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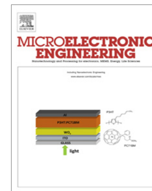

Anti-sticking layers for nickel-based nanoreplication tools

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ABSTRACT

Nickel is the preferred material for molds used in high throughput micro injection molding and roll-to-roll processes. We present different solutions for anti-sticking layers for nickel-based nanoreplication tools, which are highly desired for replication of features in the sub-micrometer and nanometer scale. Layers of fluorocarbon molecules, bound to nickel via different head groups, were evaluated via friction force and contact angle measurements, X-ray photoelectron spectroscopy and imprint tests. The robustness of fluorinated phosphates and phosphonates applied to nickel pre-treated in oxygen plasma is similar to silanes used on silicon molds.

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1. Introduction

High throughput replication by injection molding and roll-to-roll embossing is currently advancing from the micro- towards the nanometer scale. As in nanoimprint lithography (NIL), this development increases the need for robust anti-adhesive coatings [1]. This is of particular importance in the view of bio-medical applications, where the use of additives (i.e. release agents in the polymer granulate) is problematic. For such replication processes metal molds are highly desired because their mechanical properties match perfectly with the tooling requirements. For instance, in high throughput injection molding (Compact Disc molding) and roll-to-roll processes (diffractive optical elements for decoration and security features), nickel (Ni) molds are used, which are electroplated from patterned originals [2–4]. In contrast, thermal NIL preferably uses silicon (Si) molds as stamp originals because of established micromachining techniques and the identical thermal expansion coefficient between stamp and substrate to be patterned. Another advantage of Si molds is that silane based coatings can be applied as anti-sticking layers (ASL) due to their high robustness of their chemical binding to the silanol groups present on silicon surfaces [5–7]. This robustness is particularly valuable in thermal processes where the silane coating sustains repeated thermal cycles of temperatures up to 250 °C and mechanical stress by detachment and sliding during demolding. In many experiments, low surface energies – indicated by water contact angles of up to 120° – are required for detachment of nanostructures with vertical sidewalls and moderate aspect ratio. With stamps showing low water contact angles (high surface energy) not only ripping off of single structures is observed, but also detachment of entire flakes of unstructured resist. In contrast to silicon, silanes do not bind covalently to Ni, and silane-based ASLs are removed within a few cycles. Even more, the binding of silanes to oxides involves a release of HCl which may lead to corrosion of Ni. Still, there is a range of publications where the coating of silanes is proposed on Ni, on SU-8 and other materials different from SiO_2 [8]. Although it has been found that more than one imprint with sufficient release quality can be achieved, it is questionable to use a coating which works more like a lubrication film or a network of cross-linked fluoropolymers without strong binding to the substrate. These films are continuously detached from the surface and transferred onto the surface of the polymers, leading to a gradual degradation of the anti-adhesion properties of the stamp, and often already after the first imprint failure occurs.

One solution to overcome this issue is to coat the Ni mold with a SiO_2 layer in a PECVD process before a silane is applied [9]. But with this solution, not only the complexity of the coating process rises but also the original topography is modified, particularly if nanostructures with feature sizes below 100 nm have to be replicated. It has been found that a minimum thickness of 5–10 nm SiO_2 is needed to obtain maximum improvement of the anti-adhesion properties [9].

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A variety of anti-adhesive coatings for nickel, relying on the low surface energy of perfluorinated carbon chains, has been proposed. It ranges from silane based layers, which are well established for silicon stamps [6–7], to phosphates and phosphonates [10], catechols [11] and plasma-polymerized Teflon-like coatings [12]. The purpose of this work was the evaluation of suitable pre-treatment conditions of nickel surfaces and a direct comparison of layers composed of different types of chemicals as indicated in Fig. 1. For comparison plasma-polymerized Teflon-like coatings [12] and the application of silane based coatings were included in this study.

2. Experimental

As a model for Ni molds we used $2 \times 2\,cm^2$ sized silicon stamps nanostructured with electron-beam lithography (EBL) and reactive ion etching (RIE). The stamps contained various fields with line and dot structures with feature sizes down to 50 nm etched to 400 nm depth. The stamps were subsequently coated with a thin film of Ni, which enables to produce a range of identical molds needed for comparison. Furthermore, this fabrication method enabled us to fabricate stamps in a straightforward way on standardized substrates (e.g. $20 \times 20\ mm^2$ chips or 100 mm wafers) which were comparable with the silicon stamps used for silane coating. The stamps provide the same thermal expansion as Si (as long as the underlying bulk of the substrate is large in comparison to the structures) and can be cleaved for scanning electron microscopy (SEM) analysis. Furthermore they can be used in standard thermal NIL processes for better qualitative and even quantitative comparison of abrasion or distortion. As a disadvantage, the additional coating changes the overall topography of the mold and may even lead to a slight undercut due to shadowing during evaporation/sputtering. A coating of 10 nm Ni was considered thin enough to limit this modification. An oxygen plasma treatment (2 min/50 W/10 Torr) was applied to remove organic residues and to form a surface layer of nickel oxide which allows the application of the various layers via electrostatic interactions. Chemicals used are shown in Fig. 1. Heneicosafluoro-dodecylphosphate (HFDP) and tridecafluoro-octylphosphate (TFOP) were synthesized in house (see Supplementary information), perfluoro-octanephosphonate (PFOP) was purchased from Sigma–Aldrich, and N-(4,5-dihydroxy-2-penethyl)-2H,2H,3H,3H,-perfluoro-undecanamid (PFAND) was obtained from Clement Cremmel, ETHZ. All chemicals were dissolved in methyl tertiary-butyl ether (tBME) and diluted to a concentration of 10 mg/mL. The ASL were applied by immersion of the substrates within 30 min after the plasma treatment in these solutions for 2 h. The coated substrates were thoroughly rinsed with tBME and dried in a stream of nitrogen. The fluorocarbon layer (C_xF_y) was deposited in a plasma process using C_4F_8 as the process gas and the silane coating was applied in a vacuum reactor according to published procedures [7]. The long-term stability of the layers was then tested in sequences of thermal imprints into a 500 nm thick PMMA layer spin-coated ($M_W = 25$ kg/mol) onto silicon chips. Imprints were done for 10 min with an applied force of 200 kN at 180 °C. After cooling to 80 °C the pressure was released and demolding was performed manually using a razor blade. The molded structure, as well as the stamp, were checked for abrasion and residues in an optical microscope and further evaluated with SEM. The stamps were characterized after each step using water contact angle measurements.

3. Results and discussion

3.1. Stamp pretreatment

The evaluation of suitable stamp pretreatments was based on the results of a reliable coating with HFDP as described below. The primary criterion was the reproducible achievement of a high contact angle (>110°) over entire surfaces of $20 \times 20\,mm^2$. Pretreatments included cleaning with organic solvents in ultrasound to remove organic residues, and treatments in an UV/ozone cleaner as well as using oxygen plasma. Cleaning with oxidizing liquids such as piranha etches frequently used for silicon was ruled out as it would etch the nanostructures.

The organic solvents turned out to be inefficient, probably because they leave the nickel in the metallic state and unsuitable for binding chemicals via ionic or covalent bonds. In contrast oxygen plasma resulted in reliable coatings, due to surface oxidation as revealed in X-ray photoelectron spectroscopy (XPS) measurements. Ni2p spectra (see Supporting information) indicated that the surface of oxygen plasma treated nickel was in the oxidized state. Sputter profiles, however, showed that oxidized layer was less than 5 nm thick, which is acceptable with the intended replication of structures in the 100 nm range.

UV/ozone treatments resulted in less efficient coating with HFDP compared to oxygen plasma treated surfaces. Ozone efficiently oxidizes organic residues, but apparently the oxidation power is not strong enough for a quantitative transformation nickel of the topmost nickel layers into nickel oxide. This explicable by the less oxidizing power of ozone generated in an UV/ozone cleaner in comparison with oxygen radical species which are produced in a plasma.

3.2. Evaluation of the coating

In this study, chemicals with different potential binding chemistries were investigated. Phosphates, phosphonates and catechols (Fig. 1) allow electrostatic interactions between negative charge of

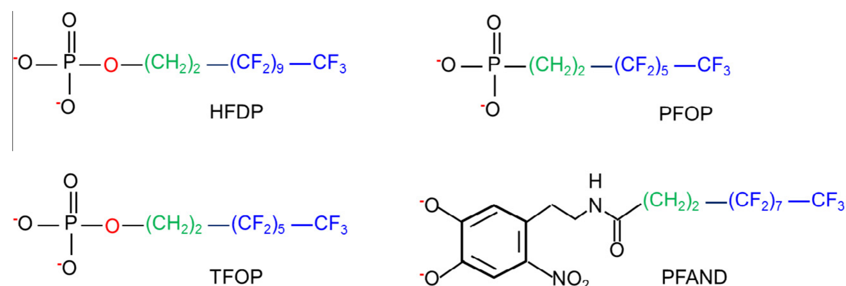

Fig. 1. Substances used for anti-sticking layers on nickel: HFDP, heneicosafluoro-dodecylphosphate; TFOP, tridecafluoro-octylphosphate; PFOP, 1H,1H,2H,2H-perfluoro-octanephosphonate; PFAND, N-(4,5-dihydroxy-2-penethyl)-2H,2H,3H,3H,-perfluoro-undecanamide.

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