



Anti-adhesive layers on nickel stamps for nanoimprint lithography

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Abstract

A new route to use silane chemistry as a means of improving anti-sticking properties of Ni stamps for nanoimprint lithography was developed. The surfaces and the corresponding anti-sticking properties for the coatings of a fluorinated silane on three different oxidized surfaces on Ni, namely oxidized Ni, oxidized Ti on Ni, and SiO₂ on Ni, were investigated using atomic/lateral force microscopy, contact angle measurement, X-ray photoelectron spectroscopy, and imprint tests. The surface energies and the friction constants for the silane coatings are found to be in the order NiO/Ni > TiO₂/Ni > SiO₂/Ni, indicating that an introduction of a SiO₂ interlayer is most effective to achieve a better anti-adhesive coating. This is also supported by simultaneous imprint tests with sinusoidal gratings of different coatings, where no failure appears for the coating with a SiO₂ interlayer.

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1. Introduction

One of the most important tasks for nanoimprint lithography (NIL) [1] is to provide stamps with good anti-sticking surface properties. A low surface energy release layer on stamp surfaces not only helps to improve imprint qualities, but it also increases the stamp lifetime significantly by preventing surface contamination. Molds made from

silicon wafers are well suited as stamps in NIL, particularly because the thermal expansion coefficient of the stamp is often identical to the substrates to be structured. The availability of high quality anti-adhesive coatings on the stamps using silane chemistry make silicon stamps ideal tools for replication. For many processes, however, flexibility and robustness higher than that of silicon is needed, and in such cases Ni stamps fabricated using electroplating are more favorable.

For Ni stamps, sputtered or plasma-polymerized teflon-like coatings have been developed and in the latter case it has been shown that some di-

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rect binding of the fluorinated polymer to the Ni surface can be achieved [2,3]. However, such coatings are still less effective and less stable in the long term than Si stamps coated with fluorinated silanes, which covalently bind to the oxide surfaces. In addition, whereas high vacuum equipment is needed for the polymerized films, the silane coating can be performed either in a solution or by vapor deposition in a simple vacuum chamber, so that the coating can be easily renewed after cleaning in unpolar solvents, e.g. when a stamp is contaminated by polymer residues. Therefore, the aim is to develop an anti-adhesive coating process for Ni stamps based on silane chemistry with similar anti-adhesion properties to that on Si stamps.

In order to achieve sufficient binding of the silanes to Ni stamps, it is necessary to produce an oxide surface on the metallic Ni. Then the chlorosilane group can react with hydroxyl groups on the oxide surface under elimination of hydrochloric acid. Coatings of a fluorinated silane on three oxide surfaces are compared, i.e. Ni oxidized in an oxygen plasma (“NiO/Ni”), Ni coated with Ti and plasma-oxidized (“TiO₂/Ni”), and Ni coated with SiO₂ (“SiO₂/Ni”). Different surface characterization methods reveal that the silane coating on SiO₂/Ni is superior to the other coating methods, which agrees with the results of simultaneous imprint tests performed using sinusoidal gratings with different coatings.

2. Experimental

2.1. Sample preparation

Two different Ni plates were used for the experiments: (i) flat plates of 200 μm thickness without structures for surface characterization; (ii) stamps with a sinusoidal grating of 1 μm period and 200 nm depth for imprint tests. The sinusoidal grating proved to be suitable because it ensures significant local polymer flow during embossing and at the same time does not induce abrasion due to undercuts and is not sensitive to slight differences in the demolding procedure. The substrates were first cleaned using acetone, isopropanol, and

deionized water and then dried with N₂ flow. Then, they were exposed into an isopropanol vapor and dried by pulling-up the substrates slowly from the bath.

NiO/Ni substrates were prepared by treating the cleaned Ni substrates with O₂-plasma for 5 min. For the preparation of TiO₂/Ni substrates, a 20 nm Ti layer was evaporated in an electron beam deposition chamber, followed by an O₂-plasma treatment for 5 min immediately after taking the samples out of the deposition chamber. For the preparation of “SiO₂/Ni” substrates, a sequential deposition of 5 nm of Ti and 20 nm of SiO₂ was done without breaking vacuum and followed by an O₂-plasma treatment. The Ti interlayer was used to enhance the adhesion between Ni substrates and SiO₂ layer. For all Ni substrates with different treatments, coatings of a perfluorinated silane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (TFS), were performed in one batch by evaporating the TFS vapor in a simple vacuum chamber, as described in [4].

2.2. Surface characterization

Different surface analytical methods are applied in an effort to obtain complementary information on surface energy, morphology, friction, and chemical composition.

Advancing contact angles of water (H₂O), diiodomethane (CH₂I₂), and ethylene glycol (C₂H₆O₂) were measured using a goniometer system (G2) from Krüss GmbH. The polar and disperse part of surface energies were calculated from the measured contact angles using the method of Owens, Wendt, Rabel and Kaelble [5].

Surface morphology and friction force were characterized by atom/lateral force microscopy (AFM/LFM, Digital Instrument Nanoscope III/Dimension 3100). A tapping-mode cantilever with a high aspect ratio tip (diameter ~20 nm, length ~4 μm) was used for acquiring topographical images with reduced tip-sample interactions and a Si₃N₄ cantilever with a force constant of 0.5 N/m was used to measure friction images and friction vs. normal force curves.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromatic

Al K α X-ray source (1486.6 eV) on a photoelectron spectrometer (VG ESCALAB 220i XL). The constant analyzer energy mode was chosen. During the measurements the distance between the samples, X-ray source, and analyzer was kept constant in order to allow comparison of absolute peak areas after normalization by the number of scans.

2.3. Imprint tests

In addition to analytical tools, imprint tests can reveal how effective the fabricated anti-sticking layers are in practice. As substrates, thin films (~ 330 nm) of polymethyl methacrylate (PMMA, molecular weight = 25 kg/mol) were spin-coated on oxidized silicon (SiO₂) substrates, followed by baking on a hot plate for 1 min at 170 °C. The sequential imprint tests using the Ni stamps with different coatings were performed simultaneously on the PMMA film for 15 min at 230 °C and 50 bar and after each imprint the quality of stamps and substrates was inspected using a microscope.

3. Results and discussion

Anti-adhesive coatings are in general characterized by low surface energies. The value of surface energy is determined mainly by surface roughness, chemical structure of coating materials such as nature and length of backbone structure and pendant moieties, and quality of the coatings such as binding mechanism to the surface, surface coverage and molecular orientation [6]. The surface roughness of Ni substrates used in this study is measured to be 3.2 nm (RMS, surface roughness for Si ~ 0.5 nm), which changes very little upon

surface modification by TiO₂ and SiO₂ deposition and/or silanization. This can be attributed to the formation of relatively homogeneous films with respect to the relatively large initial roughness of Ni substrates. Therefore, differences in surface energy occurring for silane coatings on different Ni substrates can be related exclusively to the coating qualities.

Table 1 shows surface energies (polar and disperse parts) calculated from contact angles of three different fluids before and after TFS coatings for differently treated Ni substrates. The surface energies of TFS coated surfaces depend strongly on the underlying substrates in the increasing order SiO₂/Ni < TiO₂/Ni < NiO/Ni, indicative of different nature of the binding of TFS molecules to different oxide surfaces. The value of 8.1 mN/m for the coating on SiO₂/Ni is even lower than that on oxidized Si surfaces of 12.4 mN/m. This is understandable because the high surface roughness of the Ni substrates further increases contact angles in addition to the TFS adsorption on SiO₂. The introduction of a TiO₂ interlayer, to which fluorinated silanes are reported to form covalent bonds [7,8], also results in a significant reduction in surface energy, comparable to the TFS coating on Si stamps. We have also determined friction coefficients for the coatings from the slopes of the friction vs. normal force curves using LFM, as is shown in Fig. 1. This is a measure of an AFM tip slide on the surfaces, which is closely related to the surface energy. As a result, the lowest friction coefficient was obtained for the coating with the lowest surface energy.

Consideration of the surface energy components of polar and disperse parts helps understanding of the differences in the TFS binding to the oxide surfaces. For the uncoated surfaces,

Table 1
Surface energies before and after silane coating on differently treated Ni

Surface energy/mN/m	NiO/Ni			TiO ₂ /Ni			SiO ₂ /Ni		
	σ_s	σ_s^D	σ_s^P	σ_s	σ_s^D	σ_s^P	σ_s	σ_s^D	σ_s^P
Before coating	47.7	39.9	7.8	45.7	32.0	13.7	63	29	34
After coating	21.0	12.9	8.1	12.9	12.3	0.6	8.1	7.8	0.3

The contact angles were measured in advancing mode and surface energies (total, σ_s , dispersed and polar part, σ_s^D and σ_s^P) were calculated using Owen, Wendt, Rabel and Kaelble's method.

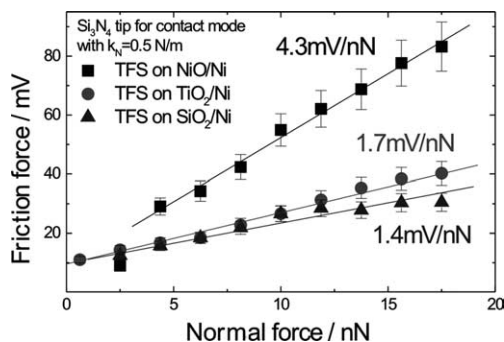


Fig. 1. Friction vs. normal force curve measured by LFM for TFS coatings on differently treated Ni substrates. Friction coefficients determined from the slope over the region showing a linear relation are included.

polar surface energy represents the amount and the strength of Ni–O, Ti–O, and Si–O surface dipoles while for the coated surfaces it shows how effectively the surface dipoles are shielded. The data show that the higher is the surface dipole before the coating, the more change of the polar surface energy occurs upon coating, indicating that the surface oxidation process has the most profound effect in determining the extent of the TFS bindings. For example, the SiO₂/Ni surface with the highest polar surface energy has the highest potential to give rise to covalent bindings of the largest number of TFS molecules.

Fig. 2 presents XPS survey spectra for the TFS coatings on differently treated Ni substrates after normalization by the number of scans. Most notably, the peak areas of the O1s core level indicating the potential binding sites to TFS molecules

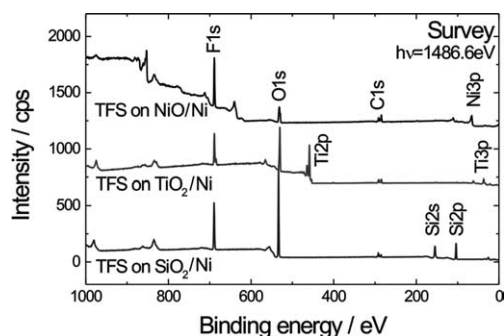


Fig. 2. XPS survey spectra for TFS coatings on the differently treated Ni substrates.

decrease in the order SiO₂/Ni > TiO₂/Ni > NiO/Ni, which correlates well with the values of the polar surface energies before the coatings. However, the F1s and C1s core levels which represent the amounts of TFS on the surface do not follow this order. Especially, the peak areas of the CF₂ and CF₃ components in the fine-scan C1s core level spectra are similar for all substrates, which indicates a similar amount of TFS molecules attached on the substrates. Therefore, the difference in surface energies occurring after the adsorption of similar amount of TFS molecules can be explained only by the difference in the ratio of silane molecules that are firmly bound to the substrate surfaces. In other words, the less effective is the oxidation of the surface, the less silane molecules can bind covalently. Accordingly, a conclusion can be drawn from results of surface characterization that low surface energy for the SiO₂/Ni substrate is not the result of the nominal coverage of TFS molecules, but due to the robustness of the coatings, which is related to the extent of the surface oxidation process.

Our TFS coating process is optimized for oxidized Si substrates. However, this cannot be the reason of the lower quality of the TFS coating on TiO₂/Ni because the similar amount of silane molecules is deposited. It is more likely that the oxidation of the Ti film could be less complete, giving rise to the insufficient binding sites for the covalent TFS adsorption.

The anti-adhesion ability of the coatings can be observed better in the imprint tests where a large local shear force is exerted on the coated surfaces by the flow of resist and during demolding of the stamp from the substrate. For all stamps, no failure was observed at the first imprint. After the second imprint, the resist is partially detached from the substrate indicating a loss of anti-adhesion on NiO or TiO₂ surfaces, while the silane coating on SiO₂ still results in a good imprint (Fig. 3). This is also an indication that loosely bound and/or unbound TFS molecules are removed from the surfaces during the first imprint, which weakens the anti-adhesion properties of the coatings giving rise to the failure at the second imprint. We have performed up to five imprint tests in sequence after cleaning of the stamps at

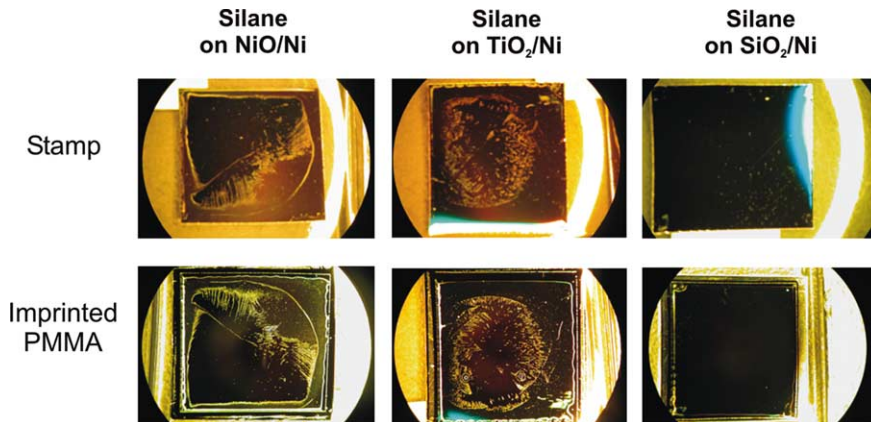


Fig. 3. Micrographs of Ni stamps with different anti-adhesive coatings and the corresponding imprinted PMMA films after the second imprint. Ripping of the PMMA is observed when TFS was coated on NiO/Ni or Ni/TiO₂ while silane coating on SiO₂/Ni results in a good imprint. The area of each structure is 18 mm × 18 mm.

each test. The SiO₂/Ni substrate shows no failure over the series of tests, which proves the superiority of the coating. For the other coatings, failure always occurs during further imprints, indicating that a loss of the coating cannot be recovered and that a renewal of the coating is needed. This is consistent with the results of surface characterization in that the amount of covalently bound TFS molecules determines the quality of the coating. This imprint tests provide only detection of failure and success. However, this method can even be further developed as a quantitative analytic tool if fluorescence materials are used as imprint resist, as in [9].

Finally, we investigated the influence of the SiO₂ interlayer thickness on the surface energy for TFS coatings because the thickness of the interlayer may be critical for extremely small nanostructures. This is shown in Fig. 4. For this series of experiments, Ni plates with slightly lower surface roughness were used, which results in slightly higher surface energies for the coating with 20 nm SiO₂ interlayer than the corresponding surface in the first series of experiments. Increase of the surface energy was observed when the SiO₂ thickness is less than 5 nm and this is the minimum thickness of the SiO₂ interlayer to obtain the improvement of the anti-adhesion properties. Therefore, it can be deduced that this method of introducing the interlayer of about 10 nm thick-

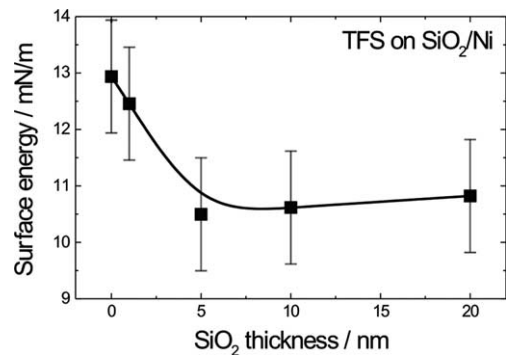


Fig. 4. Surface energy calculated from contact angles of water, diode methane, and ethylene glycol as a function of the SiO₂ interlayer thickness for TFS coatings on SiO₂/Ni substrates.

ness (including 5 nm of Ti adhesion layer) is applicable for most applications of 100 nm feature sizes and even below.

4. Conclusion

We have developed a new method of anti-adhesive coatings for Ni stamps which uses silane chemistry by introducing oxide surfaces. The TFS coating on SiO₂/Ni substrates shows lowest surface energy, lowest friction constant, and best imprint results among the different coatings investigated. The relatively low interlayer thickness

needed to improve the anti-adhesion properties makes this coating method suitable for nanostructures below 100 nm, which is sufficient for many applications. It seems that the extent of the surface oxidation where TFS molecules can bind plays an important role for this improvement. It may even be possible to improve the anti-adhesion properties further if silanes with different molecular structures and/or other oxide interlayer with higher binding force with silanes are used.

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