Journal of Colloid and Interface Science 378 (2012) 201–209

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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Self-organised microdots formed by dewetting in a highly volatile liquid

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ARTICLE INFO

Article history:
Received 24 November 2011
Accepted 3 April 2012
Available online 18 April 2012

Keywords:
Hexagonal and tetragonal order
Dewetting
Self-organisation
Iron oxide microstructure
Microdot
Stick–slip motion
Receding contact line

ABSTRACT

Dewetting induced self-organisation was used to prepare an ordered microstructure from a highly volatile liquid. Dewetting of an evaporating iron oxide precursor solute on silicon substrate resulted in arrays of microdots with nearly hexagonal and tetragonal symmetries. Ordered structures form either by stick–slip motion or fingering instability at the receding contact line of evaporating droplets. Subsequent thermal treatment at 550 °C yields crystalline Fe_2O_3 microdots with a diameter range of 1–4 μm. The size, density and shape of the microdots can be changed by using patterned substrates with different surface energies.

1. Introduction

Synthesising materials with ordered microstructures has attracted increasing interest recently. Functional materials with periodical patterns have a range of applications, for example optical devices, sensors, and photoelectrodes.

The conventional methods to pattern materials are the so called top-down techniques, which are based on fabrication of the material by removing parts of it, i.e. lithography methods. Recently, interest has turned to the so called bottom-up approaches, where the structure is formed from building blocks. Building blocks are typically organic molecules, nanoparticles, etc., which self-assemble or self-organise into larger aggregates induced by intermolecular interactions, e.g. van der Waals forces, electrostatic interactions, hydrogen bonds or hydrophobic effects. Self-assembly is a process driven by the chemical potential towards the thermodynamic equilibrium. Self-organising systems have to be kept far from the equilibrium by continuous supply of matter or energy in order to increase its entropy [1–3].

Solvent evaporation and dewetting are simple, inexpensive, bottom-up surface patterning methods to organise non-volatile materials into ordered microscopic structures. Pattern formation driven by the dewetting of an evaporating solution is a self-organisation process since the entropy of the entire system increases by the heat loss due to the evaporating solvent, even though a part of it, the solute, organises into droplets. Solvent evaporation induced dewetting can lead to the formation of micrometer-sized droplets [4]. Solvent evaporation methods based on a moving three-phase contact line have been employed to form ordered structures of materials ranging from small organic molecules [4,5] and polymers [6–9] to nanocrystalline salts, nanorods and nanoparticles [10–12]. Various models were developed to reproduce several aspects of the experimental findings [13–15]. The recession of the contact line, i.e. the edge of an evaporating liquid drop on a solid substrate, can also be non-continuous, causing a so called stick–slip motion, i.e. fast receding is followed by "pinning" [5,6,14]. At each stick–slip step, regularly spaced droplets or stripes parallel to the contact line are deposited on the substrate where the contact line was pinned. The pattern consists of droplets or lines, depending on the type [6] and the concentration of the employed materials [5]. Since dewetting is a general phenomenon of liquids, many different materials can be used: polymers [9,16,17], dye-containing polymers [18,19], nanoparticles [20], and small organic molecules in liquid phase [21]. It has also been shown that fluctuations in the solute concentration close to the contact line leads to a fingering instability [8,9,13]. The fingers recede more slowly on the substrate due to their higher concentration, i.e. higher viscosity. Therefore the fingers elongate, destabilise and break up into droplets similarly to the Plateau-Rayleigh instability found in liquid jets. In this way a 2D ordered pattern forms.

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http://dx.doi.org/10.1016/j.jcis.2012.04.011

In this paper we describe ordered iron oxide microdots with patterns reminiscent to hexagonal and tetragonal symmetry in a highly volatile iron oxide precursor solution. Pattern formation due to the receding contact line of a drop of polymer or macromolecule solution, or nanoparticle suspension has been intensively studied using single-drop deposition or dip-coating methods. Whereas spin coating as depositing technique has not been widely exploited yet for experiments with receding contact lines. During spin coating the thickness of a thin film of a volatile liquid is continuously reduced not only by evaporation but also by spinning. This combined effect can be the source of a wide variety of patterns. Here we spin coat a dilute macromolecule solution on silicon wafers. The two major processes governing the pattern formation at different stages of the spin coating process are contact line pinning and fingering instability. The receding contact lines of the drops, formed at the early stage of spin coating, shows stick–slip motion, as well as fingering instabilities. The parameters affecting the size and the order of the microdots have been investigated. The effect of the spin coating solvents has also been studied. The size, density and shape of the microdots were altered by using substrates with a pattern of different surface energies. The pattern that is obtained after spin coating consists of the solid iron oxide precursor and probably some remnant solvent. The precursor pattern is transformed to crystalline hematite pattern by following the patterning by pyrolysis at 550 °C [22].

2. Materials and methods

2.1. Materials

Iron(III)acetylacetonate (99%) and benzoylacetone (99%) were purchased from Acros Organics and Aldrich Chemicals, respectively. Methanol (gradient grade, >99.8% (GC) for HPLC) and chloroform (anhydrous, ⩾99%) were purchased from Fluka and Sigma–Aldrich, respectively. 0.45 μm, 17 mm Titan HPLC–PTFE filter membranes were purchased from Infochroma AG, Switzerland. Silicon wafers (p ⟨ 100 ⟩ >, with native oxide layer) were purchased from Si-Mat, Germany. The wafers were cleaned in acetone in an ultrasonic bath, then rinsed with ethanol and dried with compressed nitrogen. Chromium and gold pellets for metal deposition were purchased from CERAC Inc., USA. The base and curing agent for poly(dimethylsiloxane) (PDMS, Sylgard 184-Dow Corning) stamps and heptadecane-1-thiol were purchased from Troller Kunststoffe AG, Switzerland and Sigma Aldrich, respectively.

2.2. Solution preparation

The solution preparation is based on the recipe described in [23] substituting titanium butoxide with iron(III)acetylacetonate (Fe(acac)). Fe(acac) and benzoylacetone (bzac) were mixed in 1 ml methanol and stirred for 2 h at ambient temperature. To this precursor solution 3 ml chloroform (or 1-pentanol) was added and stirred for a further 15 min to produce a dilute solution for spin coating. The solution was filtered and then 0.1 ml was spin coated onto a 1 × 1 cm^2 piece of silicon wafer.

Iron(III) complexes formed with the bidentate ligands acac and bzac have similar stoichiometry (MA^{2+}, MA_2^+, MA_3) and stability on the basis of literature data [24], however, complexes of bzac represent slightly higher stability. The original form of the $[Fe(acac)_3]$ may be varied by changing its analytical (total) concentration, the acac-to-bzac ratio and the solvent; and species such as $[Fe(acac)_2]^+$, $[Fe(acac)(bzac)]^+$ can form and may become major species (for more information see Supplementary data, S2). While in the nonpolar chloroform solvent the neutral complexes, such as $[Fe(acac)_3]$, $[Fe(acac)_2(bzac)]$, $[Fe(acac)(bzac)_2]$ are probably more favourable, in polar solvents, such as alcohols, the $[Fe(acac)_2]^+$, $[Fe(acac)(bzac)]^+$ complexes may form more readily.

2.3. Spin coating

In order to prepare a thin film by spin coating a dilute solution is placed on a substrate and subjected to rotation. The spin coating process involves three stages. In the first stage, the solution spreads on the substrate and most of it is spun off due to the centrifugal force. After the first stage, a thin layer of solution remains on the substrate. In the second stage, this layer gets thinner as a result of liquid flow. The rapid evaporation of the solvent increases the viscosity of the solution and slows the shear thinning of the film. The pattern formation occurs in this stage. In the third stage, the solvent evaporation conserves the developed pattern. Generally, the structures are created in a nonequilibrium stage, resulting from the rapid solvent quench, since typical spin coating times are only 30–60 s. Due to the rapid solvent quench, the patterns solidify during spin coating and the final pattern is the dried solute (with some residual solvent).

The films were spin coated in two steps with low acceleration. In the first step 500 rpm was reached with 100 rpm/s acceleration in 5 s (spreading and hydrodynamic thinning phase). In the second step the spin coater was accelerated with 300 rpm/s to 4000 rpm (evaporative thinning). The second spin speed was varied between 2000 and 6000 rpm.

2.4. Characterisation

Images were recorded using an optical microscope (Leica) attached to a camera.

A thermographic camera (model: Cedip Jade III MWIR, from Cedip Infrared Systems, SAS, (now FLIR), France) was used to follow the temperature change during spin coating.

Laser reflectometry (laser diode from ILEE, Switzerland (www.ilee.ch), model V35MV1, lambda = 750 nm) was used to determine the initial thickness of the film prior to evaporation and to follow the thickness evolution over time [25].

The grazing incidence X-ray diffraction (GIXRD) spectra have been taken with a Siemens D5000 diffractometer with Cu K(α1) wavelength source. The incidence angle was fixed at 3° for the entire measurement and the diffraction signals were collected from 20 to 80°.

3. Results

When a solution of equimolar amounts (50 mM final concentration each) of Fe(acac) and bzac dissolved in chloroform is spin coated onto silicon wafers, highly ordered microdots form. Some areas have nearly hexagonal, others tetragonal symmetry (Fig. 1). The diameter of the dots varies between 1.4 and 4 μm and the distances between them is 2.6–10 μm, depending on the experimental parameters (discussed later). The height of the microdots is around 100–200 nm. Quantitative analysis of the AFM height profile of a representative area with dots (Fig. 1b) yields an average dot height of 110 nm ± 17.5 nm and a full width at half maximum (FWHM) of 1.61 μm. The centres of the dots are separated by 6.1 μm from each other. Fig. 1b shows the profile fitted with a series of Gaussians with 1.61 μ FWHM and separation of 6.1 μ. Fig. 2 shows the temperature transient during spin coating, obtained by a thermographic camera. Infrared radiation of a 2 mm × 2 mm area in the middle of the substrate is measured. The measured infrared radiation is corrected by the emissivity of the substrate (0.8) in order to obtain the true temperature transient. In the first 3–4 s the film and substrate cool down to a minimum temperature and in