Sensors and Actuators A 155 (2009) 253–262

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Post processing of microstructures by PDMS spray deposition

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ARTICLE INFO

Article history:
Received 11 December 2008
Received in revised form 28 August 2009
Accepted 31 August 2009
Available online 10 September 2009

Keywords:
PDMS
Spray deposition
Wafer bonding
Embossing
Soft lithography

ABSTRACT

A method of depositing polydimethylsiloxane (PDMS) onto microfabricated surfaces by spray coating is presented. Low-viscosity PDMS combinations suitable for spraying are developed by mixing Dow Corning Sylgard 184 with 200 Fluid 20 cSt, and also by dilution with hexane. Spray coating is carried out on rotating substrates using blank Si wafers. Film quality is characterised with mechanical and optical profilometry and process parameters are optimised to yield micron-scale thickness with low surface roughness. High gas pressures and substrate motion improve the quality of sprayed films. The coating process is extended to microstructures formed by lithography and etching of silicon, and it is found that heating to accelerate cross-linking improves conformal coverage. The material can be used in many applications requiring spin coated or cast PDMS. Spray coated PDMS can be used as an adhesion layer and construction of microfluidic channels is demonstrated by plasma activated bonding. The coatings can also adsorb alkanethiols and micro contact printing is demonstrated using embossed, spray coated PDMS and using spray coated etched stamps.

1. Introduction

Siloxane-based elastomers such as polydimethylsiloxane (PDMS) have been heavily exploited in microtechnology, since they are non-toxic, biocompatible and commercially available. PDMS allows low cost fabrication by casting to form structures with feature sizes down to ≈100 nm [1–3], for example for moulds and stamps for nanoimprint lithography [4–6]. Alternative structuring methods such as photocurable PDMS compositions [7] and CO_2 laser ablation [8] have also been explored. PDMS is intrinsically hydrophobic, but can be made hydrophilic by a short exposure to oxygen plasma. Freshly oxidised PDMS surfaces can be bonded to each other or to other common microfabrication materials, such as SiO_2 [9,10]. PDMS is very flexible (Young's modulus $E = 1$ MPa), but its stiffness can be increased by a supporting layer [6]. It is optically transparent at wavelengths above 300 nm. PDMS is relatively porous, with a strong tendency to adsorb certain molecules [11]. This property is disadvantageous in analytic devices, where it can lower separation efficiencies [12]; however chemical modifications can be used to tailor surface properties [13]. It is exploited in the alternative application of micro contact printing (μCP) [14,15], in which a patterned PDMS stamp is used to adsorb alkanethiol inks. The inks are then transferred to a gold surface as a self-assembled monolayer, by binding of the terminating thiol (–SH) group to the Au [16].

PDMS has found many applications in microfluidic and micro-total-analysis systems (μTAS). PDMS components range from fluid channels [17,18] to seals [19], valves [20] and pumps [21], mixers [22], cyclers for the polymerase chain reaction [23], capillary electrophoresis separators [8,24] and electrospray nozzles [25]. Pharmaceutical applications include porous PDMS membranes to control the release of drugs in dermal patches [26] and tablet coatings [27]. Exploiting its natural transparency, PDMS has been used to form optical waveguides [28,29], often for readout of μTAS. Exploiting its flexibility, PDMS has been used to form varifocal lenses [30] and tuneable gratings [31].

In most applications, a two-part heat-curable PDMS is cast or spin-coated onto micro-fabricated structures (usually formed in Si/SiO_2, SU-8 photocurable epoxy resist or glass) to form a relatively thick (10–1000 μm) substrate containing microscale features. The PDMS layer is then detached. Depending on the application, the PDMS surface is oxidised and bonded to a further substrate, or inked with alkanethiol for μCP. Casting and spin-coating are, however, inappropriate for coating deep trenches or valleys, or completed microelectromechanical systems (MEMS) such as suspended cantilevers. Furthermore, many fabrication steps involve relatively high temperatures, which may raise the PDMS above its stable range (typically 200 °C) if deposited at the start of the process. In this paper, we therefore consider the alternative of depositing PDMS by spray coating, which has the added advantage over spin coating that the film may easily be localised using a stencil.

Spray coating has been extensively investigated for deposition of photoresist onto three-dimensional microstructures [32–39], for example using the EV101 spray-coater (EV Group, Innsbruck,

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doi:10.1016/j.sna.2009.08.029

Germany) [40]. Diluted, low-viscosity resist [36,38] and a high carrier gas flow [34] are required to obtain small droplet sizes, and hence low surface roughness. Ultrasonic atomization may also be used [35]. A rapidly evaporating solvent or a heated sample is also required for conformal coverage of raised features [33,35,38], and other techniques such as resist migration can be used to reduce defects further. Spray coating has also been used for deposition of sol–gel materials [41,42], and the related method of electrospray has been investigated [43,44]. Spray coating of PDMS has, however, so far received very limited attention [27,29]; this is surprising, because the method would allow deposition at room temperature after completion of other process steps.

Here we present preliminary results for spray coated PDMS films, which demonstrate that similar conditions (rapid gas flow, low solution viscosity and rapid curing) are required to combine low surface roughness with good coverage of surface topography. Section 2 outlines the deposition process used, which involves spray coating on a rotating stage, and addresses the issues faced in preparing low-viscosity compositions and obtaining a uniform coating. Section 3 presents experimental measurements of deposited thickness and surface roughness and highlights optimum coating parameters. Section 4 investigates the coating of raised microstructures and describes the techniques used to achieve conformal coverage. Section 5 confirms the applicability of spray coated PDMS for plasma-activated bonding and alkanethiol ink transfer and demonstrates applications in microchannel construction and micro contact printing. Conclusions are presented in Section 6.

2. PDMS spray deposition process

The overall aim in spray coating is to obtain small droplets from an atomized spray, to minimise surface roughness while still achieving a uniform, pinhole-free film. In this section, we briefly review the theoretical background to atomization and introduce the materials and experimental apparatus used for spray coating. We show that the key process parameters are the spray injection pressure and the PDMS viscosity.

2.1. Atomization

Spray coating is carried out by a process akin to coaxial atomization, in which a high-speed coaxial gas stream is used to break up a liquid jet and disperse it into droplets much smaller than the jet diameter. When air is used, the process is known as air-blast atomization. A similar mechanism is used in cryogenic rocket engines, in which a liquid oxygen jet is atomized by a high-speed annular flux of hydrogen [45]. Despite considerable recent efforts, recently reviewed in [46], coaxial atomization is still relatively poorly understood. The physical processes are different to those occurring when the liquid jet discharges into stagnant gas [47]. For this case, Rayleigh investigated the break-up mechanism in 1879, and proposed a hydrodynamic instability due to surface tension. In 1931, Weber showed in turn that viscosity has a stabilising effect. For coaxial atomization, additional processes can occur by a transfer of kinetic energy from the gas to the liquid, and Varga et al. [48] have shown a series of instabilities is involved. A Kelvin-Helmholtz instability first develops in the annular shear layer at the liquid discharge nozzle, creating surface ripples in the liquid that grow into tongues and vortex sheets. Rayleigh–Taylor instabilities then develop at the crests of the tongues due to the action of the light gas pushing against the heavier fluid. The instabilities strip the fluid from the tongues as a series of fine ligaments and droplets (Fig. 1a).

The exact details of spray formation are complicated, and depend on the values of a set of dimensionless parameters.

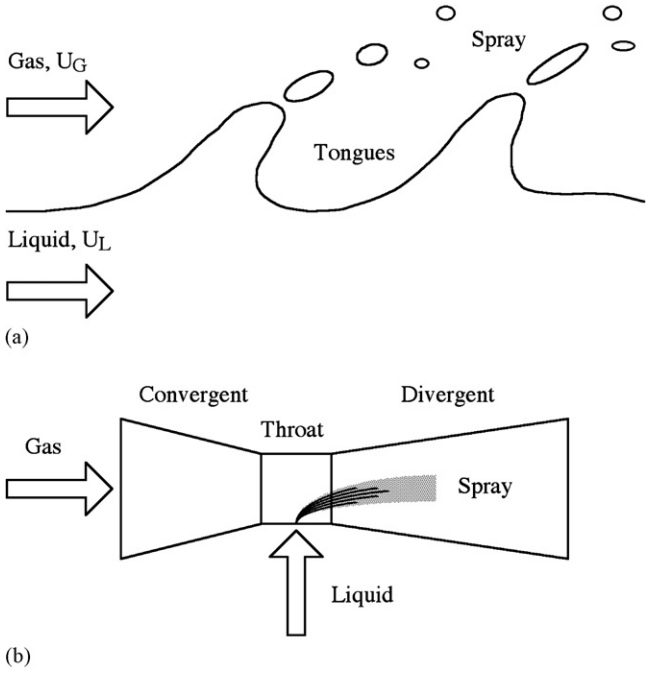

Fig. 1. (a) Schematic of the process of co-axial atomization; (b) Venturi sprayer.

These parameters include the gas and liquid Reynolds numbers $Re_G = U_G\rho_G(D_G - D_L)/\mu_G$ and $Re_L = U_L\rho_L D_L/\mu_L$, which define the ratio of inertial to viscous forces, the gas Weber number $We_G = \rho_G(U_G - U_L)^2 D_L/\sigma$, which defines the ratio between the pressure force of the gas on the liquid and the confining force of surface tension, and the Ohnesorge number $Oh = \mu_L/(\rho_L D_L \sigma)^{1/2}$, which defines the ratio between viscous and surface tension forces. Here ρ is density, μ is dynamic viscosity, σ is surface tension, U is velocity, D is the diameter of the flow, and the subscripts L and G denote liquid and gas respectively. The momentum flux ratio $M = \rho_G U_G{}^2/\rho_L U_L{}^2$ and the mass flux ratio $m = \rho_L U_L A_L/\rho_G U_G A_G$ are also important, where A is cross-sectional area of the flow. It is generally accepted that the droplet size reduces with a decrease in liquid viscosity and also with an increase in gas velocity and in the gas/liquid mass-flow ratio. However, complications arise from the use of non-Newtonian liquids [49].

Further complications arise from the use (as here) of a Venturi nozzle. Venturi scrubbers use a liquid spray to remove particles entrained in the gas, and have been again studied extensively. Different arrangements exist; in ejector scrubbers, the liquid is introduced axially into a gas flow upstream of the throat of a convergent/divergent nozzle [50], while in Pease-Anthony scrubbers, it is introduced transversely through one or more nozzles at the throat (Fig. 1b) [51]. In the latter case, the cylindrical symmetry associated with co-axial atomization may be lost. Although the atomization mechanism must be similar, theoretical models have been less detailed because of these distinctions and spray size distributions tend to be empirical. A widely-accepted expression for the Sauter mean diameter D_{32} of the drops originally proposed by Nukiyama and co-workers has the form [52,53]:

$$D_{32} = \{0.585/(U_G - U_L)\}\sqrt{(\sigma/\rho_L)} + 1.683 \times 10^{-3}\{\mu_L/\sqrt{(\rho_L\sigma)}\}^{0.45}(1000\,Q_L/Q_G)^{1.5} \quad (1)$$

Here Q_L and Q_G are volumetric flow rates, the various constants are in SI units and D_{32} is in metres. Other empirical expressions exist [54], but these and Eq. (1) again point to a need for a low liquid viscosity, a high gas velocity and a high gas/liquid mass flow ratio.