Electroplated Ni mask for plasma etching of submicron-sized features in $LiNbO_3$

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Abstract
We here report on the fabrication of electroplated nickel (Ni) masks for dry etching of sub-micron patterns in lithium niobate ($LiNbO_3$). This process allows obtaining a 350-nm thick Ni mask defining high air filling fraction holey arrays (e.g. openings of 1800 nm in diameter with inter-hole spacing of 300nm, or 330-nm diameter holes spaced by 440-nm). The mask profile is perfectly vertical (angle ≈ 90°). The obtained metallic masks are used to realize photonic and phononic crystals. High aspect ratio and dense arrays of holey patterns were defined and transferred into $LiNbO_3$ through RIE (Reactive Ionic Etching) in a sulphur hexafluoride (SF_6) chemistry. Nanometric holes exhibiting sidewall slope angles of the order of 60° have this way been etched in $LiNbO_3$. The $LiNbO_3$ / Ni selectivity is close to 6and the etch rate around 6 nm/min.

Introduction
The etching of deep structures at the submicron scale is a critical technological step in the realization of a number of devices, particularly in the field of nanophotonics,, integrated optics or radio-frequency acoustics. $LiNbO_3$, amongst other non-conventional materials, stands as key materials in these application fields as it presents excellent electro-optical, piezoelectric or acousto-optical properties. The use of non-conventional materials such as $LiNbO_3$ in these applications requires the development of specific and yet unavailable etching processes. The fabrication of very high aspect ratios structures can be carried out using several dry etching methods: ion milling [1], focused ion beam etching [2] and plasma etching [3-5]. Plasma etching is one of the most versatile, and probably the most appropriate technique in terms of etch rate, selectivity and resolution. Yet, $LiNbO_3$ etching presents one major problem: the lithium fluoride (LiF) re-deposition. This LiF deposit decreases the etch rate and the $LiNbO_3$ / mask selectivity, results in a significant decrease in the achievable sidewall slope angle, and increases the wall roughness. In order to etch deep, high aspect ratio structures, the selectivity is an important parameter. A metallic mask is essential, because organic resists are etched faster than $LiNbO_3$. Electroplated metals are an interesting alternative to sputtered or evaporated metallic masks , indeed electroplating allows obtaining high aspect-ratio, high filling fraction patterns [6].
In this paper, we present a fabrication process for electroplated Ni masks exhibiting nanometric features, The fabricated mask selectivity is also being assessed in the context of $LiNbO_3$ RIE etching.

Fabrication of metallic masks with nanometric hole arrays
Evaporated metallic masks
Metallic masks are usually obtained through lift-off processes, a very widely used technique. There is however an intrinsic limit to the achievable metal thickness: the lift-off technique imposes a limit thickness at most equal to half of the thickness of the initially patterned resist. A second drawback lies in the sidewall verticality: metal layers deposited on resists usually exhibit sloped sidewalls and the pattern edges cannot be sharply defined as the deposition step itself is rarely completely anisotropic. This particularly holds in the case of submicron-sized patterns. An example of the application of such a technique to the patterning of holey array is reported in Figure 1. Here, a negative electron-beam resist (maN 2405: 450nm thick) is covered by évaporated Cr (150nm thick).

Electroplated Ni mask: process overview
An alternative can then consist in using electroplating as a way to define the metallic mask. In such a process, the metal layer is grown inside a resist mould which allows taking advantage of the slope angle and resolution offered by lithography [6]. Electroplated Ni has here been chosen to make high-aspect ratio metallic masks featuring sub-micron patterns with a good reproducibility [7]. Both optical and electronic lithography techniques have been used to define the resist moulds.The mask fabrication steps are illustrated by a flowchart and SEM pictures are reported in Figure 2. For these experiments, a chip of $LiNbO_3$ (1,5cm × 1,5cm) in the X-crystallographic orientation is used. After a standard wet cleaningin a mixture of sulphuric acid and hydrogen peroxide (3:1 piranha), a seed layer is deposited on the sample by DC sputtering (Plassys). An Ar plasma (150W, 7.10^{-3}mb, 60s) is performed before the deposition of 10 nm of Cr and 40 nm of Ni . This conductive layer is essential to grow the Ni layer by electroplating, but also serves as a conductive layer to avoid the charge effect usually encountered on dielectric substrates during the subsequent electron-beam lithography. The seed layer thickness has to be sufficient to initiate the Ni growth, but has to remain as thin as possible to relieve the final reactive ion etching step. A thickness of 50nm is a good compromise.
An 450 nm-thick, negative-tone electron-beam resist (maN 2405) is spun (3000rpm, 4000rpm/s, 30s) with a rotating cover spinner (RC-8 Karlsuss spin coater). Thanks to a Raith e_Line system, this negative resist is exposed to a high energy electron beam (voltage: 30 kV, aperture: 7,5 µm, working distance: 7 mm, beam current: 24 pA, dose: 80-200 µC/cm²) according to a pattern previously designed. The layout consists of nanometric circle arrays (diameters of 900 nm and 160 nm; periods of 1050 nm, 380 nm respectively).
The electron-beam resist is then developed in MF-26A during 2min, and only the exposed resist stays on the sample. The high aspect-ratio (160 nm width, 450 nm height), high filling fraction (900 nm width with 150 nm spacing) patterns considered proved difficult to achieve due to significant proximity effects.
Ni could anyway be grown through electroplating until a thickness of 350 nm was reached (Fig.2-b). Before electrodeposition, a short dip in an HCl/H_2O_2 bath is performed to insure the cleaning of the metallic seed layer. Ni is then electrodeposited from a nickel sulfamate bath at 50°C (current density: 15 mA/cm²). The resist is subsequently stripped with in an N-Methyl-2-pyrrolidone (NMP) solution (Remover 1165). This way, a Ni mask with very well defined submicron patterns is obtained, as shown in Fig.2-c. SEM pictures of figures 2 and 3 reveal vertical mask profile and a smooth enough surface.

$LiNbO_3$ RIE etching
This mask was subsequently used for $LiNbO_3$ etching. Both the seed layer and the $LiNbO_3$ substrate are etched in a RIE Plassys reactor with 10 sccm of SF_6, 2 µb of pressure, and 220 W of RF power. This etching recipe involving very low pressure and high RF power, allows to obtain acceptable results [5]. Fluorine gases are indeed generally used for plasma etching of $LiNbO_3$ due to the good volatility of fluorinated niobium species at temperature around 200°C [3]. However, the major problem is the formation and re-deposition of lithium fluoride (LiF) that results in a decrease in the etching rate and in sloped sidewall profiles [7]. Figure 3-b reveals an important sidewalls roughness, due to

Ni mask and LiF deposition during the etching step. We can also notice that the electroplated Ni mask presents a significant roughness as well (Fig.2-e), probably due to the intrinsic columnar structure of the Ni. The electroplated layer is indeed here composed of cones of 100 nm in diameter which are revealed by the etching process. It should however be noted here that the electroplated nickel texture and structure depend on the growth process parameters [8]. In particular, the deposited nickel layer structure changes from columnar at low mean current densities to a granular at high current density. Therefore, we varied the current density from 15 mA/cm² to 3 mA/cm² to assess the influence of this parameter. It however occurred that these experiments had no impact on the etching selectivity ($LiNbO_3$/Ni), nor on the Ni roughness after the RIE etching.

After the dry etching step, the sample is then cleaned in a $NH_4OH/H_2O_2/H_2O$ (1:2:7) solution during 5 min in order to remove any LiF residue [3]. If this wet etching step is not performed, the Cr mask removal is not done correctly. The last stage of the process consists in removing the Ni mask by wet etching for 5 minutes in Cl_3Fe..The Cr seed layer, is eventually removed in a commercial Cr wet etching solution (Fig.2-e). In order to evaluate the etch depth and the sidewall slope angle, a FIB cross-section is performed (Fig.4). The etching angle is around 60° and the aspect ratio is around 1.

Conclusions

As a conclusion, a process for the realization of electroplated Ni masks exhibiting sub-micron sized patterns has been developed. High aspect ratio and dense arrays of holey patterns were defined and transferred in $LiNbO_3$ through plasma etching. The obtained results open interesting prospects for the realization of photonic, phononic crystals, or optical Bragg gratings.

References

[1] M. Minakata, Applied Physics Letters, 35 (1979), 40-42.
[2] N. Courjal, M.-P. Bernal, G. Ulliac, J. Dahdah, S. Benchabane, J.-M. Merolla, J. Europ. Opt. Soc. Rap. Public., 4 (2009) 09018.
[3] H. Hui, R. Ricken, W. Sohler, ECIO Eindhoven, (2008), 75-78.
[4] Z. Ren, P.J. Heard, J.M. Marshall, P.A. Thomas, S. Yu, J. of Appl. Phys. 103, (2008), 034109.
[5] S. Benchabane, L. Robert, J-Y. Rauch, A. Khelif, V. Laude, J. of App. Phys, 105 (2009), 094109.
[6] M. Bale, R.E. Palmer, j. Vac. Sci. Technol. B, 19 (2001), 2020-2025.
[7] S. Royh, L. Dellmann, G-A. Racine, N.F. de Rooij, J. Micromech. Microeng. 9 (1999), 105-108.
[8] T. Fritz, H.S. Cho, K.J Hemker, W. Mokwa, U. Schnakenberg, Microsystem Technology, 9 (2002) 87-91.

Figures

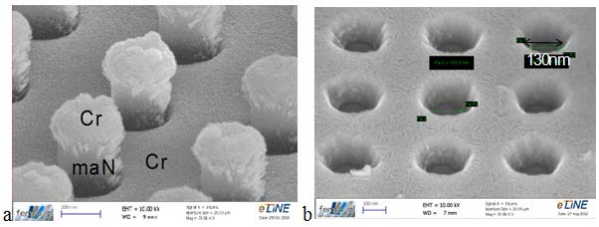

Figure 1. Lift-off drawbacks: a) resist patterns covered by a Cr layer (before lift-off); b) nanometric holes in a Cr layer (after lift-off).

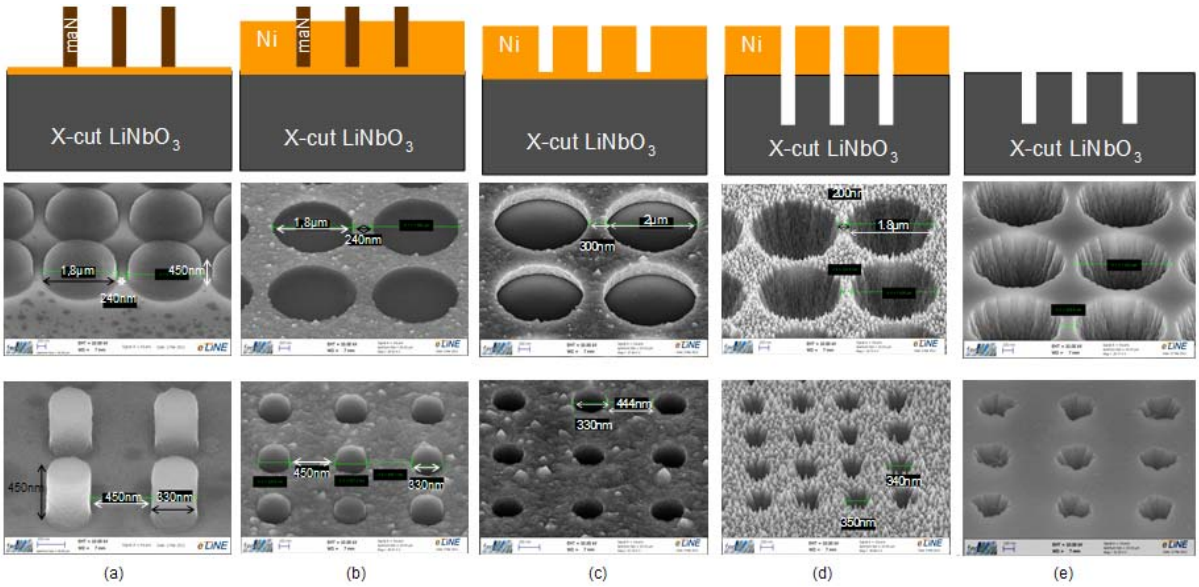

Figure 2. SEM images of different process steps for nanometric hole array fabrication:
a) Electron beam lithography of negative resist (maN: 450 nm thickness) on on a Cr/Ni seed layer (50 nm).
b) Electroplating method of Ni (350nm) using a current density of 15 mA/cm² and a temperature of 50°C.
c) Resist removal with remover1165 at 50°C
d) RIE etching of $LiNbO_3$ with SF_6 (10 sccm; RF power = 220 W; pressure = 2µm). Plassys reactor.
e) Ni mask removal by wet etching.

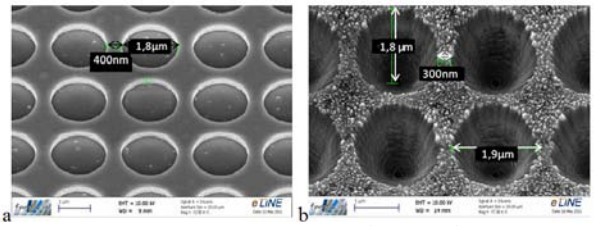

Figure 3. SEM pictures (tilt: 40° & 20°) before and after $LiNbO_3$ etching: a) Metallic mask in electroplated Ni. b) RIE (SF_6) etching.

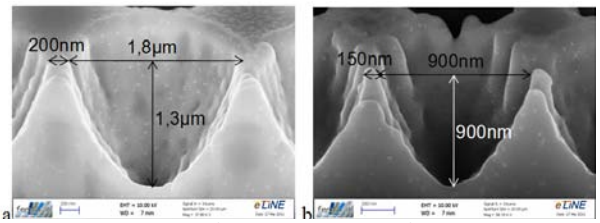

Figure 4. SEM pictures of a FIB cross section of a nanometric hole array.