Physica E 41 (2009) 1118–1121

Contents lists available at ScienceDirect

Physica E

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

Wafer-scale transfer of nanoimprinted patterns into silicon substrates

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ARTICLE INFO

Available online 14 August 2008

PACS:
81.07.−b
81.16.Nd
81.16.Rf

Keywords:
Nanoimprinting
Pattern transfer
Silicon

ABSTRACT

A simple low cost method of nanoimprinting has been developed. The technique uses a flexible disposable master and lends itself to roll-to-roll processing. Residual layer thicknesses of 5–10 nm are routinely achieved. This enables the critical step of pattern transfer into hard substrates by reactive ion etching, an essential step in the fabrication of sub-wavelength photonic device elements on a wafer-scale.

1. Introduction

Nanoimprinting provides a low cost alternative to deep ultraviolet and electron beam lithography for producing deep sub-micron features in semiconductor device fabrication [1]. Nanoimprint techniques frequently involve the formation of either a pre-patterned die of limited size, from either a hard [2] or soft material [3,4] that is then pressed into a curable lacquer spin-coated onto the target substrate. Wafer-scale or large area nanoimprinting is then achieved by stepping and repeating the impression. Frequently encountered problems include release from the master, stitching errors in the step and repeat process, damage to bowed wafers, especially in high-pressure imprint processes and clearing the inevitable residual layer when device fabrication involves pattern transfer into the underlying substrate.

A novel wafer-scale nanoimprint process and its application to pattern replication in hard substrates are described here. In principle, the nanoimprint technique reduces or even overcomes the limitations of other methods and lends itself to large-scale low cost roll-to-roll processing [4]. The technique exploits the concept of a single-use disposable master. The work also includes the development of imprint resists with low surface energy that allow easy release of the disposable master. In particular, it is shown here that the imprint resists have sufficient etch selectivity to be compatible with deep relief pattern transfer into silicon (Si) substrates via a thin intermediate silicon dioxide (SiO_2) layer by reactive ion etching.

2. The nanoimprint technique

Master structures were made on a 250 nm scale via laser interference photolithography [5] in photoresist and then transferred to nickel replicas by standard electroforming techniques. The pattern on the nickel was transferred to the surface of a polyethylene terephthalate (PET) film using a roll-to-roll UV replication process. This provides a large supply (100's of metres) of "disposable masters" for nanoimprinting. The resulting structure, shown in Fig. 1, mimics a moth eye structure and comprises a pseudo-hexagonal array of nearly sine^2 shaped features, used as an anti-reflection film for displays [6]. The peaks and depressions in the pattern have a near elliptical rather than circular cross-section.

Two types of UV-cross linking material were used in the replication process. The first was an epoxy-silicone, the second a conventional acrylate system containing a small percentage of a fluoro-acrylate. The formulation of each resist was designed so that spin-coated films have a reduced surface energy enabling clean release of the master without additional processing steps. The disposable masters are flexible, their stiffness is determined by the combination of the PET backing film and the formulation of the lacquer containing the relief. Three different masters having different period and relief height were used in this work.

The first step in the process is to spin coat the substrate with a thin film of UV sensitive imprint resist, followed by a short low

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doi:10.1016/j.physe.2008.08.014

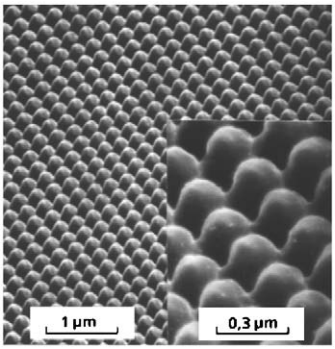

Fig. 1. SEM microphotograph of a moth eye structure roll-to-roll replicated onto a polymer substrate (a disposable master) by MacDermid-Autotype UV-nanoreplication.

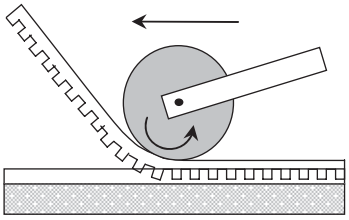

Fig. 2. Nanoimprinting by roller using a flexible disposable master.

temperature pre-bake to evaporate excess solvent and to promote adhesion of the polymer film to the wafer. The imprint step involves using a roller to press the disposable master into the resist with only light force, as shown schematically in Fig. 2. Unlike conventional imprinting, the line-contact of the flexible master makes contact pressure virtually irrelevant. In the work described here a simple hand roller is used. Our experiments have demonstrated that the degree of filling and the thickness of the residual layer are controlled by the thickness of the spin-coated layer rather than pressure.

After imprinting the next step is to cure the resist. This involves a short exposure to UV light and an optional thermal cure to complete the cross-linking of the imprint resist. Finally the disposable master is released by peeling it from the imprinted substrate. It was often found that the disposable master is already partially released after the cure, owing to the low surface energy design of the imprint resists, eliminating the need for force at a critical stage.

3. Imprint resist formulation

Two novel imprint resist formulations have been developed. One is based on oxetanyl xilsesquioxane (OXSQ) with an iodonium photo-initiator. The OXSQ molecule is shown schematically in Fig. 3. This was designed so that the Si atoms oxidise during CHF_3/O_2 reactive ion etching (RIE), a gas mixture used to clear the residual layer after imprinting.

The aim was to create a resist more able to withstand the etching required for pattern transfer into a hard substrate. The second imprint resist is based on the UV sensitive acrylate used to make the disposable master. The purpose of developing the acrylate-based resist was to ease its removal and descumming, after pattern transfer into the substrate. Flow enhancers were added to the formulation to improve wetting and spin coating of the substrates. Both types of resist were dispersed in toluene for spin coating for proof of principle trials. In later work the resists were dispersed in ethyl lactate.

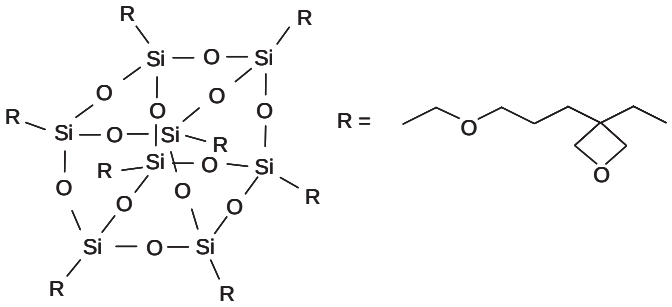

Fig. 3. OXSQ showing the Si cross-linking atoms.

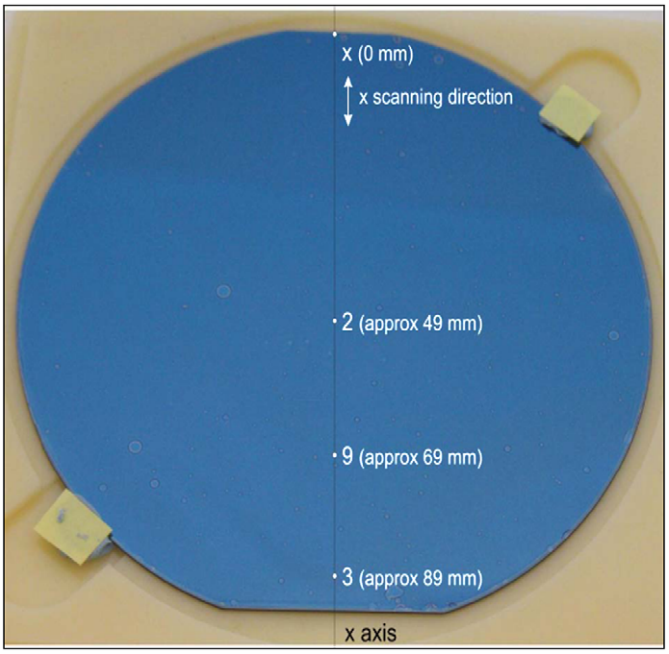

Fig. 4. Nanoimprinted 4-in diameter Si substrate. The scale markings indicate positions at which AFM measurements were performed to investigate the relief created in the imprinted resist and its uniformity across the wafer.

The thickness of the resist coating was carefully calibrated against spin speed to ensure that the spin-coated films were of optimum thickness to enable filling of the relief of the disposable master to be accomplished without leaving an excessively thick residual layer. The viscosity of both resist types was then adjusted such that any variation or error in the spin speed did not cause process critical variations in the residual layer thickness. This optimisation ensures that the residual layer thickness is always in the range 5–20 nm and, in the case of the acrylate resist, usually in the tighter range of 5–10 nm.

Fig. 4 shows a photograph of a 4-in Si wafer coated with OXSQ resist and imprinted using a disposable master having pseudo-hexagonal symmetry with a period of 450 nm. This sample was chosen for illustration as the minor circular blemishes provide evidence of the presence of the imprinted resist film. Typically the imprinting occurs without such blemishes. Fig. 5 shows a $5 \times 5\,\mu m^2$ AFM scan of a section from this sample measured at one of the points along the meridian shown in Fig. 4. The imprinted pattern is regular and shows good filling of the relief on the master.

Two-in diameter Si wafers with or without a 100 nm thick layer of SiO_2 deposited by CVD were used in the following imprinting results. Significantly, we have also shown that the

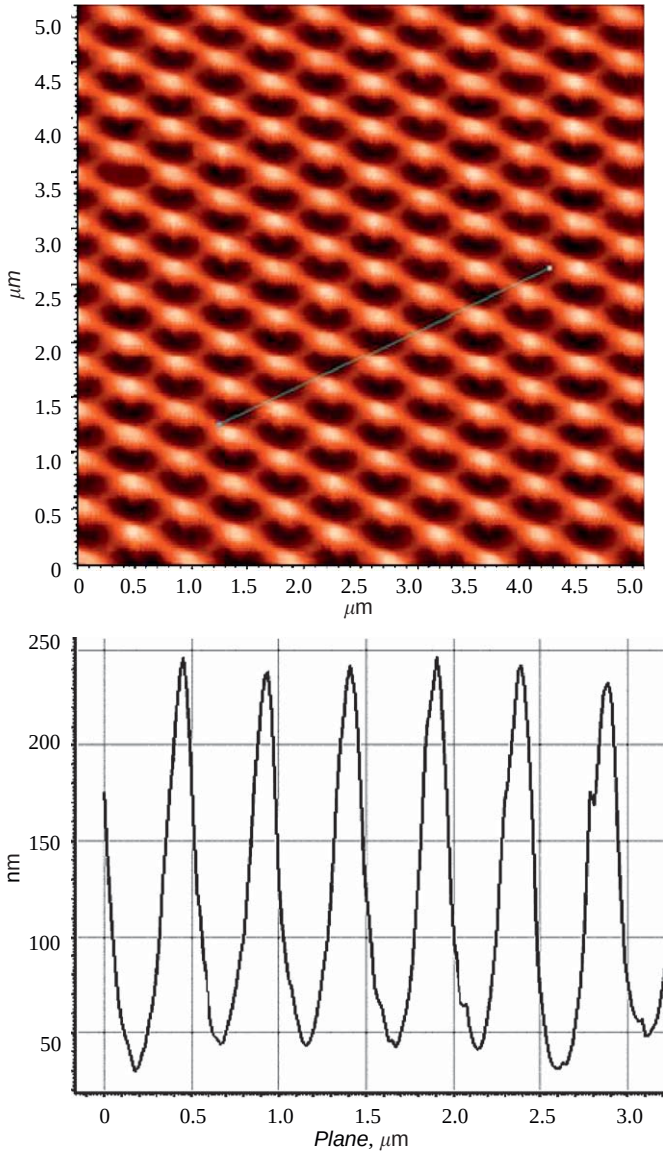

Fig. 5. AFM scan of a $5 \times 5\,\mu m^2$ from the imprinted 4-in wafer shown in Fig. 4.

technique works equally well on 4-in diameter and, in other contexts, $250 \times 250\,mm^2$ samples have been successfully replicated. Fig. 6(a) shows a SEM microphotograph of an imprinted OXSQ film of original thickness 165 nm. The pattern is an inverted near replica of the relief in the surface of the disposable master, which has pseudo-hexagonal symmetry with a period of 450 nm. The filling of the relief is complete and the residual layer thickness is <20 nm, which is the worst case. This shows good optimisation of the spin-coating process and the viscosity of the resist. Under these conditions with the 450 nm period master, near perfection replication is achieved by this low cost process, with typical residual layer thicknesses in the 5–15 nm range.

Disposable masters with 300 and 230 nm period have also been used, again with complete filling of the relief when the thickness of the resist film is optimised. In addition linear gratings and square symmetry patterns have been imprinted successfully with similar fidelity of the master and infill of the master relief by the imprint resist.

Fig. 6(b) shows the effect of CHF_3/O_2 RIE to remove the residual layer. The thickness of the resist is reduced by $\sim$70 nm by the descumming process. The edge profile of the imprinted resist is not vertical. At first sight, this looks unpromising for an etch mask.

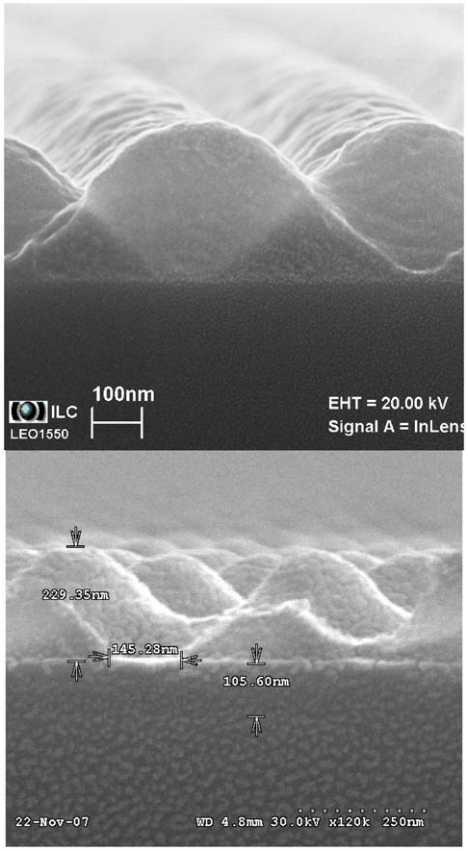

Fig. 6. (a) Nanoimprinted OXSQ. The imprinted film is an near exact replica of the master, with pattern period = 450 nm, relief height $\approx$300 nm; (b) after descumming with O_2 RIE to remove the residual layer where the relief height is reduced to 230 nm.

However, as will be seen, the 9 nm/min etch rate of OXSQ in the SF_6/CHF_3 plasmas used to reactive ion etch SiO_2 and Si was low enough to enable pattern transfer into both these materials.

4. Pattern transfer in silicon

In pattern transfer, the removal of the residual layer (typically $\leqslant$20 nm) is the critical but controllable step. Fig. 7(a) shows the effect of removing sufficient of the OXSQ residual layer to form a pseudo-hexagonal array of holes in the resist for pattern transfer into the Si by Ar^+ RIE. Fig. 7(b) shows the impact of more extensive CHF_3/O_2 RIE that leaves isolated islands of OXSQ. Here SF_6/CHF_3 RIE was used to create a structure in the Si with an undercut edge, showing the resilience of the OXSQ to SF_6/CHF_3 RIE.

Whilst OXSQ is a resilient resist for working with dielectric substrates, its chemical make-up is unsuitable for metallic surfaces. An acrylate-based resist has been developed for general purpose nanoimprinting.

The performance of the acrylate nanoimprint resist as a dry etch mask was tested by subjecting imprinted samples to the following sequence of RIE processes: removal of the residual acrylate layer by O_2 RIE (no CHF_3 is needed), etching through a $\sim$100 nm thick SiO_2 layer using CHF_3 RIE, and pattern transfer into the underlying Si by SF_6/CHF_3 RIE for 3 min.

Fig. 8(a) shows the surface of the acrylate after these three RIE steps and Fig. 8(b) shows the side view through the acrylate/SiO_2/Si structure. Whilst the etching of the SiO_2 is not anisotropic, RIE of the Si results in the formation of vertical sided, flat bottom holes on a highly regular lattice. Vertically-sided holes in the Si as

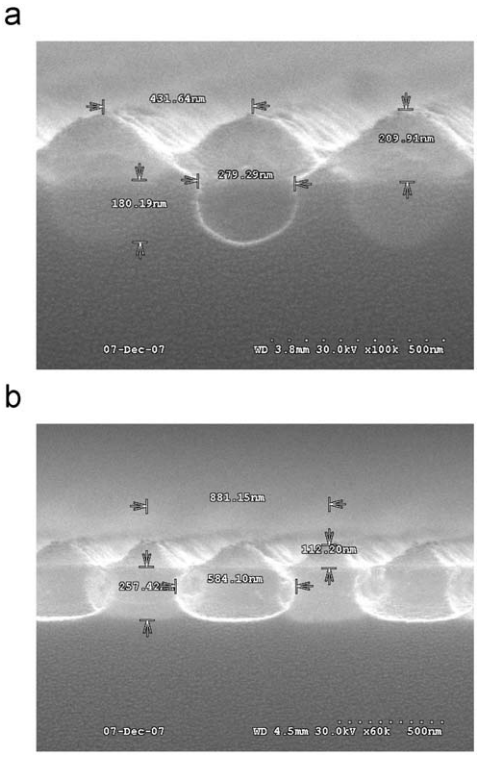

Fig. 7. (a) Edge profile of 2D photonic structure etched into Si using SF_6/CHF_3 RIE with nanoimprinted OXSQ as the etch mask; (b) The effect of over-widening the holes during removal of the residual layer by CHF_3/O_2 RIE.

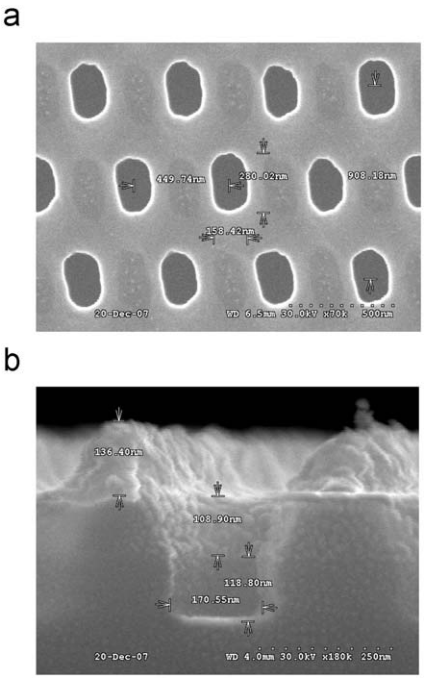

Fig. 8. (a) Surface view of nanoimprinted acrylate resist after removing ~20 nm thick residual layer, subsequent CHF_3 etching to clear the SiO_2 and 3 min SF_6/CHF_3 RIE to transfer the pattern into Si and (b) side view of the same sample.

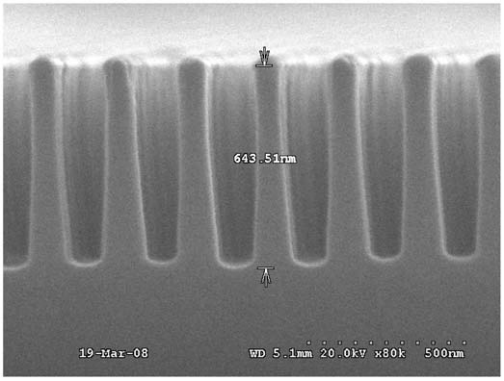

Fig. 9. Deep etched linear grating formed in Si. The period of the grating is 450 nm and its depth is 643 nm. The grating ridges are still capped by the residue of the etch mask.

deep as 600 nm have been achieved when longer etch times have been used with the acrylate resist mask.

The combination of nanoimprinted acrylate and a 100 nm thick CVD SiO_2 layer is sufficiently resilient to SF_6/CHF_3 RIE to enable much deeper patterns to be defined in the Si substrate. Fig. 9 shows a deep etched linear grating transferred into Si using the combination etch mask. The depth of the etched air gaps in the Si exceeds 640 nm. Whilst the etch mask is eroded, remnants of it can still be seen on top of the Si ridges.

5. Conclusions

A flexible nanoimprint process capable of wafer-scale pattern transfer into Si substrates has been demonstrated. The technique is based on the novel concept of a disposable soft master with matching imprint resist formulations. Both the resists developed enable the transfer of vertical sided, nearly flat-bottomed features in Si substrates. The process is a promising method for low cost formation of photonic crystal structures in hard substrates and for numerous other nano-structure applications. In particular, it is potentially very suitable for high volume production.

Acknowledgement

The Authors wish to acknowledge support from the European Union under Framework 6 Contract number 017481, STREP "N2T2" and partial support from the Slovak Research and Development Agency Grant APVV-RPEU-0005-6. DWEA is deeply grateful to the Royal Academy of Engineering (UK) and Leverhulme Trust for providing a Senior Research Fellowship.

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