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Towards greener nanoimprint processes

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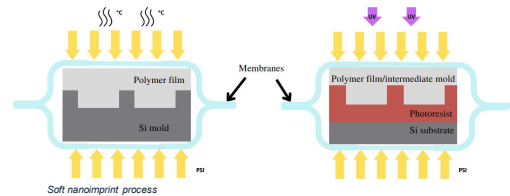
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CONTEXT

Surfaces nanostructuring is commonly used in biomedical applications and also in renewable energy applications. For bio-systems, approved bio-materials have to be used with biocompatibility and/or biodegradability properties depending on their utility. For components dedicated to renewable energy applications, the use of greener polymers makes sense compared to petrochemicals materials. Moreover, reducing the use of polluting and harmful materials in micro and nano-technology processes is of great interest in terms of health and environmental issues.

The purpose of this work is to develop nanoimprint processes using "greener" polymers: Poly Lactic Acid (PLA) and Poly Vinyl Alcohol (PVA). PLA, a bio-sourced, bio-degradable and bio-compatible polymer, will be directly nano-structured via a thermal nanoimprint process (T-NIL). PVA, a synthetic bio-compatible and bio-degradable [1] polymer, will be used as water-soluble sacrificial layer in a lift-off process.

Soft nanoimprint lithography is a simple, very fast and cheap 2-step process. Patterns are first replicated in a polymer film by thermal nanoimprint. Then the structured film is used to pattern the substrate with photosensitive resist.



MATERIALS & METHODS

PVA water-soluble sacrificial layer in a lift-off process

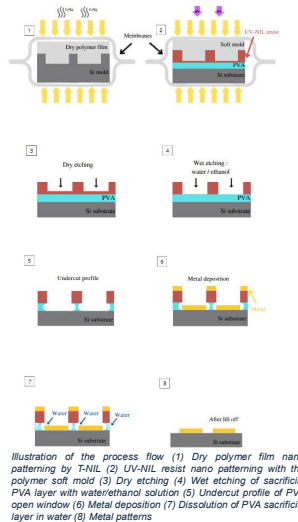
Lift-off process with a PVA underlayer has several advantages : its water-solubility and the benefit of a wet etching. Wet etching is an isotropic process, this makes it possible to create an interesting underetching profile for the lift-off step, called a cap profile. This profile implies a discontinuity of the metal deposit therefore avoiding the creation of metal bridges.

PVA (13-23 kg/mol) is dissolved overnight in water (concentration 5%) in a 70°C water bath (+/-10°C). To obtain 70 nm thick layer, PVA is deposited on a silicon substrate at 4000 rpm for 30 seconds. Sample is annealed 2 min at 110°C. The photoresist NILUV135 [2] is coated at 4000 rpm for 30 seconds to obtain a 130 nm thick layer and annealed 1 min at 95°C.

Sample is shaped using nanoimprint process explained just above.

Resist pattern residual layer is removed by dry oxygen plasma etching. Etching speed is 20 nm/min, plasma lasts 3 min.

Then, to remove the PVA pattern residual layer, a wet etching is carried out. 2 structured samples are immersed during 1 min and 5 min respectively, in a mixture of 44% water / 56% ethanol under vacuum degassing. Samples are rinsed with pure ethanol and annealed for 2 minutes at 90°C.



PLA films structuration

COP films usually used are replaced with polylactic acid films.

Commercial films (Goodfellow) and home calendered films (based on Total Corbion granules) were introduced into nanoimprint process presented above with following parameters.

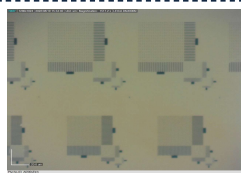
- 5 min thermal nanoimprint using a pressure of 450 PSI (30 bars) and a temperature of 70°C.
- 3 min UV nanoimprinting using a pressure of 200 PSI (14 bar) at room temperature.
- PLA anti-adhesive surface treatment for unmolding is composed of a few nanometers SiO₂ deposit followed by a per fluoro decyl trichloro silane self-assembled monolayer grafting.

RESULTS

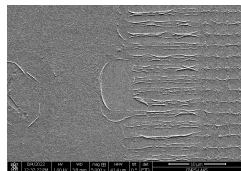
This process allows patterns replication with good resolution and same depth as the initial mold. Total mask thickness (PVA + resist) is 200 nm (+/-2 nm measured by atomic force microscopy).

Total mask thickness after dry etching is measured at 150 nm (+/-2 nm), the PVA layer has been opened.

- 5 min immersion time dissolves too strongly PVA layer and suspends the resist.
- 1 min immersion time is not sufficient and does not allow to dissolve PVA in the patterns. The mask is measured at 115 nm (+/-2 nm) in height and the patterns at 110 nm (+/-2 nm) in depth.



Optical image of patterns consisting of 500 nm, 200 nm or 100 nm wide squares and lines with variable pitch replicated in UV-NIL resist / PVA bilayer system.

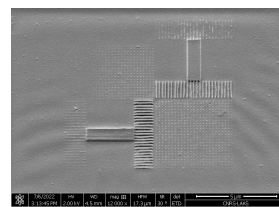


SEM image of patterns consisting of 500 nm wide lines with 2 μm pitch replicated in UV-NIL resist / PVA bilayer system after 5 min wet etching

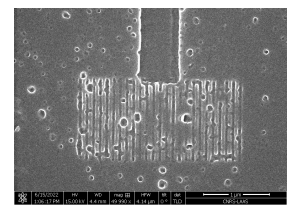
Both structured PLA films contain bumps defects probably coming from water condensation during calendering.

These films are used to structure a layer of resist by UV nanoimprinting.

Patterns of 20 nm wide and 100 nm pitch are perfectly replicated up to defects (holes).



SEM image of patterns consisting of 50 nm or 20 nm wide squares and lines with variable pitch replicated in PLA film



SEM image of patterns consisting of 20 nm wide lines with 100 nm pitch replicated in UV NIL resist

CONCLUSION

- To carry out lift-off step, wet etch step duration should be adjusted to obtain the desired profile.
- We demonstrate that it is possible to use PLA films for nanoimprint process to replicate patterns with very good resolution.
 - Ready to use in biology applications
 - For microelectronics field use, PLA film fabrication process should be improved to remove film defects.

[1] Chiellini, E., Corti, A., D'Antone, S., & Solaro, R. (2003). Biodegradation of poly (vinyl alcohol) based materials. In *Progress in Polymer Science (Oxford)* doi.org/10.1016/S0079-6700(02)00149-1

[2] Jean Baptiste Doucet, 'A UV-NIL resist developed for a transitional soft mold process and the subsequent dry etch transfer into hard materials', 43rd International Conference on Micro- and Nano-engineering (MNE 2017), Braga, Portugal, Sep. 2017.