

# Influence of ion implantation on optical properties of thin Pd films on lithium niobate

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Significant increase of absorption and decrease of reflectance of thin Pd films on lithium niobate as a result of ion implantation as well as modification of the films surface structure was revealed. Formation of craters on the surface of Pd films, their amorphization and intensive ion intermixing on the interface film-substrate make spectral response nonselective in the infrared ( $\lambda = 1-15 \mu\text{m}$ ) range of spectrum. Adhesion of Pd film to lithium niobate becomes at least 2 orders higher. The effects revealed were successfully applied for development of pyroelectric detectors.

Обнаружены эффект существенного увеличения поглощающей способности и уменьшение коэффициента отражения тонких Pd пленок на ниобате лития, а также модификация поверхностной структуры образцов в результате ионной имплантации. Формирование кратеров на поверхности Pd пленок, их аморфизация и интенсивное межатомное перемешивание на границе пленка-подложка делают спектральную чувствительность образцов неселективной в инфракрасной области спектра ( $\lambda = 1-15 \mu\text{м}$ ) и адгезию Pd пленки к ниобату лития как минимум на 2 порядка выше. Это успешно было применено для разработки пироэлектрических приемников излучения.

## 1. Introduction

Lithium niobate has variety of applications in optics and optoelectronics. High pyroelectric coefficient, stability to environment, long-term durability and high optical damage threshold make lithium niobate irreplaceable to be used for pyroelectric photodetectors and power meters operating with power radiation [1]. The only improvement required is to increase sensitivity by deposition appropriate absorbing layer on the surface of lithium niobate. Golden black coating despite of non-selective absorption increase time constant due to its big thickness ( $d = 1-10 \mu\text{m}$ ). In this case thermal wave spends more time to reach pyroelectric crystal. Deposition of metallic coatings especially Pd gives advantage in thickness (usually from 20 to 50 nm) and compar-

tively good absorption value. But all above mentioned coatings have low adhesion to lithium niobate what significantly limits optical damage threshold of entire sensing system.

The idea of the present work was to provide appropriate modification of the surface structure of the samples and investigate their optical properties to find the optimal parameters of the samples structure modification. Ion implantation is known as novel method of materials processing. Depends on ions energy and dose, materials of film and substrate the following effects can be observed: defects generation, their interaction, radiation-accelerated diffusion, implantation of recoil atoms, atom intermixing in the transition layer, and other related effects.

## 2. Experimental

The Monte-Carlo method was applied for determination of a distribution of  $\text{Ar}^+$  ions and recoil atoms per depth of thin Pd films on lithium niobate substrate for ions energy of 50, 100 and 150 keV. As shown on Fig. 1 the majority of ions accelerated to 50 keV stops at 20 nm from the sample's surface. For ions with energies of 100 and 150 keV the ions distribution peaks will be at 40 and 60 nm from the sample's surface accordingly. The dose of ions should be from  $10^{15}$  to  $10^{16} \text{ cm}^{-2}$  for effective modification of samples structure. Obtained results were used for production and further processing of the samples.

Slices of lithium niobate single crystal with thicknesses of 100  $\mu\text{m}$  were coated by Pd films with thicknesses 15, 20, 30, and 40 nm by ion plasma method [2]. Ion implantation of thin Pd films on lithium niobate was made by  $\text{Ar}^+$  ions with energies from 50 to 100 keV depending on Pd film thickness in accordance with the Monte-Carlo calculations.

Spectral investigations of optical properties were performed by UR-20 spectrophotometer in wide wavelength range from 0.2 to 15  $\mu\text{m}$ .

Surface structure of the samples was examined by Scanning Electron Microscopy and Atomic Force Microscopy methods.

## 3. Results and discussion

Optical properties, in particular reflectance and transmission spectra of thin Pd films on lithium niobate non-implanted and

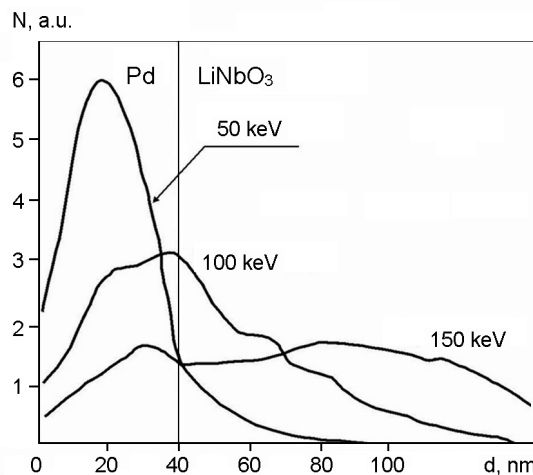


Fig. 1. Distribution of stopping range of implanted  $\text{Ar}^+$  ions by depth (energy 50, 100, and 150 keV) in the system thin Pd film-lithium niobate substrate.

implanted by  $\text{Ar}^+$  ions were measured in wide wavelength range (0.2–15  $\mu\text{m}$ ). Transmission spectra show that two absorption bands are observed near  $\lambda = 5.5$  and 6.2  $\mu\text{m}$  (Fig. 2a) for both implanted and non-implanted samples, that is related with presence of H–O–H groups in  $\text{LiNbO}_3$  and by oscillation of  $\text{H}_2\text{O}$  molecular complexes and other inclusions. In the wavelength range near  $\lambda = 10.5 \mu\text{m}$ , an intensive absorption band causes decrease in transmission. This band is related with valence bridge oscillations of oxygen in the octahedron  $\text{NbO}_6$ . These oscillations are fundamental phonons of lithium niobate single crystal [3]. As shown in Fig. 2 ion implantation causes rise

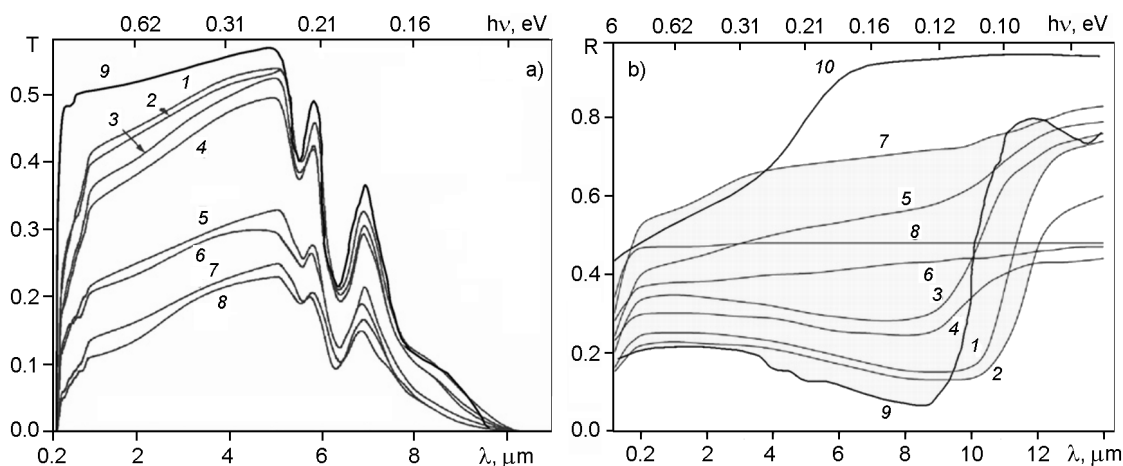


Fig. 2. Transmission (a) and reflectance (b) spectra of thin Pd film with thicknesses of 15 (1, 2), 20 (3, 4), 30 (5, 6), and 40 nm (7, 8) before (1, 3, 5, 7) and after ion implantation (2, 4, 6, 8) in comparison with lithium niobate single crystal (9) and bulk Ni (10, b).

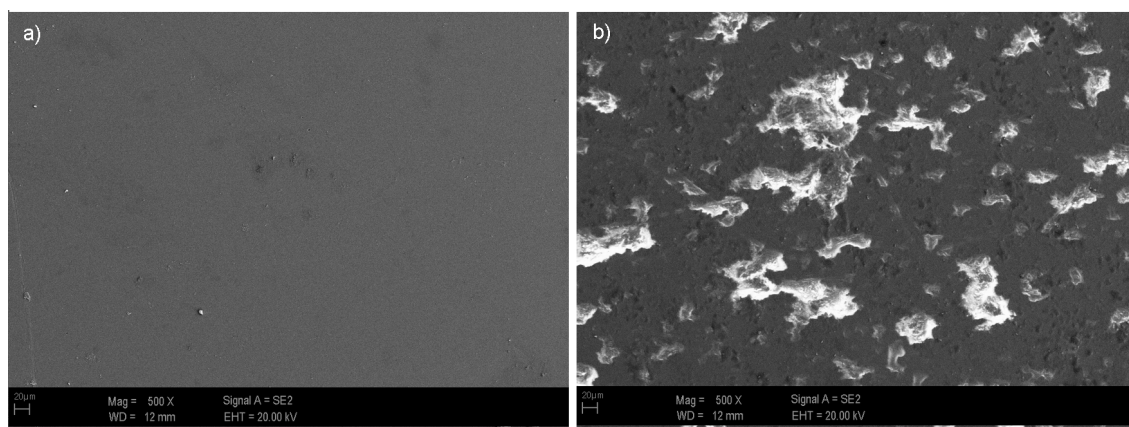


Fig. 3. SEM image of thin Pd film (40 nm) on lithium niobate before ion implantation (a) and after implantation by  $\text{Ar}^+$  ions (b).

of transmission of Pd–LiNbO<sub>3</sub> in visible and near infrared (0.4–6.0  $\mu\text{m}$ ) spectral region that is result of widening the transitional layer film-substrate and disordering the near-surface structure of the metal film and substrate.

Results of spectral investigations of reflectance for Pd–LiNbO<sub>3</sub> nonimplanted and implanted by  $\text{Ar}^+$  ions in the wide spectral range ( $\lambda = 0.2\text{--}15\ \mu\text{m}$ ) show that reflection coefficient decreases in whole the spectral range after ion implantation and for Pd film thicknesses of 30 and 40 nm it becomes non-selective in the infrared (1–15  $\mu\text{m}$ ) range [4]. To explain such difference of the results of ion implantation an investigation of surface structure of the samples by SEM and AFM method was carried out.

In SEM investigations (Fig. 3) it was shown that smooth thin Pd film 40 nm on lithium niobate before ion implantation (a) totally changed its surface structure after 100 keV  $\text{Ar}^+$  ion implantation (b), in particular crater-like blisters as well as amorphization of Pd film and subsurface layer of lithium niobate substrate were observed. Blisters appeared are result of Argon exit from the film depth during thermal annealing after ion implantation [5]. In comparison with other metals for absorbing coatings, only Pd led to the crater formation making absorbing coating more effective

and non-selective in the wide spectral range like golden black [6].

As shown in Table Pd is characterized by the lowest value of damage threshold and coefficient of surface tension among other transition metals mentioned. High values of damage threshold and coefficients of surface tension for Ni and Mo resulted in Argon coming outside the film depth. In the case of Pd films, otherwise, Argon destroys blisters that transform to the craters.

Additionally, investigations have shown that adhesion between Pd film and LiNbO<sub>3</sub> substrate becomes at least 2 orders higher after ion implantation owing to ion intermixing process which take place during ion implantation at transition layer Pd film-substrate. The revealed effects can be used for development of pyroelectric photodetectors sensing system and power meters with enhanced radiation stability, sensitivity and non-selective response in the infrared [7] range.

#### 4. Conclusion

In the current study it was found that ion implantation of thin Pd films on lithium niobate causes the reflectance decrease and absorption increase in the wide wavelength range ( $\lambda = 0.2\text{--}15\ \mu\text{m}$ ) owing to the processes of: 1) blisters formation on the samples surface increasing diffuse scattering and absorption of the sample; 2) decrease of

Table. Mechanical properties of Pd in comparison with Ni and Mo

Metal	Ni	Mo	Pd
Surface tension	1810 erg/cm <sup>2</sup>	2050 erg/cm <sup>2</sup>	1600 erg/cm <sup>2</sup>
Damage threshold	500–600 N/m <sup>2</sup>	800 N/m <sup>2</sup>	185 N/m <sup>2</sup>

heterogeneity on the interface film-substrate by ion intermixing; amorphization of subsurface layer of the film and substrate. Ion implantation led to crater-like structure formation with average diameter of craters about 10  $\mu\text{m}$ . Type of surface structure of implanted system thin metal film-lithium niobate depends on mechanical properties of metal film and in particular its damage threshold and coefficient of surface tension. Sensing system on the base of thin Pd film-lithium niobate implanted by  $\text{Ar}^+$  ions was developed for application in pyroelectric photodetectors. Their characteristics such as sensitivity, detectivity, radiation stability, time constant, durability are not worse than the corresponding characteristics of the best analogues. Spectral sensitivity of implanted thin Pd films on lithium niobate is non-selective in the infrared (1–15  $\mu\text{m}$ ) range that demonstrates variety of perspective use of the sensing system.

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## Вплив йонної імплантації на оптичні властивості тонких Pd плівок на ніобаті літію

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Виявлено ефект суттєвого збільшення поглинальної здатності та зменшення коефіцієнта відбивання тонких Pd плівок на ніобаті літію, а також модифікація поверхневої структури зразків внаслідок йонної імплантації. Формування кратерів на поверхні Pd плівок, їх аморфізація та інтенсивне міжатомне перемішування на межі плівка-підкладка роблять спектральну чутливість зразків неселективною в інфрачервоному діапазоні спектра ( $\lambda = 1-15$  мкм), і адгезію Pd плівки до ніобату літію щонайменше на 2 порядки вище. Це успішно було застосовано для розробки піроелектричних приймачів випромінювання.