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Nano-imprinting of highly ordered nano-pillars of lithium niobate (LiNbO₃)

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Abstract

Lithium niobate (LiNbO₃) is used in applications such as in optoelectronics, surface acoustic wave devices and transducers. In this paper nano-patterning of LiNbO₃ wafers at the wafer scale is investigated using a novel low cost and large-area nano-imprinting technique. The formation of nano-scale pillars is presented by nano-imprinting an ordered nickel etch mask by lift-off on a y-cut LiNbO₃ wafer. The process lends itself to the development of novel sensors or high temperature nano-scale harvesting structures. Since one potential application for nano-pillars of piezoelectrics is energy harvesting, calculations of relevant figures of merit for LiNbO₃ based composites are also presented.

Keywords ferroelectric, piezoelectric sensitivity, nano-scale, lithium niobate, processing

PACS: 77.65.-j: Piezoelectricity and electromechanical effects; 77.84.-s: Dielectric, piezoelectric, ferroelectric, and antiferroelectric materials

Title for the running head: **Nano-imprinting of lithium niobate**

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1. INTRODUCTION

Lithium niobate (LiNbO₃) is a ferroelectric material that is used in a variety of applications including optical switching [1], integrated optical devices [2] and surface acoustic wave (SAW) filtering [1]. Lithium niobate also has potential as a high-temperature transducer material for applications such as acoustic measurements, ultrasonic drills and high temperature accelerometers [3,4,5]. The material possesses relatively large electro-mechanical coupling coefficients, a pre-requisite for efficient energy conversion, and an extremely high Curie temperature of 1142-1210°C [4,6]. The upper operating temperature of a ferroelectric is typically half of the Curie temperature, hence

LiNbO₃ based transducers have the potential to operate at temperatures of 600°C, or even higher [7]. Transducers manufactured using high purity z-cut LiNbO₃ single crystals have been successfully tested at temperatures up to 1000°C with no significant oxygen loss or resistance change at temperatures over 600 °C [6]. Cochran et al. created high temperature 1-3 piezocomposites consisting of relatively coarse 0.7mm diameter rods of z-cut LiNbO₃ embedded in a high temperature cement matrix using a dice and fill method. The transducer devices were tested at temperature of up to 360°C for high temperature non-destructive testing applications [7]. Since the material is used in single crystal form it is anisotropic and the specific crystal cuts often employed for transducers are z-cut and 36° y-cut [8]. Fraser et al. used a y-cut plate to create a shear-mode transducer [4].

Recently, there has been growing interest in creating nano-structures of piezoelectric or ferroelectric materials for applications related to energy harvesting. Nam Cha et al. [9] created piezoelectric ZnO based nano-wire generators for harvesting energy from acoustic vibrations. The ZnO nano-wires were grown by chemical vapour deposition and were ~10µm long and 150nm in diameter. Su et al. [10] formed GaN nano-rods to harvest energy from mechanical vibrations at ambient temperatures for self-powered systems. The nano-rods were grown on a silicon substrate by plasma-assisted molecular beam epitaxy. The high Curie temperature of LiNbO₃ makes it an interesting material for harvesting energy from mechanical vibrations at high temperatures. For example, macro scale plates of 36° y-cut LiNbO₃ were investigated by Bedekar et al. [5] for harvesting applications above 500°C. The creation of nano-scale rods of lithium niobate is therefore of interest for high temperature energy harvesting applications, such as self-powered near-engine or geothermal sensors [5].

This paper therefore aims to use a novel nano-imprinting technique using a disposable master to generate large areas (wafer scale) of ordered lithium niobate nano-pillars. This approach is particularly suited to this material since high quality lithium niobate wafers and crystals are commercially available, unlike some other piezoelectric materials such as GaN or ZnO. Preliminary calculations of relevant figure of merit for energy harvesting are also presented for LiNbO₃ based composites.

2. NANOIMPRINTING LiNbO₃

Highly ordered arrays of nano-pillars were fabricated in LiNbO₃ using nanoimprint lithography (NIL) with a lift-off process, providing a hard mask for successful dry etching of the substrate. The process has been initially demonstrated on silicon and GaN substrates [11, 12]. Figure 1 shows an outline of the process. A 4inch y-cut LiNbO₃ wafer (Fig. 1a) was initially spin coated with a resist (Fig. 1b). A polyethylene terephthalate (PET)

disposable master [11] was then applied to imprint a positive nano-dot structure onto the LiNbO_3 surface into the softer UV cured polymer resist (40nm depth). The disposable master structures were made via laser interference photolithography [11] in a photoresist and transferred to nickel replicas by standard electroforming techniques. The pattern on the nickel was transferred to the surface of a 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 disposable master was applied to the resist using a simple hand roller (Fig. 1c), providing a route to low cost formation of large areas of nanostructured surfaces. After UV curing the imprinted resist, the master was removed by hand (Fig. 1d), leaving a positive imprint on the lithium niobate substrate. Deposition of a second material, hydrogen silsesquioxane (HSQ), was carried out for the planarisation and in-filling of the imprinted relief (Fig. 1e). The structure depth was ~200-300nm as measured by a Dektak 6M system. HSQ was selected for its low etching in O_2 and is free of organic compounds. The layer was then etched back to the imprint level by a CHF_3 plasma (Plasmalab 80 RIE, Oxford Instruments Plasma Technology), with an O_2 plasma etch for removal of the exposed imprint resist. This allowed removal of the initial resist imprint, leaving a negative HSQ imprint pattern on the substrate surface (Fig. 1f). Ni was then deposited by electron beam evaporation (Edwards EB3) onto the negative imprint surface (Fig. 1g), followed by a conventional lift-off technique of a buffered oxide etch to reveal a metal nano-dot array on the LiNbO_3 surface (Fig. 1h). Fig. 2 shows examples of the Ni nano-dot array on the surface of lithium niobate with nano-structures of up to 350nm in height and a pitch of 600nm (equivalent to the master). Since a hand roller was employed the process was easily applied across the whole 4inch wafer. Etch selectivity between the nickel dot mask array and the LiNbO_3 substrate then allowed for the fabrication of LiNbO_3 nano-pillars by dry etching. The substrate was selectively removed using reactive ion etching (RIE) and inductive coupled plasma (ICP) etching tools (Oxford Instruments Plasma Technologies ICP180 system) with a hybrid of SF_6/Ar gases (Fig.1i). ICP etching of the LiNbO_3 has reached ~200nm/min at 1000W ICP with selectivity to Ni being ~10 [13]. The final nano-pillars of LiNbO_3 achieved by this NIL approach can be seen in Figs. 3 and 4. Typical nano-pillar heights achieved were 500nm to 1 μm with a pitch equivalent to the imprint master (600nm).

3. FIGURES OF MERIT OF LiNbO_3 BASED COMPOSITES.

One potential application for nano-structured piezoelectrics is energy harvesting. In the off-resonance mode, a material with high $d_{ij} \cdot g_{ij}$ product and high g_{ij} constant will generate a high voltage and power when the piezoceramic is used for energy harvesting and sensing [14]. To examine the potential for LiNbO_3 based energy harvesting, calculations were carried out using the effective field method [15]. Room-temperature electromechanical constants of

single-domain LiNbO₃ single crystal (3m class) were taken from [16]. Fig. 5 outlines the type of structure considered. We initially consider the case when the piezoelectric coefficient e_{22} (or d_{22}) is effective along the OX_3 axis of the composite and we assume a square arrangement of rods with the crystallographic axes X_j° of the single-domain LiNbO₃ rod oriented as follows: $X_1^\circ \parallel OX_2$, $X_2^\circ \parallel OX_3$ (i.e., parallel to the rod's generatrix) and $X_3^\circ \parallel OX_1$. In this case we exploit the larger piezoelectric activity as a result of the e_{22} or d_{22} along the OX_3 axis. The LiNbO₃ rods can be embedded in a porous polymer represented as a matrix containing spherical air inclusions distributed regularly with the volume fraction (porosity) m_p . The volume fraction of the LiNbO₃ rods is m over the composite sample. The predicted harvesting figure of merit, $(Q_{33}^*)^2 = d_{33} \cdot g_{33}$, in Fig. 6 are relatively large and are comparable to those achieved in 1–3s based on lead zirconate titanate (PZT). The material is lead free and also has very high Curie temperature. The high $(Q_{33}^*)^2$ figure of merit is relatively surprising given the relatively low piezoelectric (d_{ij}) constant of the material (Fig 6a). However LiNbO₃ exhibits relatively large g_{33} values due to its low permittivity; which also leads to high $(Q_{33}^*)^2$ values (Fig. 6b).

4. CONCLUSIONS

The work outlined here has presented the successful fabrication of nano-pillars in lithium niobate using a disposable master for nanoimprint lithography. The combination of using a disposable master available in large areas and using a simple hand roller provides a novel route to the formation of low-cost and large-area nanostructured surfaces. This work may be taken forward with investigations into the Ni mask thickness and its effects on the etched profile of LiNbO₃ nano-pillars. Our NIL approach allows for future investigations into nano-scaled structures in LiNbO₃ for applications such as energy harvesting at elevated temperatures and optoelectronic devices. Preliminary modelling shows that LiNbO₃ based systems have the potential to achieve relatively high $(Q_{33}^*)^2$ as a result of the low permittivity of the material.

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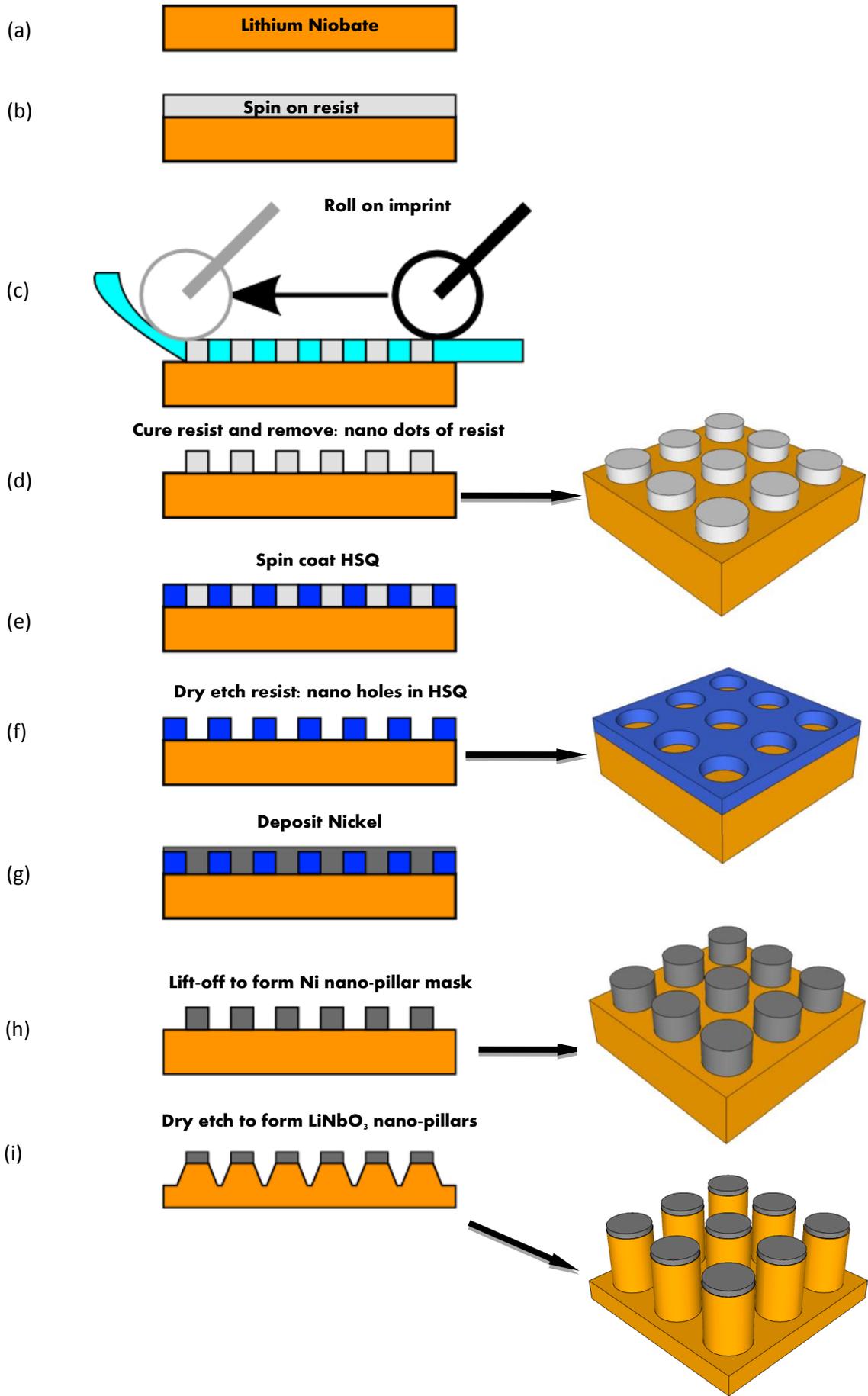


Figure 1. Schematic of nano-imprinting process (a-i)

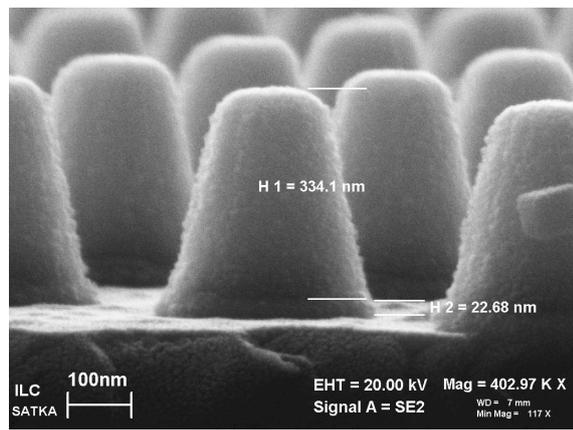
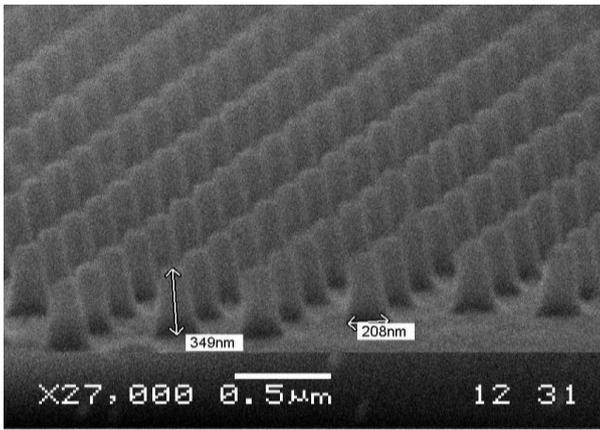


Figure 2. SEM images of nickel resist on LiNbO₃ (corresponding to Fig. 1h in schematic).

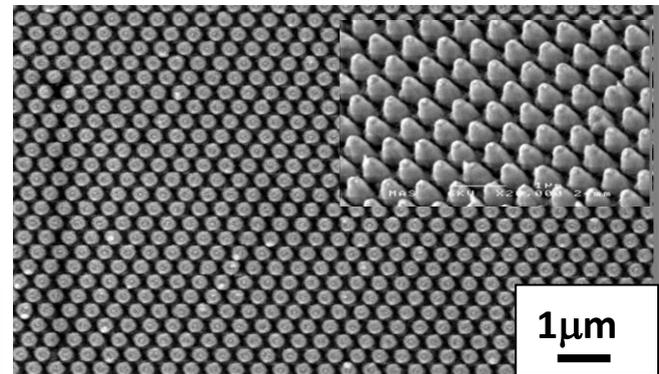
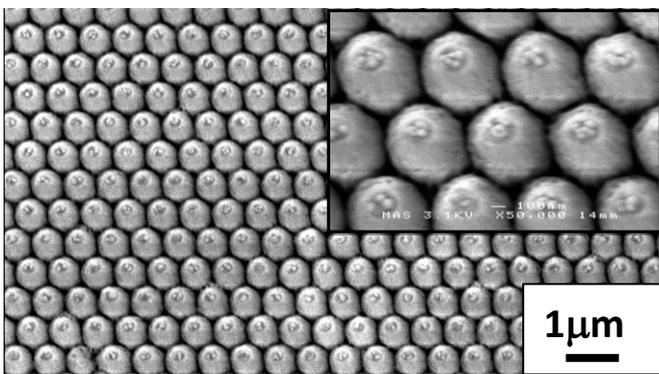


Figure 3. LiNbO₃ nano-pillars (corresponding to Fig. 1i in schematic)

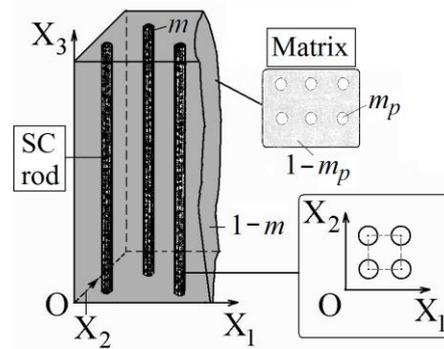
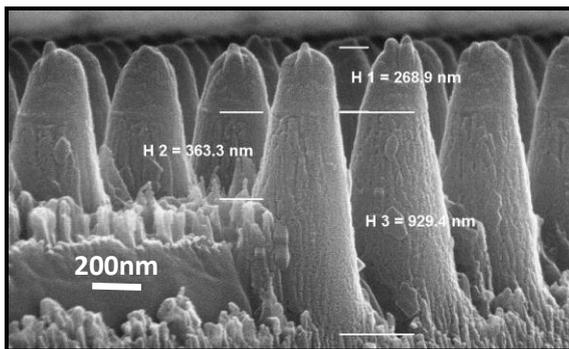


Figure 4. LiNbO₃ nano-pillars (corresponding to Fig. 1i in schematic)

Fig. 5. Schematic of the 1-3-type SC-based composite

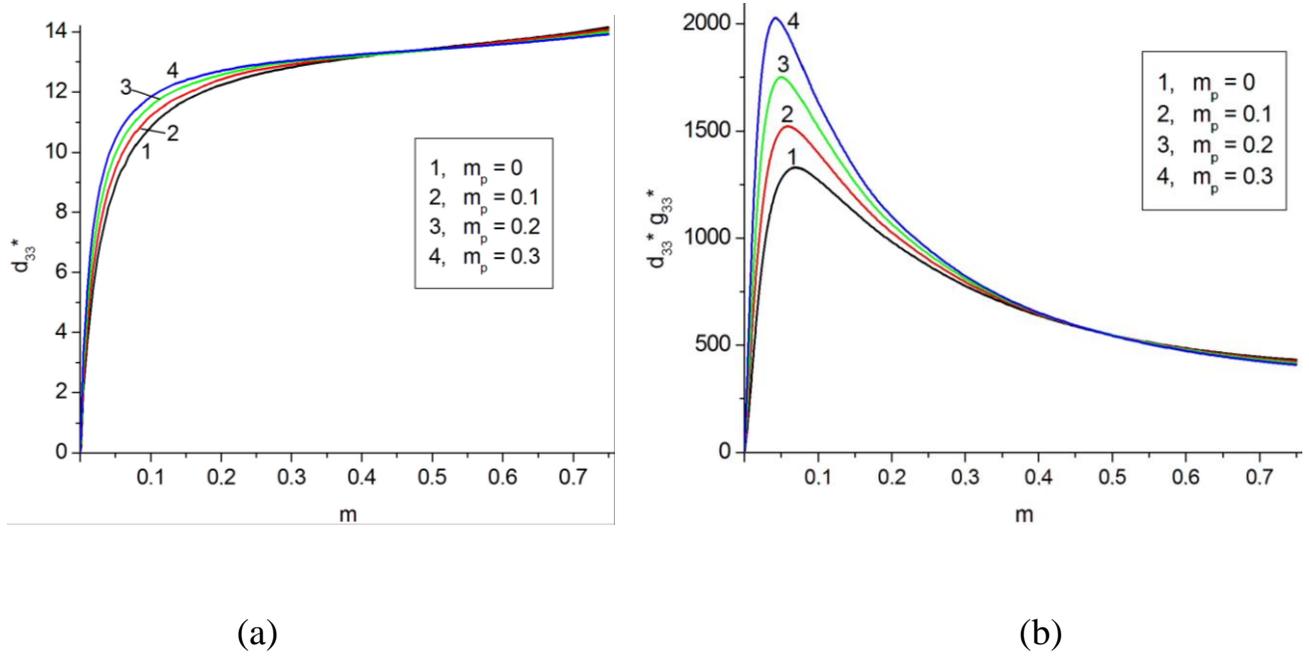


Fig. 6

(a) d_{33}^* in pC / N at $X_2^\circ \parallel OX_3$

(b) Squared figure of merit $(Q_{33}^*)^2 = d_{33}^* g_{33}^*$ (in 10^{-15} Pa^{-1}) of the 1–3 LiNbO₃ single crystal / porous epoxy composite at $X_2^\circ \parallel OX_3$.