

by cooling. Furthermore, the concentration of the free charge carriers in layer 1 must be such that the thickness of the depletion region is greater than the thickness of the high-resistance layer. The latter condition is satisfied at concentrations $<10^{14} \text{ cm}^{-3}$. We note in conclusion that, owing to the high resistivity of the semiconductor layer in nonstationary depletion operation, it becomes possible to match the parameters of the narrow-band photoconductor with the parameters of the scanning system.

LITERATURE CITED

1. N. F. Kovtonyuk and V. G. Fadin, Zh. Prikl. Spektrosk., 18, No. 1, 127 (1973).
2. N. F. Kovtonyuk, V. A. Morozov, D. G. Sikharulidze, I. F. Usol'tsev, V. G. Fadin, and M. I. Brodzeli, Zh. Prikl. Spektrosk., 22, No. 3, 539 (1975).
3. N. F. Kovtonyuk, A. R. Gililov, and B. M. Lavrushin, Radiotekh. Élektron., 18, No. 6, 1316 (1973).

CHANGES IN THE OPTICAL PROPERTIES OF FILMS OF SILICON NITRIDE, SILICON OXINITRIDE, AND SILICON OXIDE UPON ION IRRADIATION

N. N. Gerasimenko, T. I. Kovalevskaya,
V. G. Pan'kin, K. K. Svitashv, and G. M. Tseitlin

UDC 535.32

Films of silicon nitride and silicon oxinitride on quartz or silicon substrates covered with an oxide film are now being used as dielectric lightguides [1]. The manufacture of various integrated optical elements on those films will be the next step in the production of optical microcircuits. The refractive index of a well-specified section of the lightguide must be modified when certain optical elements such as prisms, diffraction gratings, etc., are to be produced. It is a well-known fact that the index of refraction of oxinitride layers depends strongly upon their composition, mainly upon the ratio of the nitrogen and oxygen concentrations in the layers [2]. The goal of the present work was to study the possibility of changing both the composition and the index of refraction of oxinitride, oxide, and nitride layers by incorporating nitrogen and oxygen ions.

We used films of pyrolytic silicon nitride and oxinitride and thermally produced oxide films with a thickness $d = 80 \text{ nm}$ on silicon substrates. Ions with energies of 20-45 keV were used for the irradiation; the current density was $\sim 10 \mu\text{A}/\text{cm}^2$. The annealing took place for 30 min in a nitrogen current at 800°C . The doses were selected so that the concentration of the atoms incorporated was comparable with the concentration of the atoms in the target and that the composition of the films could be noticeably modified. It is easy to estimate that under the irradiation conditions selected, the dose of incorporating atoms must be $\sim 10^{17} \text{ cm}^{-2}$. The refractive index n was determined with a laser ellipsometer at the wavelength 632.8 nm.

The changes which the irradiation with oxygen ions at a dose $D = 2 \cdot 10^{17} \text{ cm}^{-2}$ effected in the refractive indices of the nitride and oxinitride films were as follows: $n_{\text{initial}} = 1.96$ and 1.53 and $n_{\text{irr}} = 1.63$ and 1.50 , respectively. The irradiation of the nitride and oxinitride films with oxygen ($D = 2 \cdot 10^{17} \text{ cm}^{-2}$) substantially reduces n (at doses $D = 10^{16} \text{ cm}^{-2}$ and smaller doses a decrease in n was not observed). The refractive index decreased further (by 0.01) after annealing.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 26, No. 1, pp. 164-166, January, 1977. Original article submitted November 24, 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

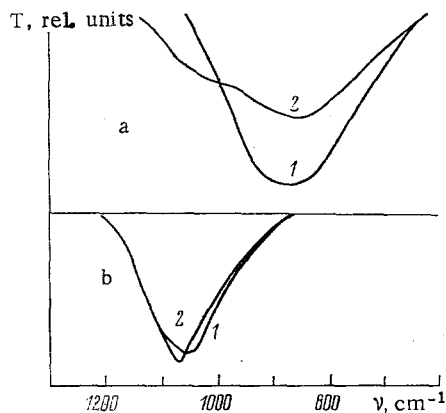


Fig. 1. Change in the infrared absorption spectrum (in relative units) of a) a silicon nitride film and b) a silicon oxinitride film after irradiation with oxygen ions at a dose of $2 \cdot 10^{17} \text{ cm}^{-2}$. Infrared spectrum before (1) and after (2) ion irradiation.

The changes in both the structure and the composition of the films were observed via the infrared spectra recorded in the region of the basic absorption bands ($1200\text{--}800 \text{ cm}^{-1}$). The spectra were recorded with a DS-402G spectrophotometer. Figure 1 shows the infrared spectra recorded from the silicon nitride samples. The basic absorption band, which results from the valence oscillations of the Si-N bonds and which is normally located at 850 cm^{-1} , had a reduced intensity after irradiation with ions. Besides that, the band became broader because the absorption at $1000\text{--}1070 \text{ cm}^{-1}$ had been increased; the absorption at $1000\text{--}1070 \text{ cm}^{-1}$ is normally caused by oscillations of the Si-O bonds. This change in the absorption spectra indicates that when Si_3N_4 films are irradiated with oxygen ions, new chemical bonds of the type of Si-O are formed so that, after irradiation, the film has a composition close to oxinitride.

After irradiation with the oxygen ions, the basic absorption band of the oxinitride films had been shifted toward shorter wavelengths (see Fig. 1b); the absorption at $950\text{--}1000 \text{ cm}^{-1}$ was slightly reduced. According to [3, 4], these results indicate that the amount of oxinitride in the film was reduced by increasing the oxide concentration. The observed changes in the infrared spectra of the nitride and oxinitride films irradiated with oxygen ions were even more pronounced after annealing. This also indicates that these changes are associated with changes in the composition resulting from the chemical interaction of the ions incorporated with the matrix molecules rather than with radiation-induced defects in the films.

The infrared spectra of the SiO_2 films were noticeably modified by irradiation, but the modifications were practically the same in the implanting of nitrogen or an inert gas (argon) and must be ascribed to radiation-induced defects, as observed in [5]. A quantitative analysis of the infrared spectra with proper regard for the changes in the form of the infrared bands (according to [3, 4]) by radiation-induced defects has shown that the concentration of oxinitride in the films can be at most 10% of the concentration corresponding to the dose of the nitrogen incorporated. Changes in the substrate temperature ($23\text{--}600^\circ\text{C}$), changes in the dose ($10^{16}\text{--}5 \cdot 10^{17} \text{ cm}^{-2}$), and subsequent annealing rendered the same results, i.e., a large portion of the nitrogen incorporated does not interact with the target molecules.

These experiments, in which Si_3N_4 and oxinitride films were irradiated with oxygen ions, indicate that the nitrogen atoms are displaced by oxygen from the matrix molecules irradiated with ions. This is obviously caused by the chemical activity of the oxygen atoms and ions, which is greater than the chemical activity of nitrogen. The displacement of nitrogen atoms from Si_3N_4 molecules by oxygen was also observed when oxygen ions were incorporated in Si_3N_4 films in anodic oxidation [6]. It cannot be ruled out that when SiO_2 is irradiated with nitrogen ions, Si-N bonds are formed, but subsequently the nitrogen is expelled by oxygen ions and the composition of the film remains practically unchanged.

Thus, it was observed that when silicon nitride and silicon oxinitride layers are irradiated with oxygen ions, the refractive index decreases, with the decrease reaching -15% in the case of Si_3N_4 . This decrease is accompanied by a change in the composition of the films. Accordingly, the irradiation of certain sections of silicon nitride and silicon oxinitride waveguides (sic) can be used to produce thin-film prisms, diffraction gratings, and other integrated optical elements.

The authors thank L. S. Smirnov for useful discussions and V. V. Voskoboinikov for providing the silicon nitride and silicon oxinitride films.

LITERATURE CITED

1. M. J. Rand and R. D. Standley, *Appl. Opt.*, 11, 2482 (1972).
2. D. M. Brown, P. V. Gray, F. K. Heumann, H. R. Philipp, and E. A. Taft, *J. Electrochem. Soc.*, 115, 311 (1968).
3. Yu. I. Kol'tsov, N. G. Kol'tsova, and G. I. Zhuravlev, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 7, 521 (1971).
4. Yu. I. Kol'tsov, N. G. Kol'tsova, G. I. Zhuravlev, and N. V. Korobov, *Zh. Prikl. Spektrosk.*, 16, 474 (1972).
5. C. R. Fritsche and W. Rothemund, *J. Electrochem. Soc.*, 119, 1243 (1972).
6. O. D. Goryunova, E. P. Kurazaev, and O. V. Sopov, *Elektron. Tekh.*, Ser. 2, No. 4, 38 (1969).
7. E. M. Zolotov, V. A. Kiselev, and V. A. Sychugov, *Usp. Fiz. Nauk*, 112, 231 (1974).