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SIMS-depth profile and microstructure studies of Ti-diffused Mg-doped near-stoichiometric lithium niobate waveguide

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Abstract

Ti-diffused planer waveguides have bcen fabricated on pure and Mg-doped near stoichiometric lithium niobate (SLN). Secondary ion mass speetroscopy method was applied to study the Ti diffusion in 1 mol% Mg-doped Z-cut SLN crystal. 100nm Ti film has been deposited on LN substrate by e-beam evaporation at room temperature. Diffusion constant value for Mg-doped SLN is lower (1.84×10^{-13} cm^{-2}/s) than that of pure SLN. Mg-dephd CLN also possesses iow diffusion eonstant value of 1.27×10^{-13} cm^{-2}/s due to higher doping concentration of Mg (5 mol%). AFM topographic observation. reveals that Mg-doped SLN shows lower sutface roughness than Mg-doped CLN. The roughness (peak to valley) of the Ti-diffused Mg:SLN is 20nm compared to 62nm for the congruent LN waveguide. These features make Mg:SLN highly attractive for the fabrication of efficient waveguides.

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1. Introduction

Most of the research on integrated optics has been devoted to the fundamental problems of component design and material development. A variety of materials have been used for the formation of integrated optical components such as modulators, switches, filters, polarization controllers, etc. Among them, ferroelectrics like $LiNbO_3$ (LN) and $LiTaO_3$ (LT) offer high optical quality and both electro-optic and piezoelectric effects for active interaction with the optical wave. The enhanced photorefractive sensitivity in optical waveguides is based on the incorporation of transition metals [l] and the surface doping techniques such as ion implantation, ion exchange and in-diffusion process [2,3]. In order to realize an integrated component, it is essential to fabricate a high refractive index region in $LiNbO_3$ matrix and this increase, of refractive index is usually achieved by the methods of Ti in-diffusion and proton exchange.

Diffusion of titanium into LN single crystal substrate at high temperature ($T > 1000^{\circ}$C) is essential for practical wave-guide fabrication in second harmonic generation and optical parametric process similar to Ti:LN waveguides [4] with periodic ferroelectric domain inversion for quasi phase matching [5,6]. The diffusion of Ti into LN creates sufficient stresses to generate. both misfit dislocations and cracks within the diffused layers [7]. The diffused Ti site and valence site were investigated by X-ray photoelectron spectroscopy (XPS). Diffusion constants along surface or in bulk were obtained in substrates with different crystallographic orientations [8,9]. Ti and Li concentrations in diffused layers have beeh studied by secondary ion mass spectroscopy [10]. It is well known that in the temperature region between 550 and 900°C, lithium triborate normally

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precipitates on the substrate of $LiNbO_3$ with congruent composition irrespective of the oxygen, N or Ar atmosphere and $LiNb_3O_8$ Phase vanishes at the temperature above 900 °C.

In spite of extensive studies on optlcal properties of Ti:$LiNbO_3$ diffused layers, many fundamental issues in Ti diffusion process of stoichiometric and congruent LN at higher temperature > 1000 °C are not well understood and hence further investigations are required. In the present work, we aim to study the characteristics of Ti in-diffusion in MgO-doped and non-doped stoichiometric $LiNbO_3$ by high temperature annealing treatment and surface morphology of the LN waveguides using SIMS and AFM analyses.

2. Experimental procedure

Polished and chemically cleaned Z cut $LiNbO_3$ substrates were used in this experiment. Thick Ti films of 100 nm were prepared by e-beam evaporation at room temperature on the -Z surface of $LiNbO_3$ crystals. Planar waveguide was prepared by the thermal diffusion of Ti into the substrates. The samples were annealed for 23 h to enhance diffuslon of Ti at 1080°C with three zone tube furnace. The heating and cooling rates were 9 and 3 °C/min, respectively. All experiments were carried out in dry atmosphere (80:20;N_2:O_2). To prevent the reduction of the samples, dry carrier gas was flown throughout annealing process. Titanium in-depth profiles were measured by the secondary ion mass spectrometry (SIMS) technique with an IMS 4f mass spectrometer using a 14.5keV Cs^+ primary beam (100nA) rastered over a 125 × 125 μm^2 area, and by negative secondary ion detection. The charge build-up profiling was compensated by an electron gun. To avoid electrical charging during analysis, samples were coated with about 50Å of gold and for the same reason negative oxygen ions were used in the sputtering beam for SIMS analysis taken with a CAMECA IMS 3f ion microanalyser.

The diffusion coefficient D has been estimated by comparing titanium ion concentration profile measured by SIMS to the solution of Fick's law. The concentration profile $C(x,t)$ depends on the diffusion depth x and the annealing time t. The diffusion process is based on the Fick's law:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}. \quad (1)$$

For the thin film case, it has a semi-Gaussian shape:

$$C(x,t) = C_0 \operatorname{erfc}\left(\frac{x}{d}\right), \quad (2)$$

where

$$d = 2\sqrt{Dt_{\text{diff}}}$$

'd' is thickness of Ti film coated on LN substrate.

The surface morphology of annealed samples was examined by atomic force microscopy (AFM) using a SPI-3700 system of Seiko Corp. The AFM observation was performed at room temperature in air atmosphere using a micro-fabricated cantilever in contact mode without any bias.

3. Results and discussion

3.1. Ti in-diffusion characteristics

The parameters that affect and control the dopant concentration depth profiles are the initial thickness of the film, annealing time and diffusion temperature. In order to get the anisotropy of the diffusion processes, Mg-doped and non-doped stoichiometric and congruent lithium niobate single crystals were chosen. Table 1 shows the experimental process parameters for four different Ti-coated LN samples. Fig. 1a depicts the normalized SIMS depth profiles of titanium in 1 mol% of MgO-doped stoichiometric $LiNbO_3$ (Mg:SLN) with h = 100nm annealed for 23h at 1080°C. For the as-prepared sample, it does not show any abrupt slope change at the interface of Ti and $LiNbO_3$, which is due to the mixing of elements during coating. However, Ti diffusion slightly starts at 500 °C-annealed sample in comparison with as-prepared sample. Instead, at T > 1000°C, as it clearly emerges, the dopant profile can be well approximated by a semi-Gaussian function [11]. SIMS measurements reveal that at this temperature a strong modification in the material composition takes place, as shown in Fig. 1a. In all the profile data, the magnesium and niobium signals remain constant, but the Ti concentration decreases to minimum. Fig. 1b shows the normallzed SIMS depth profile of Ti for 1 mol% Mg:SLN, 5mol% Mg:CLN, non-doped

Table 1
Annealing condition and diffusion constant for Ti-diffused LN samples

Samples	Ti film thickness (nm)	Annealing temperature (°C)	Annealing time (h)	Atmosphere	Ti/Nb concentration I[48Ti]/I[Nb]	Diffusion constant cm^{-2}/s
Mg:SLN	100	1080	23	Dry air	0.14–0.15	$3.30E^{-13}$
Mg:CLN	100	1080	23	Dry air	0.30–0.38	$9.18E^{-13}$
SLN	100	1080	23	Dry air	0.18–0.21	$6.23E^{-12}$
CLN	100	1080	23	Dry air	0.35	$1.15E^{-12}$

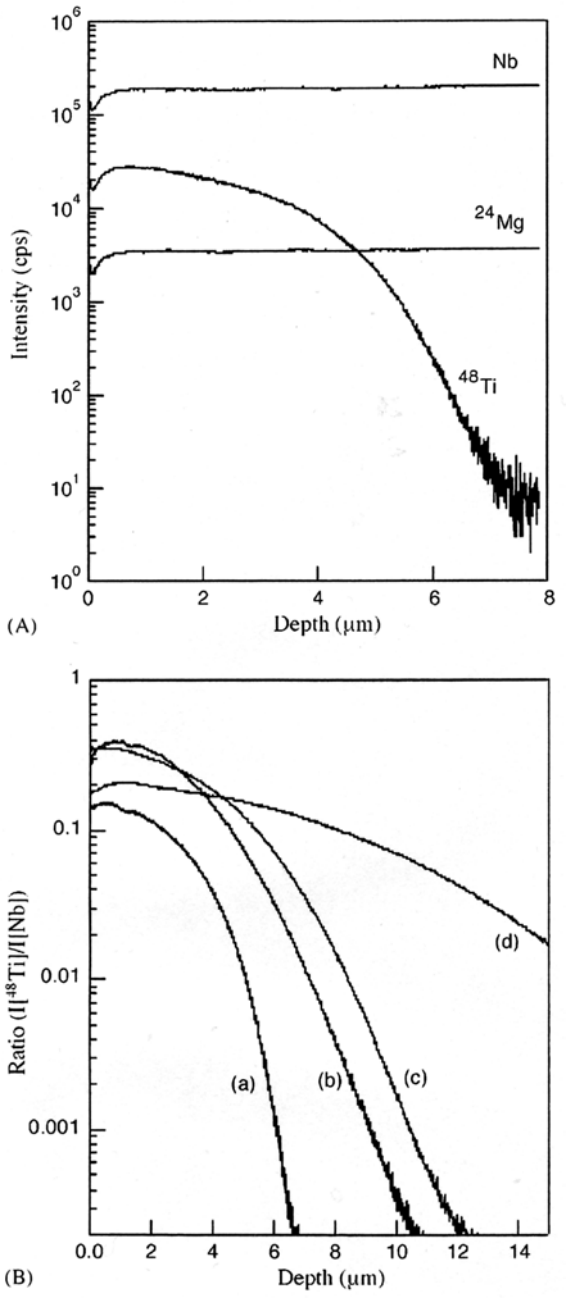

Fig. 1 . (A) SIMS depth profiles of Ti, Nb and Mg in 1 mol% MgO-doped $LiNbO_3$ after annealing at 1080 ˚C for 23 h. (B) SIMS depth profiles of Ti in (a) (1 mol%) Mg:SLN (b) (5 mol%) Mg:CLN (c) non-doped SLN and (d) CLN after Ti diffusion at 1080˚C for 23 h.

stoichiometric (SLN) and congruent lithium niobate (CLN) slab waveguides. The depth of Ti diffusion varies and it is very less in Mg:SLN compared to that of congruent lithium niobate waveguide. Ti diffusion in Mg-doped congruent lithium niobate (Mg:CLN) and stoichiometric lithium niobate (SLN) has almost same trend and this may due to high concentration (5mol%) of Mg in congruent LN waveguide. From the Ti and Nb yields, it is possible to obtain a ratio between Ti and Nb atomic concentrations in the surface layer compound as shown in Table 2. For longer annealing time at T = 1080 ˚C, the Ti surface concentration lowers as titanium diffuses further into the substrate and removal of lithium accumulation at the surface is also realized at higher diffusion temperatures.

Fig. 2 shows the depth profile of Ti in-diffusion into (1 mol%) Mg-doped stoichiometric lithium niobate with different annealing time (a) 2 h (b) 4h (c) 8 h and (d) 23 h.

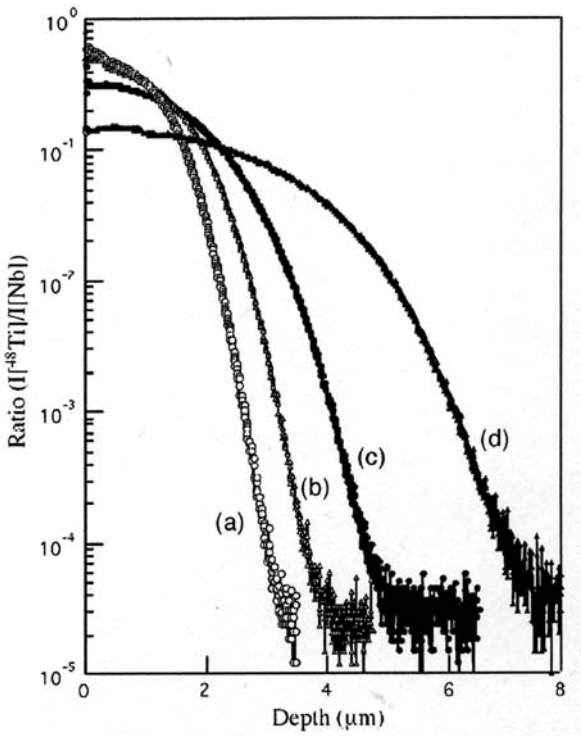

Fig. 2. SIMS depth profile of Ti in (1 mol%) Mg:SLN annealing at l080 ˚C for different annealing time (a) 2 h (b) 4 h (c) 8 h and (d) 23 h.

Table 2
Annealing condition and diffusion constant for Ti-diffused Mg:SLN in dry air atmosphere with different annealing time

Sample	Ti film thickness (nm)	Annealing temperature (°C)	Annealing time (h)	Ti/Nb concentration I[48Ti]/I[Nb]	Diffusion constant cm^{-2}/s
Ti diffused Mg:SLN	100	1080	2	0.63	$6.92E^{-13}$
	100	1080	4	0.50	$4.84E^{-13}$
	100	1080	8	0.32	$4.08E^{-13}$
	100	1080	23	0.14–0.15	$3.30E^{+13}$

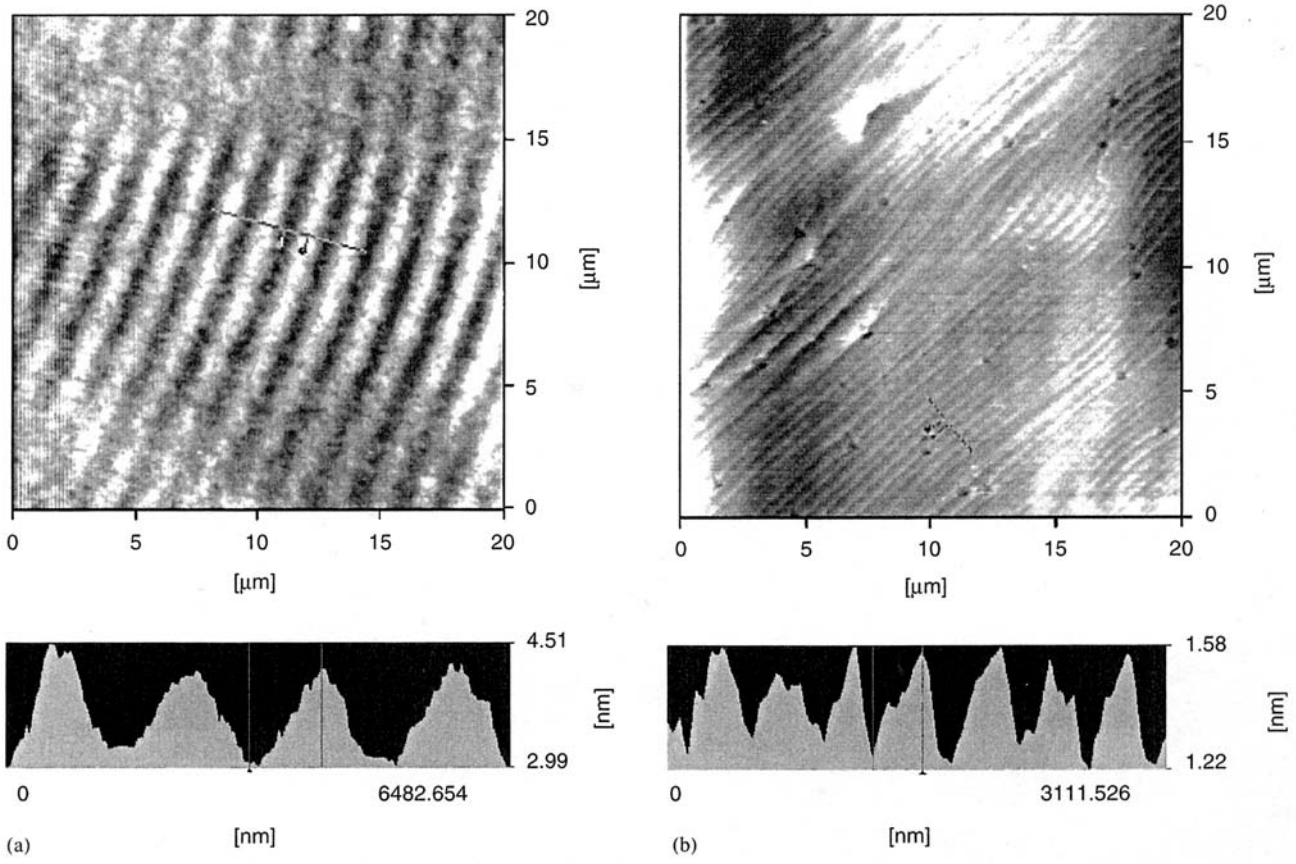

Fig. 3. AFM images and surface profile of Mg:SLN (a) before and (b) after annealing.

The diffuslon depth of titanium increases with annealing time and it is evident that the density of Mg-diffused LN has the increasing tendency of with longer diffusion time. This phenomenon of lattice distortion is probably related to the mechanism of Ti ion diffusion [12]. The diffusion constant in the case of Ti-diffused Mg-doped SLN increases with annealing time as shown in Table l. As a result of the fit procedure, it is found that the diffusion constants are compatible within the experimental errors to those obtained at lower anneallng times. This may be due to the variation in defect density of the crystals.

3.2. AFM observation on Ti-diffused LN substrates

Fig. 3a and b denotes the AFM observation on the surface of Mg-doped SLN substrate before and after annealing. This polished surface contains surface damages such as scratches and corrugations on atomic scale on the top most surface. The peak to valley roughness on the pre-annealed surface is estimated to be 1.14nm rather than 0.28 nm over 20μm. The surface smoothness of the annealed substrate is improved five times compared to that of the as-prepared substrate. Figs 4a–d show the AFM images and cross-sectional profiles of Ti-diffused surface of Z-cut Mg-doped and non-doped stoichiometric lithium niobate (SLN) and congruent lithium niobate (CLN) substrates annealed at 1080°C. The surface roughness of Mg-doped SLN is drastically improved to atomically flat type compared to congruent lithium niobate waveguides. The atomic step height of Ti-diffused Mg-doped SLN Substrate is as low as 1.9–5.8±0.02 nm, and uniform over the whole substrate as compared with Mg:CLN (6.25–55.60±0.02nm). The fonnation of smooth surface and a terrace-and-step structure is explained based on the faceting process [13]. During the annealing process, a thermodynamically unstable surface is converted into equillbrium crystal Surfaces by rearrangement of surface atoms. Aiso, either hill-and-valley or terrace-and-step surface structure is deveioped from faceting, depending on the orientation of the original surface.

The peak to valley roughness on the surface of Ti-diffused Mg-doped and non-doped SLN and CLN substrates were estimated over an area of 20μm^2. This height corresponds to the dist,ance between oxygen triple layers, which suggests that the top most layer of the annealed Z-cut substrates conslsts of oxygen layers [14,15]. Fig. 5 represents the surface image of annealed but not diffused side of Mg-doped LN substrate and it Is observed that the Mg-doped SLN possesses smooth surface (0.28 nm) compared to other Substrates. A stable surface of stoichiometric lithium niobate waveguide with the particular orientation via the thermal faceting process gives rise to the improvement of surface smoothness in order to reduce the overall surface free energy.

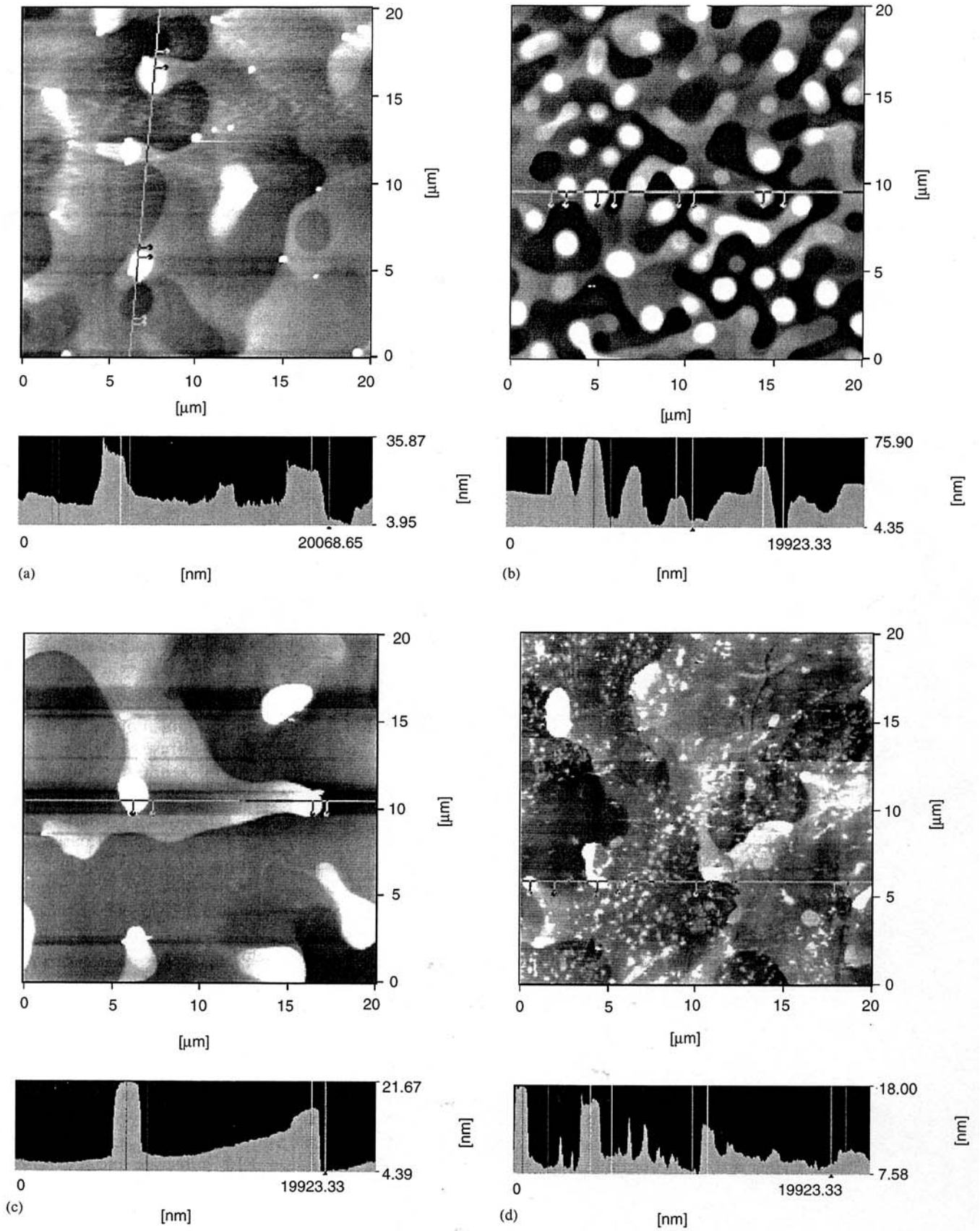

Fig. 4 AFM images and surface profile of Ti diffused (a) Mg:SLN, (b) Mg:CLN. (c) SLN and (d) CLN substrates annealed at 1080°C for 23 h.

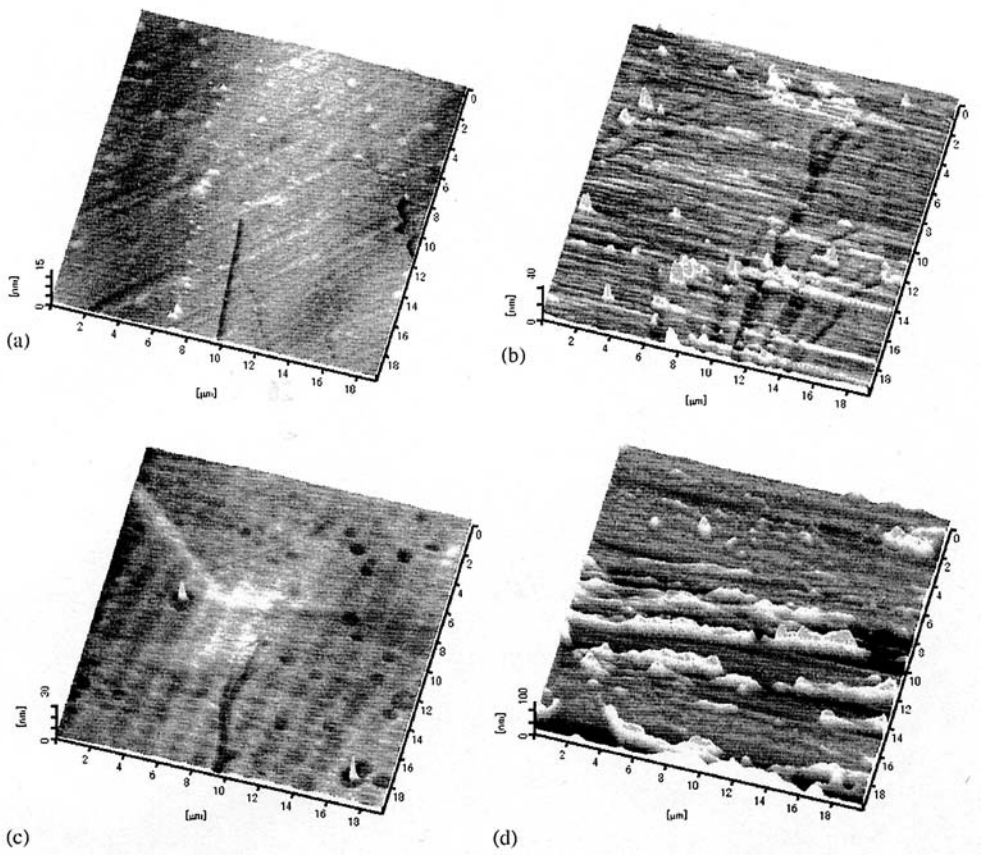

Fig. 5. AFM image of annealed surfaces of (a) Mg:SLN. (b) Mg:CLN, (c) SLN and (d) CLN substrates annealed at 1080˚C for 23 h.

The topmost layer of the annealed substrates can also be elucidated through the relationship between characteristic height of atomic step on the ultra-smooth terrace and crystallographic orientation of the substrate, which is of great importance in the viewpoint of operation of acoustic and electro-optic devices.

4. Conclusions

A systematic investigation on the compositional and surface structural properties of Ti-diffused -Z cut Mg-doped and non-doped, stoichiometric and congruent lithium niobate crystals has been carried out. Ti was diffused into MgO-doped and non-doped $LiNbO_3$ by annealing at 1080˚C for 23 h in dry atmosphere. In all experiments, Ti ion profiles could be fitted well with a Gaussian equation, and the penetration depth of Ti is found to decrease with increasing annealing time. The titanium diffusion coefficients have been estimated with best conditions. It is shown that when the titanium film deposited on the substrate diffuses completely into the matrix, a compressive deformation was found in the lattice cell. Atomically smooth surfaces with atomic step structure were obtained on Mg:$LiNbO_3$ substrates by high-temperature annealing. Using the substrates of this ultra-smooth surface, high-quality optoelectronic devices based on Mg-doped SLN substrates can be fabricated.

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