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A scalable anti-sticking layer process via controlled evaporation

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ABSTRACT

We developed a novel process for the deposition of anti-sticking layers from the gas phase based on the use of evaporation cells. The cells are prepared from Teflon and consist of small silane containers with an orifice. Temperature is used to provide a silane-containing gas phase in the containers; the temperature is well below the boiling point of the silane. The number of cells can be varied to improve the uniformity with respect to surface energy, to scale-up the process to larger diameters and to reduce the processing time required. The impact of cell number, processing temperature and processing time is investigated with respect to uniformity and with respect to the minimum times and temperatures required. The concept works well and shows potential for the control of surface energy beyond anti-sticking purposes.

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1. Introduction

Nanoimprint as a contact process ultimately requires anti-sticking layers in order to provide a low adhesion and thus a preferred separation at the stamp-polymer-interface. It is well known that in order to be long-living [1], these layers have to be bonded to the stamp surface. Additionally, they should be thin (preferably monolayers) in order not to affect the dimensions of the stamp and thus the dimensional fidelity of the replication [2,3]. Fluorinated silanes are suitable materials, as (i) they provide the low surface energies (typically 15–20 mN/m) required for low adhesion, as (ii) they can be attached to an OH-terminated Si- or SiO_2-surface via chemical bonds and as (iii) they form monolayers in the nanometer range as long as self-polymerization of the silane is avoided by providing a water-free environment during processing. Being independent from solvent wetting of small capillaries, deposition from the gas phase is superior to a deposition from the liquid phase, in particular with stamp cavities in the nanometer range [2,3].

Gas phase deposition processes are well described and well characterized in the literature. The process according to Beck [2] works at atmospheric pressure, where the silane is dropped besides the sample in a Petri dish and deposition proceeds at 200–250 °C; the process described by Jung [3] operates with a flow of evaporated silane under vacuum, and the whole process consists of three consecutive steps of silane and water evaporation; a further process described by Schift [4] also works under vacuum, where the liquid silane is injected into the vacuum chamber via a syringe through a membrane. Processes combining vacuum and temperature are also described [5].

We developed a different process based on the use of evaporation cells. The cells are prepared from Teflon and consist of small silane containers with an orifice. Temperature is used to provide a silane-containing gas phase in the containers, but the temperature chosen is well below the boiling point of the silane. Thus a low, but constant volume stream of silane is provided through the orifice throughout the whole process if a sufficient amount of silane is deposited in the container at the beginning of the process. This is different from the gas phase process of Beck [2], where the silane volume provided quickly decreases with deposition time in an uncontrolled way as the silane droplet surface area decreases. Our deposition process is slow and allows the formation of a uniform layer. This is also different from a situation, where the liquid silane evaporates in the vacuum abruptly, like in the process of Schift [4]. In-house experiments have shown that direct evaporation into a vacuum, without valve control, results in splattering and may lead to silane clusters at the sample surface. The vacuum process of Jung [3] avoids this issue. There, the silane is evaporated in a remote cell and the silane vapor is guided to the processing chamber, where a constant stream of silane is provided during the deposition time (3 times for 30 min). Our process is similar to the process of Jung, as we want to provide stationary, well-controlled deposition conditions throughout the whole processing time. But the components are simple and do not require corro-

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sion-resistive vacuum components (during silane binding HCl is formed). In addition, our process requires limited resources of silane, only. The whole process is operated within a capped Petri dish and does not suffer from corrosion of non-glassy components of the deposition system.

In addition, our process is scalable. Scalability here concerns two issues. First, we intend to develop a simple process that is up-scalable for samples of 10–15 cm diameter and provides uniform layers. To our knowledge, no uniformity investigation of anti-sticking layers is presently at hand. Second, we intend to develop a process that also allows scaling the surface energy itself. This matters for an application beyond the preparation of simple anti-sticking layers, where low surface energies (in the range of 10–20 mN/m) are asked solely. For example, with surface preparation for block copolymer self-assembly, the surface energy has to be tuned in the range of 25–40 mN/m in order to provide a 'neutral' non-preferential surface [6]. Thus, scalability of the sample size as well as of the surface energy is addressed here.

For both purposes, the concept of evaporation cells is tested here by investigating the impact of processing temperature and of processing time. In view of the uniformity of the layer across 10 cm diameter samples also the number of evaporation cells is varied. The concept is well suitable to provide uniform, low energy anti-sticking layers, working even well with undercut trenches [7]. The concept is also well suitable for a scaling of the surface energy in a time-controlled process at adequate temperature.

2. Experimental

As an anti-sticking agent $CF_3(CF_2)_5(CH_2)_2SiCl_3$ (Fluorooctatrichlorosilane, FOTS, Sigma–Aldrich) was used. Its boiling point at atmospheric pressure is at 192 °C (data sheet). Literature values [8] (vapor pressure of 0.3 Torr at room temperature) allow to provide curves of the vapor pressure as a function of temperature as shown in Fig. 1, assuming a constant enthalpy of evaporation within this temperature range. As our deposition process includes a water step, also the vapor pressure for water is given.

The deposition procedure consists of a UV-exposure (172 nm) to generate OH-groups at the Si surface in an air environment at average humidity [9], the thermal evaporation of the silane itself, followed by a thermal evaporation step with DI-water. During FOTS evaporation the fluorinated silane chemically bonds to the OH-terminated Si surface and forms a monolayer under the formation of HCl. The subsequent water evaporation provides additional OH-groups to the silane by reacting with the Cl-groups still present – it has to be assumed that only one of the three Cl-bonds forms a bridge to the Si surface. In a final temperature step the OH-groups react among themselves to crosslink the layer and to provide long-term stability. All deposition steps are performed in a glove box under dry nitrogen flow to provide controlled humidity and thus to avoid a self-polymerization of the FOTS.

The evaporation cells are prepared from Teflon, a non-corroding material, and consist of small containers with a definite orifice (0.8 mm ø, 2.4 mm long) in a detachable top cover (see Fig. 2a). Typical loading for one cell is about 50 µl of FOTS. Within the container the initial liquid height is about 1 mm and offers a constant evaporation surface of about 0.5 cm^2 throughout the process – with a loading of 50 µl there is still FOTS remaining in the container after a 90 min process at 120 °C. (The contact angle of FOTS to Teflon is around 35°, thus the container is wetted.) The total amount of FOTS atoms per cell loading is about 10^{20} (molar mass 480 g/mol, density 1.3 g/cm^3). The orifice limits the outflow of FOTS-vapor from the cell. With the geometries realized (see Fig. 2a) the maximum solid angle for direct transmission amounts to $\Omega = 0.4$ rad (6% of the full solid angle of 2π). Within the small container volume (0.45 cm^3) the silane vapor pressure is almost instantly provided, and the small orifice guides only a small amount of the evaporated FOTS molecules into the processing chamber, the Petri dish, so that the equilibrium within the cells is only marginally affected. (Similar cells are used for the subsequent water process. Here, the DI-water loading is uncritical (300 µl) and the cells are used without the cover lid.) The free path for N_2 collisions at atmospheric pressure is in the range of some micrometers, only. We expect that collisions of FOTS with N_2 are elastic and do not deplete the amount of FOTS available for deposition. As all walls have temperatures below the boiling point of FOTS, adhesion will occur there, with potential re-emission when no chemical bond is formed. In order to assure constant processing conditions, the orifice is cleaned before every process.

For an up-scaling to samples of 100 mm diameter up to 12 cells are arranged symmetrically around the wafer, held in place by a ring (see Fig. 2b) The whole assembly is operated in a closed Petri dish (diameter 16 cm, inner height 3 cm).

The procedure for anti-sticking layer deposition is as follows. 100 mm diameter Si substrates are prebaked for 15 min at 200 °C on a hotplate in order to evaporate the H_20 from the surface, followed by UV-exposure for 2 min (XERAFEX®20, OSRAM), 3 mm apart from the lamp housing. For thermal evaporation, FOTS is supplied from up to 12 evaporation cells. The whole assembly is placed in a closed Petri dish and transferred onto a pre-heated hotplate in a glovebox purged with dry N_2. After the processing time envisaged the wafer is transferred inside the glovebox into a similar second Petri dish prepared with the same number of cells, but loaded with DI water. As soon as the hotplate has reached the processing temperature for the water process (50 °C), the second Petri dish is placed on the hotplate and processed for 10 min. The final temperature step is performed on a hotplate outside the glovebox,

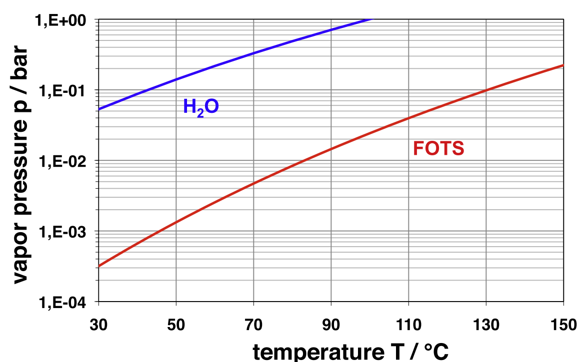

Fig. 1. Vapor pressure dependence on temperature for DI-water and FOTS. The calculation for FOTS is based on a boiling point of 192 °C at ambient pressure and a vapor pressure of 0.3 Torr at room temperature [8].

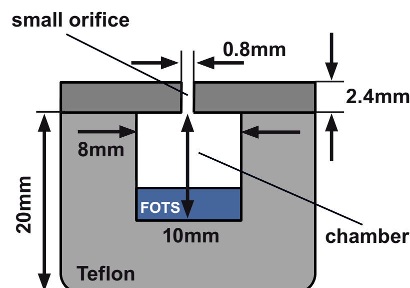

Fig. 2a. Schematics of evaporation cell. The evaporation cell is made from Teflon, a non-corroding material. It consists of the container, providing the supply of vaporized material, and a removable top-cover with a small orifice, providing a constant outflow of the vapor.

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