

phys. stat. sol. (a) **172**, R3 (1999)

Subject classification: 66.30.Jt; S11

## Copper Diffusion into Lithium Niobate

J. HUKRIEDE<sup>1</sup> (a), B. GATHER (b), D. KIP (a) and E. KRÄTZIG (a)

(a) Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück, Germany

(b) Universität Osnabrück, Institut für Chemie, D-49069 Osnabrück, Germany

(Received February 23, 1999; accepted March 11, 1999)

Holographically recorded refractive index gratings in lithium niobate crystals are of potential use for applications in integrated optics. In this field commercially available wafers serve as the substrate material for waveguide fabrication. To increase the number of photorefractive centers [1] the wafers can be surface-doped by additionally indiffusing [2] a thin layer of a transition metal, e.g. iron. Iron-doped substrates have been used to fabricate reflection filters for infrared light in LiNbO<sub>3</sub>:Ti channel waveguides [3] for dense WDM applications or laser diode wavelength stabilisation. Also DBR waveguide lasers [4] have been realized in LiNbO<sub>3</sub>:Fe utilizing holographically recorded laser mirrors. A main disadvantage of the indiffusion of iron is its small diffusion constant even at high temperatures. As an alternative, in this contribution we investigate copper diffusion at  $T = 1000^\circ\text{C}$  into lithium niobate.

The sample was prepared in the following way: An undoped polished lithium niobate wafer of congruently melting composition was cut into pieces of  $x_0 \times z_0 = 8 \times 10 \text{ mm}^2$ , the  $c$ -axis of the crystal pointing along the larger side. The direction of the  $y$ -axis was parallel to the top face normal. The thickness  $y_0$  of the sample was 1 mm. A 500 nm-thin layer of copper was deposited by thermal evaporation on the top face of the crystal. We successively indiffused the layer into the substrate at  $T = 1000^\circ\text{C}$  in air. The annealing steps were  $\Delta t = 1 \text{ h}$ , 1 h, 1 h, 2 h and 2 h, resulting in a total diffusion time of  $t = 1 \text{ h}$ , 2 h, 3 h, 5 h and 7 h. After each annealing step the  $c$ -face of the sample (orientated rectangular to the top face) was precisely polished. Then it was scanned in the  $y$ -direction by the focused electron beam of a microprobe (focus diameter  $< 1 \mu\text{m}$ , acceleration voltage 25 keV) to determine the distribution of copper atoms in the sample. As a reference the signals of oxygen and niobium atoms were also checked. One scan step of the beam was  $\Delta y = 1 \mu\text{m}$ . After 1000 steps the whole sample was scanned and the copper indiffusion was carried on with the next annealing step  $\Delta t$ .

For a total annealing time below  $t = 7 \text{ h}$  the evaporated copper layer had not yet indiffused completely into the sample. An additional sharp peak on the top appeared in the copper signal during the microprobe scan. This indicates that up to this point indiffusion from an infinite source had taken place. The solution of Fick's laws results in

$$c_{\text{Cu}}(y) = \hat{c}_{\text{Cu}} \operatorname{cerf}(y/\varrho), \quad \varrho = 2\sqrt{Dt}, \quad (1)$$

where  $\operatorname{cerf}(\xi) = (2/\sqrt{\pi}) \int_{\xi}^{\infty} e^{-t^2} dt$  is the complementary error function. The diffusion constant is denoted by  $D$ ,  $t$  is the total diffusion time,  $\varrho$  the penetration depth and  $c_{\text{Cu}}(y)$  the local copper concentration in the crystal.

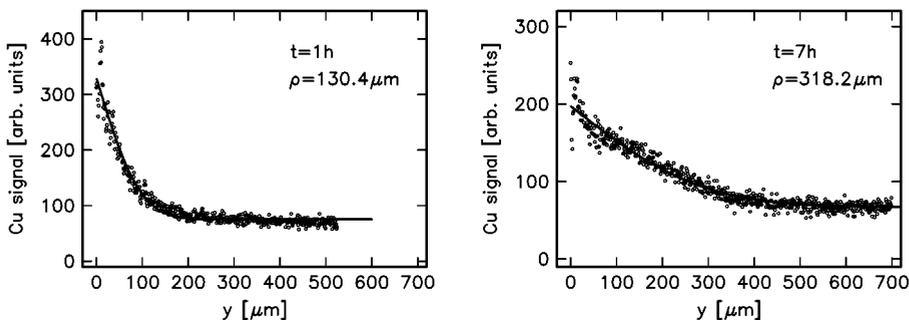


Fig. 1. Copper signal (symbols) detected with the microprobe and best fitting curve (solid line) after a total annealing time of 1 h (left part) and 7 h (right part)

<sup>1</sup>) Supported by the Deutsche Forschungsgemeinschaft, grant SFB225/D9.

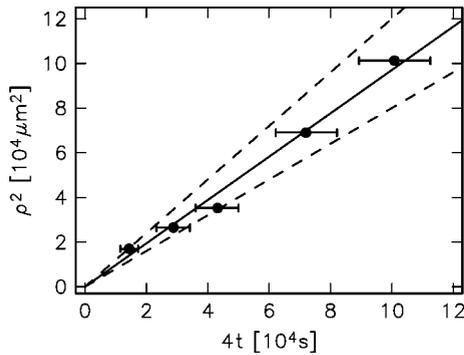


Fig. 2. Diffusion depths  $\rho^2$  extracted from the measurements versus time  $4t$ . The solid line is a linear fit according to Eq. (1). The two dashed lines indicate the deviation of  $\pm 0.2 \mu\text{m}^2 \text{s}^{-1}$ , the horizontal lines represent error bars

As an example the left part of Fig. 1 shows the measured copper distribution in the sample after a total diffusion time of  $t = 1$  h. The strong copper peak resulting from the remaining evaporated layer has been subtracted. The copper signal is well described by Eq. (1) if we add a constant value  $c_{\text{Cu}}^0$  to take into account the present background signal. The solid line indicates the best fitting curve. In the right part we present the same measurement after a total diffusion time of  $t = 7$  h. Here the copper signal of the remaining layer has just vanished but the curve is still well described by Eq. (1). Diffusion from an exhaustive source would result in a Gaussian shaped curve which does not describe the measured data in a convincing manner. Fig. 2 represents the square of the extracted diffusion lengths  $\rho^2$  versus the quadruple diffusion time  $4t$ . According to Eq. (1) a linear fit yielded the corresponding diffusion constant  $D$ . We derived  $D = (1.0 \pm 0.2) \mu\text{m}^2 \text{s}^{-1}$  for copper diffusion into lithium niobate along the  $y$ -axis at  $1000^\circ \text{C}$ . This is more than 500 times higher than the diffusion constant of iron in lithium niobate under the same conditions [4].

The derived diffusion constant is high enough to produce surface-doped waveguide substrates of adequate impurity concentration for holography within a few hours of annealing time. This is of great advantage to minimize surface modifications of the material resulting from, e.g., lithium out-diffusion during long diffusion times. It also seems possible to dope even volume crystals with a thickness of one or two millimeters homogeneously by indiffusion of thin evaporated copper layers. For example, our investigated crystal would reach an impurity level of  $c_{\text{Cu}} = 2000$  molppm if all of the copper is uniformly redistributed. This requires an annealing time of 50 to 100 h which is still in the practicable range.

## References

- [1] G. E. PETERSON, A. M. GLASS, and T. J. NEGRAN, *Appl. Phys. Lett.* **19**, 130 (1971).
- [2] W. PHILLIPS, J. J. AMODEI, and D. L. STAEBLER, *RCA Review* **33**, 94 (1972).
- [3] J. HUKRIEDE, I. NEE, D. KIP, and E. KRÄTZIG, *Opt. Lett.* **23**, 1405 (1998).
- [4] C. BECKER, A. GREINER, T. OESSELKE, A. PAPE, W. SOHLER, and H. SUCHE, *Opt. Lett.* **15**, 1194 (1998).
- [5] D. KIP, B. GATHER, H. BENDIG, and E. KRÄTZIG, *phys. stat. sol. (a)* **139**, 241 (1993).