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Modelling Ti in-diffusion in LiNbO₃

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Abstract. This work presents theoretical results on the modelling of Ti in-diffusion in LiNbO₃ assuming the Ti activation energy to be spatially dependent along the diffusion depth direction as consequence of the Li concentration depletion due to its out-diffusion. The model also considers that Ti diffusion occurs as an ion exchange process in which Ti⁴⁺ ions substitute Nb⁵⁺ ions located in Li sites. The resulting diffusion equation is numerically solved according to initial and boundary conditions chosen to describe as close as possible the experimental scenario. The results show that this approach leads to highly asymmetrical Ti concentration profiles within the LiNbO₃ crystal, as already determined experimentally.

1. Introduction

Channel waveguides are important components for manufacturing opto-electronic devices, such as modulators [1], switches [2] and interferometers [3]. They are also important for many applications in signal generation, transmission and processing in telecommunication, and in integrated optics in general. Ti in-diffusion in LiNbO₃ is a well established technology as are others such as proton exchange [4]. Although the process of Ti in-diffusion in LiNbO₃ is widely used and well controlled, some physical aspects of this technique remain to be studied as result of controversial or inconclusive explanations. One point still unclear concerns the way Ti diffuses in LiNbO₃: whether it is through Li and/or Nb sites, as discussed in the models presented by Buchal *et al* [5], Sugii *et al* [6], Hauer *et al* [7] and Kollewe and Kling [8]. Another point not definitely closed is the description of the large anomalous lateral diffusion experimentally observed in *z*-cut wafers [9]. This effect was tentatively explained by Burns *et al* [10] and Fukuma and Noda [9] as a consequence of the anisotropy of the LiNbO₃ lattice, resulting in an anisotropic Ti diffusivity, *D*, but this is not in agreement with experimental results of Holmes and Smith [11]. Alternatively, the enhanced lateral diffusion was theoretically described by Fontaine *et al* [12] by solving the two-dimensional diffusion equation, under Fick's approach, with a spatially dependent diffusivity along the depth direction, mainly related to local defects, vacancies or compositional variations in the crystal, induced during the diffusion process. In order to have an analytical solution using the finite integral transform technique [13], Fontaine assumed *D* to be a step-like function, having a higher value in a region just 0.01 μm below the surface and a lower value deeper in the bulk. Later, Nunes *et al* [14] proposed an alternative description for the one-dimensional Ti in-diffusion based on experimental results of Kollewe and Kling [8]. Considering that the diffusion process occurs with Ti⁴⁺ ions replacing Nb⁵⁺ ions located in Li sites and assuming no source or sink of charges

inside the crystal, the model uses the principle of charge neutrality and applies the Nernst–Planck conceptualization. This naturally leads to a spatially dependent effective diffusivity of Ti in LiNbO_3 . The resulting diffusion equation was numerically solved for a planar geometry using the finite-element collocation technique [15] with appropriate boundary conditions. This numerical method was extended by Silva to the two-dimensional diffusion problem [16], but the results indicated that even with a spatially dependent diffusivity only a small asymmetry is achieved, as will be shown later.

This work intends to present a more complete description of the Ti in-diffusion process, but before going into further detail, let us make some comments with respect to the approach adopted by Fontaine *et al* [12]. They initially assume a diffusivity that is exponentially dependent on the diffusion depth but, in order to have an analytical solution, the exponential is approximated by a steplike function, which is not physically rigorous. Besides, they consider as boundary conditions that all Ti film is initially within the crystal. In the present work, the Ti in-diffusion process is modelled by considering the Ti activation energy to be spatially dependent along the direction perpendicular to the crystal surface where the Ti film is deposited, as a consequence of the Li out-diffusion [17, 18], causing an asymmetry in the dynamical behaviour of the diffusion process. This assumption follows the experimental results of Holmes and Smith [11] showing that the Ti diffusivity in LiNbO_3 increases when the Li molar percentage decreases. The payback of this approach is that no analytical solution for the diffusion equation is available and the problem has to be solved numerically, which can be done with the two-dimensional finite-element collation technique [16]. With this method, the initial and boundary conditions can be chosen as close as possible to the experimentally situation. It is considered that at the initial time ($t = 0$) no Ti is present inside the crystal and the film acts as a continuous source of this element up to a time τ_s (switching time) when all the surface phase will be completely diffused within the LiNbO_3 crystal. For $t \geq \tau_s$, a second diffusion stage takes place in which the Ti mass in the crystal is conserved and the diffusion leads to the equalization of the gradient concentration for very long diffusion times. On the other hand, aiming to introduce a more complete description of the physical phenomena taking place in the diffusion process, the model presented here also considers the possibility of ion exchange [14]. This comes from the fact that the ions participating in the Ti in-diffusion process (Ti and Nb) have different valencies which might lead to an internal electrical local field. Although this process may actually be occurring during the Ti diffusion, we show here that it is not as important as the activation energy spatial dependence to explain the highly asymmetrical Ti concentration profile.

2. Model formulation

This section presents the formulation of the model employed to calculate the Ti in-diffusion in LiNbO_3 . Figure 1 shows the Cartesian system relative to the crystal, x being the direction parallel to the surface where the Ti film is deposited and y the depth diffusion direction. As in [14], it is assumed that Ti diffuses through Li sites occupied by Nb and, since the ions have different valencies (Ti^{4+} and Nb^{5+}) [8, 11], charge balance should occur. The time required for charge balance is assumed to be much shorter than the time required for the concentration front to advance appreciably and the charge balance equation can be formally expressed as:

$$pC_{\text{Ti}} + qC_{\text{Nb}} = C_0 \quad (1)$$

where $p = 4$ and $q = 5$ are the valencies of the Ti and Nb ions, respectively, C_0 is an equivalent global concentration and the other terms are the concentration of the ions

identified by the subscripts. According to the Nernst–Planck approach, and considering that the internal electrical field and the gradients of Ti and Nb concentrations are collinear, each ion mass flux is given by:

$$\mathbf{J}_i = -D_i \left[\nabla C_i + \frac{z_i F C_i}{KT} \mathbf{E} \right] \quad (2)$$

where i stands for Ti or Nb, z_i is the valence of i th ion (p for Ti and q for Nb), F the Faraday constant, K the Boltzmann constant, T the temperature and \mathbf{E} the internal electric field. By considering that no source or sink of charges exists, the fluxes of both ions (Ti and Nb) have to satisfy the condition:

$$p\mathbf{J}_{Ti} + q\mathbf{J}_{Nb} = 0 \quad (3)$$

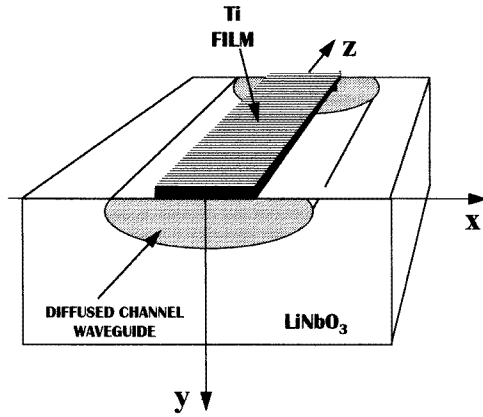


Figure 1. The geometry adopted to describe the Ti in-diffusion in LiNbO₃.

Upon substitution of equation (2) into equation (3), and using equation (1) to express C_{Nb} in terms of C_{Ti} one obtains:

$$\frac{F\mathbf{E}}{KT} = \frac{p}{q} \left[\frac{1-r}{1-\alpha \frac{C_{Ti}}{C_0}} \right] \frac{\nabla C_{Ti}}{C_0} \quad (4)$$

where $r = D_{Ti}/D_{Nb}$ and $\alpha = p(1-rp/q)$. Substituting this equation into equation (2) we obtain:

$$\mathbf{J}_{Ti} = -D_{eff} \nabla C_{Ti} \quad (5)$$

where

$$D_{eff} = D_{Ti} \left(\frac{1 - \beta \frac{C_{Ti}}{C_0}}{1 - \alpha \frac{C_{Ti}}{C_0}} \right) \quad (6)$$

and $\beta = p(1-p/q)$. Considering the continuity equation:

$$\frac{\partial C_{Ti}}{\partial t} = -\nabla \cdot \mathbf{J}_{Ti} \quad (7)$$

and using the expression for \mathbf{J}_{Ti} given in equation (5), we obtain a nonlinear partial differential equation for the Ti diffusion:

$$\frac{\partial C_{Ti}}{\partial t} = \frac{\partial}{\partial x} \left(D_{eff} \frac{\partial C_{Ti}}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{eff} \frac{\partial C_{Ti}}{\partial y} \right). \quad (8)$$

This equation is general for describing the diffusion of a given ion in a crystal where exchange with another ion occurs. When the valencies of these ions are equal ($p = q$) $\beta = 0$, but the parameter α can be different from zero in cases where the ions diffusivity are not equal, and we may still define an effective diffusivity. This means that when the ions participate in the diffusion process with different valencies, or with different mobilities, the charge balance requirement leads to an effective diffusivity for the in-diffused ions. On the other hand, if $r = 1$, we have $\alpha = \beta$, $E = 0$ and the effective diffusivity becomes the titanium diffusivity. In this situation, therefore we re-obtain the usual diffusion equation, under Fick's approach, without ion exchange.

In our model the real diffusivity has a spatially dependent activation energy \mathcal{E}_i due to the Li out-diffusion and is usually written as:

$$D_i = D_{0i} \exp\left(\frac{\mathcal{E}_i}{KT}\right) \quad (9)$$

where again i stands for Ti or Nb and D_{0i} is a term proportional to the jump distance and frequency inherent to the diffusion mechanism in the crystal. Here, the activation energy will be expressed with the assumption that only variations along the direction perpendicular to the crystal surface will exist, as also considered in reference [12]. This means that the out-diffusion of Li is assumed to be the same along the entire crystal surface, even through the Ti film deposited on the crystal surface. Under this hypothesis, the activation energy, \mathcal{E}_i , is written in the form:

$$\mathcal{E}_i = E_i - \Delta_i(y) \quad (10)$$

where E_i is the unperturbed activation energy (without Li out-diffusion) and $\Delta_i(y)$ is a monotonically decreasing function, conveniently chosen to describe the spatial variation of the perturbation in the activation energy. References [19] and [20] show that the concentration depletion of Li is well fitted by different functions such as exponential, error function and integral-error function, and since $\Delta_i(y)$ is assumed to be proportional to the Li concentration, it may also be described by these functions. For simplicity, we will assume $\Delta_{Ti}(y) = \Delta_{Nb}(y)$, such that r does not depend on the y -coordinate and the subscript i can be dropped. Although this assumption is not crucial to obtain the enhanced lateral diffusion, as we have verified in our numerical calculations, it simplified the solution and makes easier the analysis of the situation where the ion exchange is not present. In this case, we have just to set $r = 1$, as discussed previously.

It is usual to express the diffusion equation in a dimensionless form. Taking L as the substrate thickness we define: $\tau = D_{Ti}t/L^2$, with $D_{Ti} = D_{Ti}^0 \exp\{-E_{Ti}/KT\}$, $\xi = x/L$, $\chi = y/L$ and $u = C_{Ti}/C_0$, and using equation (9), the dimensionless diffusion equation will be:

$$\frac{\partial u}{\partial \tau} = e^{\delta(\chi)} \left\{ \frac{\partial}{\partial \chi} \left[\frac{1 - \beta u}{1 - \alpha u} \frac{\partial u}{\partial \chi} \right] + \frac{\partial}{\partial \xi} \left[\frac{1 - \beta u}{1 - \alpha u} \frac{\partial u}{\partial \xi} \right] + \frac{\partial \delta(\chi)}{\partial \chi} \left[\frac{1 - \beta u}{1 - \alpha u} \frac{\partial u}{\partial \chi} \right] \right\} \quad (11)$$

where $\delta(\chi) = \Delta(\chi)/KT$. For $\delta(\chi) = 0$ (unperturbed activation energy) one recovers the equation with just the ion exchange [16]. Equation (11) can be solved numerically by the two-dimensional finite-element collocation technique, which allows the use of several different functions to describe $\Delta(y)$.

3. Numerical results

This section presents results of the numerical solution of (11). The activation energy perturbation is described by an exponential function of the type $\Delta(y) = \Delta_0 \exp(-y/\sigma)$, or

in the dimensionless form

$$\Delta(\chi) = \Delta_0 \exp(-\chi/\sigma') \quad (12)$$

where $\sigma' = \sigma/L$. Other functional descriptions can be used, such as Gaussian and others, with no extra computational problem.

The initial condition is $C(0, \xi, \chi) = 0$. Therefore, no Ti has been diffused inside the crystal at $\tau = 0$ ($t = 0$). On the other hand, the boundary conditions used in our calculations are the following: (i) for $\tau < \tau_s$, $u(\tau, \xi, 0) = 0.25$ for $|\xi| < w/2$, $(\partial u/\partial \chi)_{\chi=0} = 0$ for $|\xi| > w/2$ and $(\partial u/\partial \chi)_{\chi=1} = (\partial u/\partial \xi)_{\xi=-1/2} = (\partial u/\partial \xi)_{\xi=1/2} = 0$, and (ii) for $\tau > \tau_s$, $(\partial u/\partial \chi)_{\chi=0} = (\partial u/\partial \chi)_{\chi=1} = (\partial u/\partial \xi)_{\xi=-1/2} = (\partial u/\partial \xi)_{\xi=1/2} = 0$. Here, w is the film width and τ_s is the instant of time when all the Ti deposited on the LiNbO₃ wafer surface has been totally diffused into the crystal. The condition $u(\tau, \xi, 0) = 0.25$ is the same as used in [14] and is obtained from (1) assuming that at the interface where the Ti film is deposited $C_{Nb} = 0$, which leads to $u(\tau, \xi, 0) = 1/p$. This time can be obtained by integrating the mass of Ti diffused within the crystal (m_d) and comparing with that deposited (m_0) on the wafer surface. When $m_d = m_0$, with a precision conveniently chosen in the computer program, τ_s is obtained and the boundary conditions are changed. For $\tau < \tau_s$, our boundary conditions impose that the Ti concentration on the surface is constant and equal to the normalized concentration C_{Ti}/C_0 . It is also imposed that no flux of mass exists through the surface located at $\chi = 1$, which is opposite to that where the Ti film was deposited and from the other lateral surfaces. After the switching time τ_s , the boundary conditions are changed to the new set and the concentration at the surface where the Ti film was deposited is free to vary while no flux of mass exists at any other crystal surface.

Figure 2 shows the concentration distribution as a function of x and y obtained with $r = 0.5$ and $\delta_0 = 5.0$, where $\delta_0 = \Delta_0/kT$. This result corresponds to the case where both the activation energy perturbation, given by the exponential function, and the ion exchange occur. For $\delta_0 = 5.0$, the activation energy perturbation $\Delta(y)$ at the surface corresponds to a decrease of about 20% of the bulk activation energy. In these calculations, we have used $\sigma' = 0.032$ for the exponential activation energy distribution, which corresponds to a depth penetration $\sigma = 5 \mu\text{m}$ for a wafer $160 \mu\text{m}$ thick. This value for σ is somewhat smaller than the results of Li effusion reported in [19], but it is significantly higher than the value of $0.01 \mu\text{m}$ used by Fontaine *et al* [12]. We have found that both the asymmetry and the switching time depend strongly on the parameters δ_0 and σ . In this way, it is possible to increase the value of σ by increasing δ_0 and still have a highly asymmetrical profile. However, in this case, the switching time decreases to very small values, much lower than what is obtained experimentally (a few hours, depending on the film thickness and the diffusion temperature, as measured in [21]).

Figure 3 shows the time evolution of the concentration profile as a function of x and y for two values of the energy perturbation. Along the x direction (parallel to the surface) the calculated profiles agree with experimental results of Fukuma and Noda [9], while along the y direction they are in agreement with those reported by Minakata *et al* [22]. It is interesting to point out that, in this later situation, both our theory and their results present a bump inside the bulk, whose position depends on the diffusion time.

The asymmetry in the diffused Ti profile can be more easily seen in figure 4, where topographic concentration curves are shown for different Ti diffusion cases, namely (a) without activation energy perturbation ($\delta_0 = 0$) and with ion exchange ($r = 0.5$), (b) without ion exchange ($p = q$) and with activation energy perturbation ($\delta_0 = 5.0$ and $\sigma = 5 \mu\text{m}$) and (c) both effects being considered ($\delta_0 = 5.0$, $\sigma = 5 \mu\text{m}$ and $r = 0.5$). The experimental values of δ_0 , σ and r are not known, but we are using numbers with

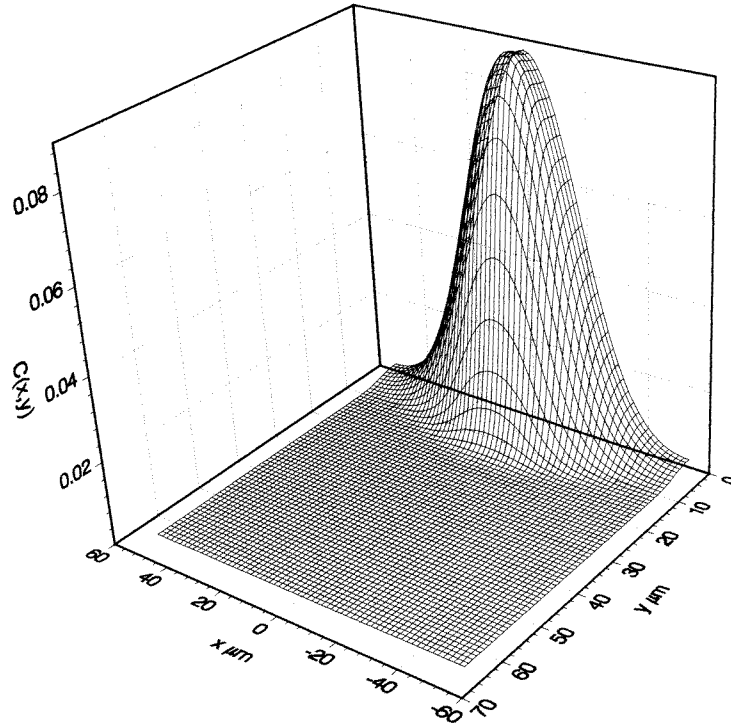


Figure 2. The three-dimensional concentration distribution with activation energy perturbation ($\delta_0 = 5.0$ and $\sigma = 5 \mu\text{m}$) and ion exchange ($r = 0.5$), for $w = 16 \mu\text{m}$ and $t = 7 \text{ h}$.

physically meaningful magnitudes. The curves corresponding to the spatially dependent activation energy are much wider than those for a constant value of \mathcal{E} , but even in this case an asymmetry arises due to the film width. These results indicate that a smaller asymmetry should be expected in the Ti concentration profile only as a consequence of the spatial dependent diffusivity caused by the ion exchange diffusion process. The model presented here was also applied to other functions describing $\Delta(y)$, such as Gaussian and negative slope straight line. The results obtained were qualitatively the same as the one obtained with the exponential function. Therefore, we suggest that the asymmetrical Ti concentration profile arises not due to asymmetries of LiNbO_3 properties nor due to the ion exchange process, but as a consequence of the diffusion process which induces perturbations on the wafer properties as a consequence of the Li effusion, building up an asymmetric behaviour in the diffusion process.

4. Conclusions

This work has presented a theoretical model for Ti in-diffusion in LiNbO_3 assuming that the Ti activation energy is perturbed by the Li effusion that occurs as a consequence of crystal heating together with the ion exchange during the diffusion process. The effusion causes a Li depletion that is function of the depth and this concentration gradient produces the perturbation on the activation energy. A behaviour similar to this was also observed during the diffusion of divalent ions in doped alkali halides [23]. The ion exchange between Ti

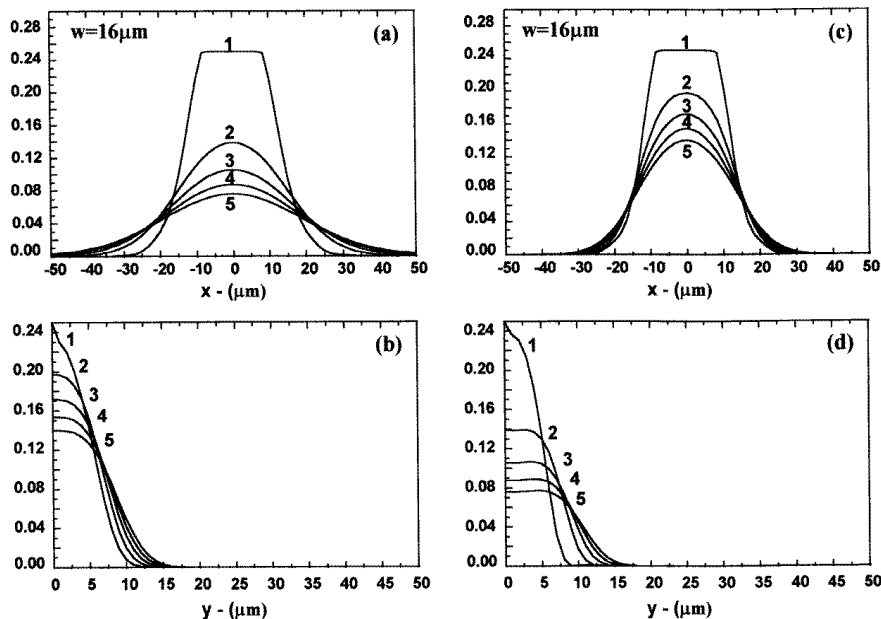


Figure 3. The evolution of concentration profiles with ion exchange ($r = 0.5$) for two values of energy perturbation (with $\sigma = 5.0 \mu\text{m}$) along the direction parallel to the wafer surface at $y = 0$ and along the depth diffusion at $x = 0$. In (a) and (b) $\delta = 2.5$, and in (c) and (d) $\delta = 5.0$. The curve labels indicate the diffusion time (1, $t = \tau_s$; 2, $t = \tau_s + 3 \text{ h}$; 3, $t = \tau_s + 5 \text{ h}$; 4, $t = \tau_s + 7 \text{ h}$; 5, $t = \tau_s + 9 \text{ h}$).

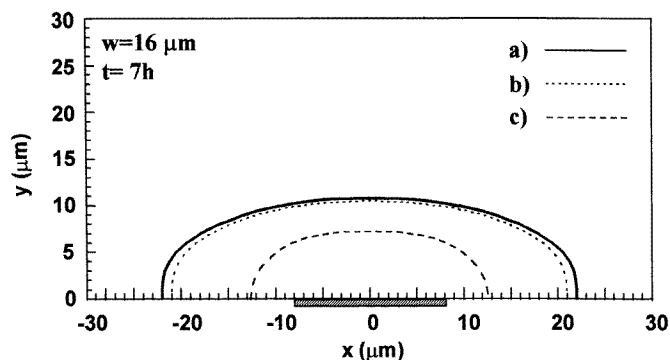


Figure 4. Topographical curves at half-maximum concentration for $\delta_0 = 0$ and $r = 0.5$ (a), $p = q = 0$, $\delta_0 = 5.0$ and $\sigma = 5.0 \mu\text{m}$ (b) and $\delta_0 = 5.0$, $\sigma = 5.0 \mu\text{m}$ and $r = 0.5$ (c).

and Nb ions is directly related to the necessary neutrality of charges that must occur within the crystal bulk. Adopting initial and boundary conditions that fit as closely as possible the physical phenomena taking place during diffusion, our model leads to the asymmetrical Ti concentration profile observed experimentally. In our model some improvements are in progress, for example considering the effusion of Li taking place together with the Ti diffusion. This approach will lead to coupled non-linear diffusion equations, significantly increasing the degree of calculation level, and will be reported in a future work. The main

conclusion we obtained is that the asymmetrical Ti concentration profile is not a result of intrinsic asymmetries in the physical properties of LiNbO₃. Instead, the asymmetrical Ti concentration profile results from the induced phenomena caused by the effusion of Li which has its origin in the crystal heating and, to a lesser extent, in the ion exchange that occurs during the diffusion process. Finally, we should point out that for other types of cut, the diffusion would occur for directions different from the y direction and in this case the value of Δ_0 could change according to the diffusion direction. As a consequence, the asymmetry of the Ti concentration profile could be smaller than the one studied here, as experimentally observed by Fukuma and Noda [9].

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