterning. Most of this work has been done with thermoplastic polymers, especially poly (methyl methacrylate) (PMMA) and polystyrene (PS), but other materials have also been used, such as UV-curing polymers and sol-gels [4–7].

In EHD patterning, a fluid is applied to one electrode in a flat plate capacitor which is separated from the second electrode by an insulator such as air (Fig. 1A). A voltage is applied across the two electrodes, which creates an electric field both in the polymer and the insulator. It is the mismatch between these two fields that creates an electrostatic pressure at the interface and destabilises the surface of the fluid (Fig. 1B). Pillars or disks can then form, and when the fluid is solidified the structures are permanent (Fig. 1C).

A range of wavelengths initially exists at the interface, which grow in amplitude at different rates. The interaction between

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Fig. 1. (Blue: electrode; red: spacer; yellow: patternable fluid.) (A) no applied voltage. (B) initial instability. (C) fully-evolved structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrostatic stress and capillary pressure means that a certain wavelength, characteristic of the fabrication parameters, grows most quickly and dominates the overall structure and centre-to-centre spacing of the final column array.

In comparison to other methods, the simplicity of this technique is a great advantage and it has the potential to produce patterns on the micro- and nanoscales without the need for expensive lithographic equipment. Functional surfaces using EHD patterning have already been produced, such as substrates for surface-enhanced Raman scattering spectroscopy (SERS), micro lens arrays and surfaces for use in vapour sensors [8–10].

In addition to its simplicity, EHD patterning technique is very versatile: any fluid can potentially be used, and although a variety of substances other than thermoplastics have been examined, there are still a great many materials that could be tested. The process itself offers a number of readily-modified parameters that may be used to provide control over the patterns produced.

Previous work in this area has both used plain, unpatterned electrodes and electrodes with a patterned surface of raised conductors. Using plain electrodes, EHD patterns in thermoplastics (PMMA and PS) with wavelengths of 2–3 μm have been produced. However, the heights of these patterns, limited by the electrode spacing, were between 200 and 500 nm, creating disks rather than pillars such as those of Schäffer et al. and Lau and Russel [4,11,12]. Other research by Dickey et al. has used plain electrodes to pattern a photocurable polymer, creating wavelengths of around 17 μm with disk heights of 2.5 μm [6].

When a patterned electrode is used, the raised patterning creates areas between the electrodes where the electric field is greater. The long-range order of the pattern can be controlled in this way, which may be advantageous for some applications, but processing the patterned electrodes can be expensive and requires specialist equipment. Patterned electrodes have been used with thermoplastics by Wu et al., who created disks with wavelengths of about 4–5 μm and heights around 200 nm in PMMA [13]. Sol-gel precursors have been used with patterned electrodes to produce inorganic oxide features with wavelengths around 2.5 μm and a height of 38 nm [5].

The objective of the present work was to use EHD instabilities to produce micro-patterned surfaces without the use of photomasks, since to some extent the benefit of the technique is vitiated by the use of electrodes that need to be patterned by photolithography. Our study has explored the scope for scale reduction of the patterns that can be obtained using simple flat plate electrodes with a room-temperature curing epoxy resin as the patternable polymer and air as the gap material.

This paper describes a method for patterning a two-part epoxy resin at the micro-scale by a simple benchtop method that could be replicated in any laboratory. A comparison of the practical results with those derived from current theory is also presented. Some effects that interfere with the production of a regular array of columns are also reported and discussed, such as the coarsening of the patterns and some possible reasons for this phenomenon.

2. Materials and methods

The basic experimental cell had a simple flat-plate capacitor configuration, as shown in Fig. 1. The cell was approximately 20 mm × 20 mm in basal area.

2.1. Patternable polymer

Many EHD patterning studies reported by other groups have used thermoplastic polymers which require a heating and cooling cycle to process the polymer. In some cases, where high molar mass polymers were used, patterning took several days to complete [4,12]. UV-curing polymers have been tested to overcome the need to heat the substrate, although they clearly need a UV source [6], and the polymers can be expensive and sensitive to ambient light. In this study, Bostik Evo-Stik Control® epoxy resin was used as the patternable fluid (Fig. 1a). It is a two-part commercial resin that does not require thermal or UV curing, with a nominal setting time of 2 h at room temperature.

The two components of the resin were very viscous, so in order to obtain a homogeneous spin-coatable liquid, they were dissolved in a solvent and then spin-coated. The hardener fully dissolved in toluene, whereas the resin would only dissolve fully in acetone. Therefore each part was dissolved in the appropriate solvent and then the two solutions were combined (to give the recommended 1:1 ratio) and freed from traces of suspended matter using a 0.22 μm filter. The mixed solution was then capable of being spin-coated and the thickness of the coating was controlled by adjusting the viscosity of the initial solutions and the spin speed (1000–4500 rpm). The viscosity was of course dependent on the concentration of the solution, which ranged from 150 to 320 g L^{-1}. Smooth, homogeneous layers of resin with thicknesses ranging from 0.1 to 40 μm were prepared in this way.

2.2. Electrode fabrication

The bottom electrodes of the EHD cell were constructed from n-type doped silicon wafers (conductivity typically 100 S m^{-1}), and