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# Impact of laser pulse repetition frequency on nucleation and growth of $LiNbO_3$ thin films

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This paper reports the impact of the laser pulse repetition frequency on growth processes, morphological and electro-physical parameters of nanocrystalline $LiNbO_3$ thin films obtained by the pulsed laser deposition technique. It was found that the nucleation process in $LiNbO_3$ films could controllably change by increasing the laser pulse repetition frequency. The film obtained at the repetition frequency of 4 Hz consists of local islands and clusters with a diameter of 118.1 ± 5.9 nm. Nanocrystalline films, grown at the repetition frequency of 10 Hz, possess a continuous granular structure with a grain diameter of 235 ± 11.75 nm. Achieved results can be used for the development of promising "green" energy devices based on lead-free piezoelectric energy harvesters.

*Keywords*: Thin films; lead-free ferroelectrics; pulsed laser deposition; energy harvesting; piezoelectrics.

## 1. Introduction

The global environmental pollution and energy crisis arise from the increased energy consumption from nonrenewable sources prompted researchers to start exploring alternative energy technologies based on environmental energy conversion into electricity.[1] In turn, the rapid development of nanotechnology leads to a gradual decrease in the size and energy consumption of electronic devices, which opens up the possibility of using environmental energy as sources for powering the devices.[2,3] One of the promising ways of converting mechanical energy into electricity is piezoelectric-nanostructured-materials-based energy harvesters.[2,4] Using lead-free materials in such devices are of utmost importance for biocompatibility and medical applications of energy harvesters.[5] Lithium niobate ($LiNbO_3$) is one of the potential lead-free piezoelectric materials with high Curie temperature.[6] Therefore, the compatibility of piezoelectric $LiNbO_3$ energy harvesters with modern technologies of micro- and nanoelectronics can be achieved by using thin-film methods for obtaining nanocrystalline materials. However, $LiNbO_3$ is a multicomponent oxide, and its properties (optical, piezoelectric parameters, and surface morphology, as well as resistance, concentration, and mobility of charge carriers) depend on the stoichiometric composition and structure, which are determined by fabrication method and the formation modes.[7,8]

Nanocrystalline $LiNbO_3$ thin films can be grown by various techniques: spin coating,[9] MOCVD,[10] reactive sputter deposition,[11] and pulsed laser deposition (PLD).[12–16] PLD is one of the most promising growth methods for metal oxide thin films fabrication as it has advantages related to multicomponent oxides formation.[17,18] However, the wide variety of piezoelectric energy harvesters manufactured by integral technology based on $LiNbO_3$ films is still limited due to the technological difficulties of obtaining films with controlled properties.[19–21] Additionally, growth mechanisms of complex oxides crystallization have not yet been established.[22]

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However, it was previously shown that the $LiNbO_3$ films obtained by PLD exhibit piezoelectric properties.[23]

During the PLD, many ablated particles are instantly deposited on the substrate surface. The particles can diffuse and aggregate on the surface of the substrate. In contrast to other methods, PLD allows one to combine rapid deposition velocity with intervals of no deposition in a periodic manner. At the same time, in the growth process, a low deposition rate (low repetition frequency) means that the ablated particles will have more time to complete nucleation.

In this paper, we demonstrate the impact of laser pulse repetition frequency on the growth processes regularities and parameters of $LiNbO_3$ thin films.

## 2. Materials and Methods

Nanocrystalline $LiNbO_3$ films were fabricated using Neocera Pioneer 180 PLD module (Neocera LCC, USA) of NANOFAB NTK-9 nanotechnological complex (NT-MDT, Russia).

Initially, the growth chamber of the module was pumped down to a pressure of $1 \cdot 10^{-5}$ Torr. Oxygen with a pressure of $1 \cdot 10^{-2}$ Torr was used as a background atmosphere. KrF excimer laser (Coherent Inc., USA) with a laser radiation wavelength $\lambda$ = 248 nm was used for target ablation. The laser pulse repetition frequency was varied from 4 Hz to 10 Hz. Target-substrate distance during deposition was set to 100 mm. The design of the heater allows deposition in an inert and reactive atmosphere with a maximum possible substrate temperature of 950 °C. $LiNbO_3$ thin films deposition was carried out on Si substrates.

To examine the surface morphology of the grown samples, we used the NTEGRA Probe Nanolaboratory (NT-MDT, Russia), which makes it possible to study the surfaces of solids by atomic force microscopy (AFM) technique.[24,25] The thickness and morphology of the obtained films were also examined by scanning electron microscopy (SEM) using a Nova NanoLab 600 (FEI Co., Netherlands). $LiNbO_3$ films thickness study was carried out by measuring the "step" height

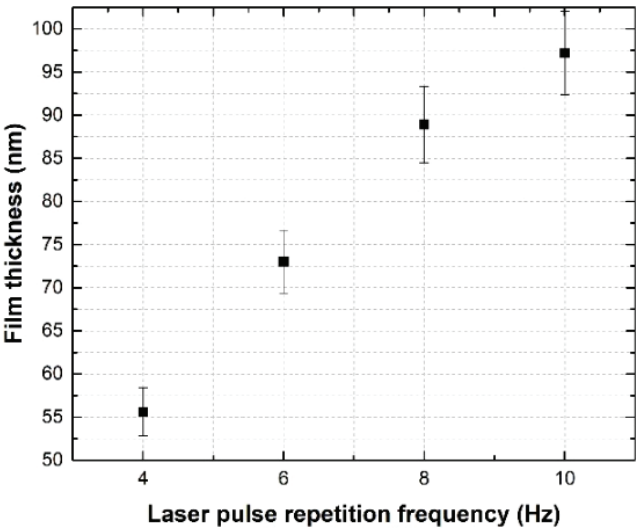


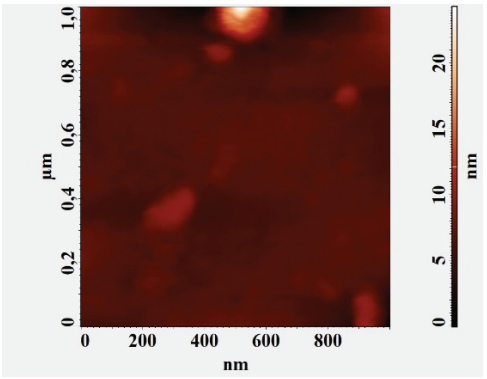

Fig. 1. Dependence of $LiNbO_3$ films thickness as a function of laser pulse repetition frequency.

obtained by etching a lamella in the films using a focused ion beam.[17,26] Electro-physical parameters of the obtained films were measured using the HMS-3000 Hall Effect measurement system (Ecopia Corp., Republic of Korea), which allows use Van der Pauw method to determine the resistivity and Hall coefficients, the type of film conductivity, and the mobility ($\mu$) and concentration ($N$) of charge carriers in the films. Aluminum (Al) top contacts with dimensions of 10 × 10 mm were formed according to the developed technology, which provides ohmic contact to $LiNbO_3$, to study the electro-physical parameters of nanocrystalline $LiNbO_3$ films.[27]

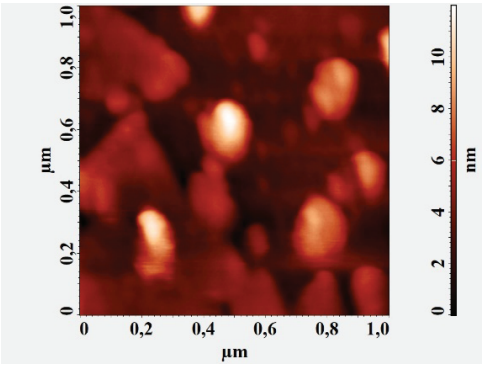
## 3. Results and Discussion

Figure 1 demonstrates the dependence of $LiNbO_3$ films thickness as a function of laser pulse repetition frequency.

Figure 2 shows AFM images of nanocrystalline $LiNbO_3$ thin films obtained on Si substrates.

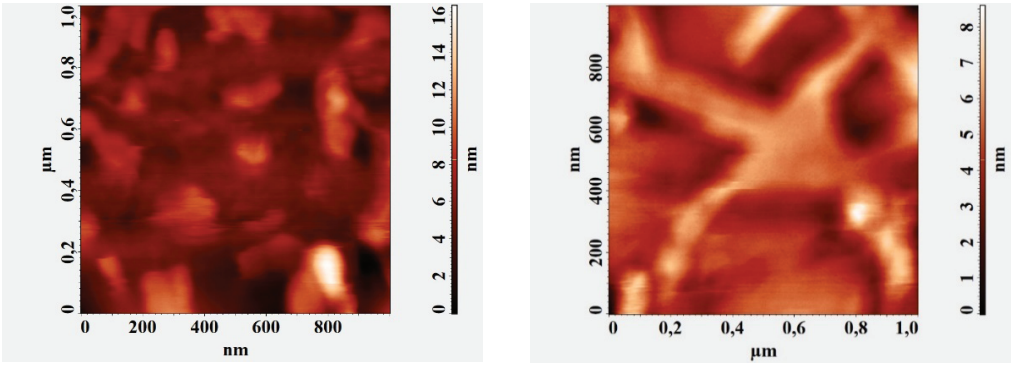



(a)




(b)

Fig. 2. Morphology of $LiNbO_3$ films obtained on Si substrates at different laser pulse repetition frequencies: 4 Hz (a), 6 Hz (b), 8 Hz (c), and 10 Hz (d).




(c) (d)

Fig. 2. (*Continued*)

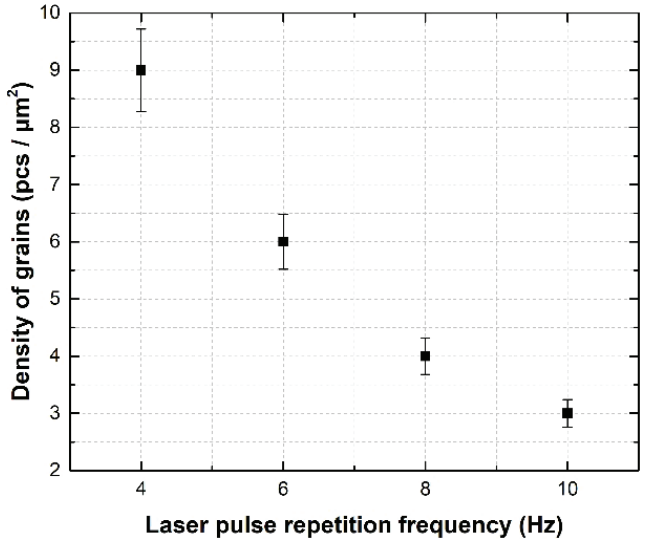



Fig. 3. Dependence of the grain density of nanocrystalline $LiNbO_3$ films on the laser pulse repetition rate.

Obtained results show that increasing the laser pulse repetition frequency from 4 Hz to 10 Hz results in increasing $LiNbO_3$ film thickness from 55.6 ± 7.8 nm to 97.2 ± 3.5 nm. The thickness of grown films increasing is a consequence of gain in the kinetic energy and the flux of ablated particles, as well as a decrease in the influence of the thermalization process.[28] It was found that $LiNbO_3$ film obtained at a laser pulse repetition frequency of 4 Hz consists of local islands and clusters with an average diameter of 118.1 ± 5.9 nm. The increase in the repetition frequency from 4 Hz to 10 Hz results in the formation of nanocrystalline films with a continuous granular structure and an average grain diameter of 235.1 ± 11.6 nm. The results presented in Refs. 12 and 29 shows that $LiNbO_3$ films obtained by PLD have a nanocrystalline structure.

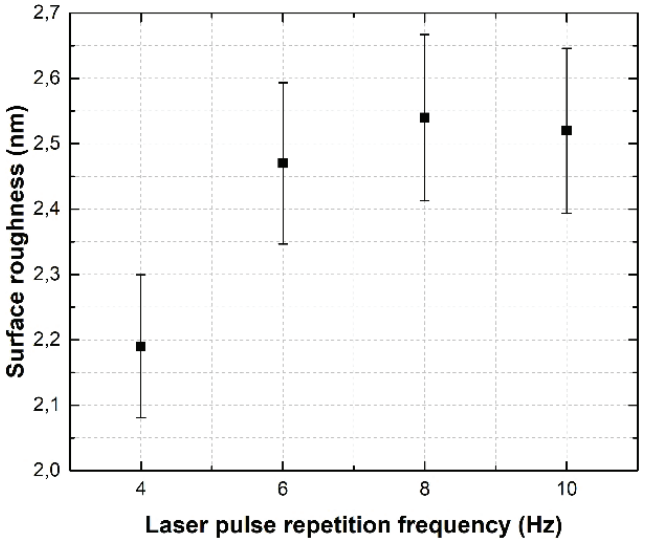
Figure 3 shows the dependence of grain density on laser pulse repetition frequency.

It is found that the grain density decreasing by a factor of 3 (from 9 pcs/$\mu$m$^2$ to 3 pcs/$\mu$m$^2$) with the increase in the laser pulses repetition rate from 4 Hz to 10 Hz. This effect is attributed to the growth in the grain's diameter associated with the increase in the laser pulse repetition frequency. The results are confirmed by AFM and SEM studies [Figs. 2 and 5].

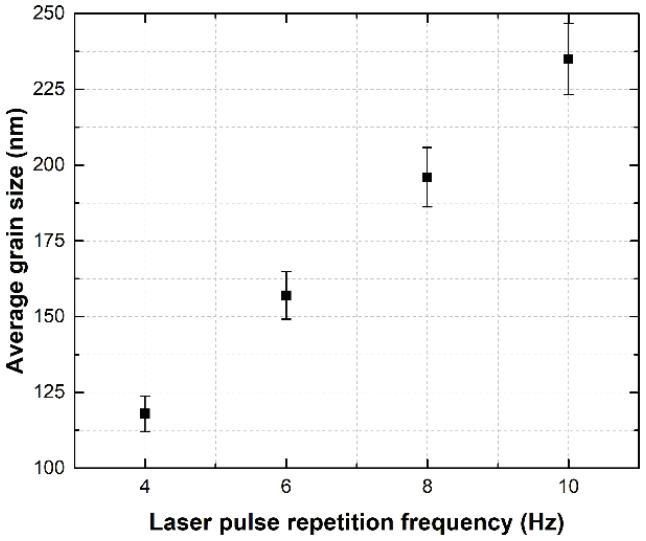
Figure 4 shows the morphological parameters of $LiNbO_3$ films obtained at various laser pulse repetition frequencies.

The roughness of the films slightly increases from 2.2 ± 0.1 nm to 2.5 ± 0.1 nm [Fig. 4(a)], which may be associated with a decrease in the mobility of adatoms.[30] Along with AFM, SEM is also a prospective tool for studying ferroelectric films.[31,32] Figure 5 shows the results of $LiNbO_3$ thin films SEM study. According to the results of SEM images analysis, it was found the film obtained at a laser pulse repetition frequency of 10 Hz has a textured and rougher surface compared to $LiNbO_3$ thin films obtained at a laser pulse repetition frequency of 4 Hz. It is attributed to the increasing in the average size of the drop-shaped structures on the film surface with an increase in laser pulse repetition frequency. The film obtained at a laser pulse repetition frequency of 4 Hz is characterized by the formation of separately standing clusters. The clusters intensely coagulate with increasing in laser pulse repetition frequency [Figs. 2 and 3(b)]. Comparison of the grain density obtained by SEM images analysis with the results of AFM studies shows their good correlation, the discrepancy does not exceed 10%. Detailed SEM studies of $LiNbO_3$ films can be found in Ref. 33.

Based on the obtained results, films fabricated at a laser pulse repetition frequency of 4 Hz are formed according to the island mechanism, whereas increasing the laser pulse repetition frequency to 10 Hz, the growth mechanism changes to a more complex, due to nonequilibrium processes of heat and mass transfer in the laser plume.[12] The low repetition frequency of laser pulses leads to the formation of smaller islands [Fig. 4(b)]. In line with Ref. 34, the difference in size can be linked to the intensification of the nucleation process following every pulse resulting from the amount of material

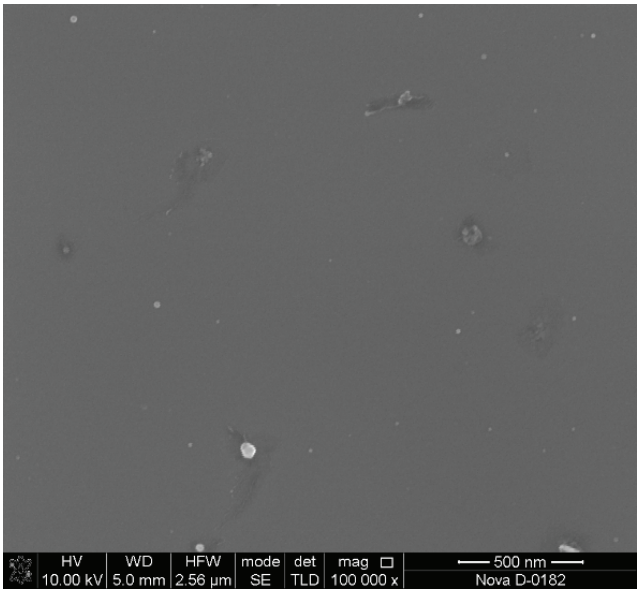



(a)

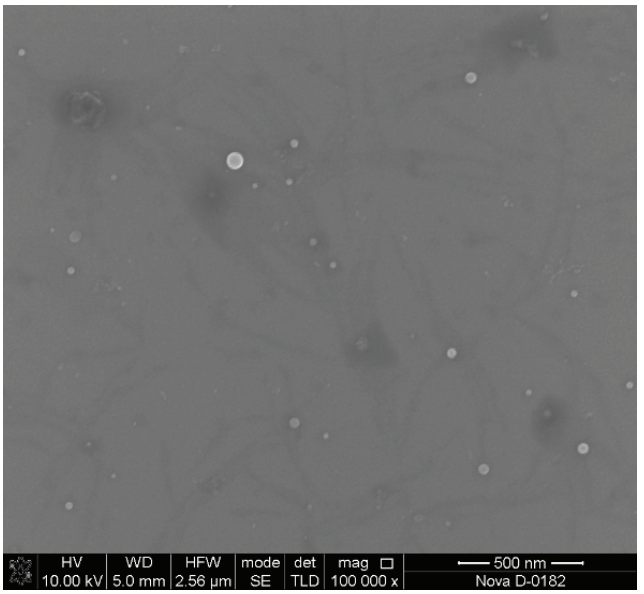



(b)

Fig. 4. Surface roughness (a) and average grain diameter (b) of the obtained $LiNbO_3$ films as a function of laser pulse repetition frequency.




(a)




(b)

Fig. 5. SEM images of nanocrystalline $LiNbO_3$ films obtained at different laser pulse repetition frequencies: 4 Hz (a), 10 Hz (b).

deposited per pulse. For $LiNbO_3$ films obtained at a repetition frequency of 10 Hz, a more homogeneous structure is observed, which represents $LiNbO_3$ (the data of AFM and SEM studies on Figs. 2 and 5). The film shows the formation of small islands obtained in the process of coalescence.[34]

Figure 6 shows the dependences of $N$ and $\mu$, as well as the resistivity ($\rho$) of $LiNbO_3$ films on the laser pulse repetition frequency.

$N$ of charge carriers in nanocrystalline $LiNbO_3$ films increases from $(1.35 \pm 0.06) \times 10^{13}$ cm$^{-3}$ to $(4.42 \pm 0.22) \times 10^{13}$ cm$^{-3}$, by increasing the repetition frequency of laser pulses from 4 Hz to 8 Hz. In this case, the $\mu$ of charge carriers decreases from $12.94 \pm 0.65$ cm$^2$/(V·s) to $4.60 \pm 0.23$ cm$^2$/(V·s). The charge carriers mobility can change with an adjustment of the $LiNbO_3$ stoichiometry: congruent $LiNbO_3$ (the ratio of Li to Nb is ~ 94%) has lower electron mobility than a stoichiometric crystal (the ratio of Li to Nb is 1).[35] This fact can be associated with a change in the stoichiometric composition of $LiNbO_3$ films: decreasing in the content of metallic Li and an increase in the defectiveness of the films.[12] The ability to control and manage the dynamics of carriers in materials used for energy harvesting is of great importance for optimizing the energy efficiency of energy converters.[36] It was shown that the high concentration and

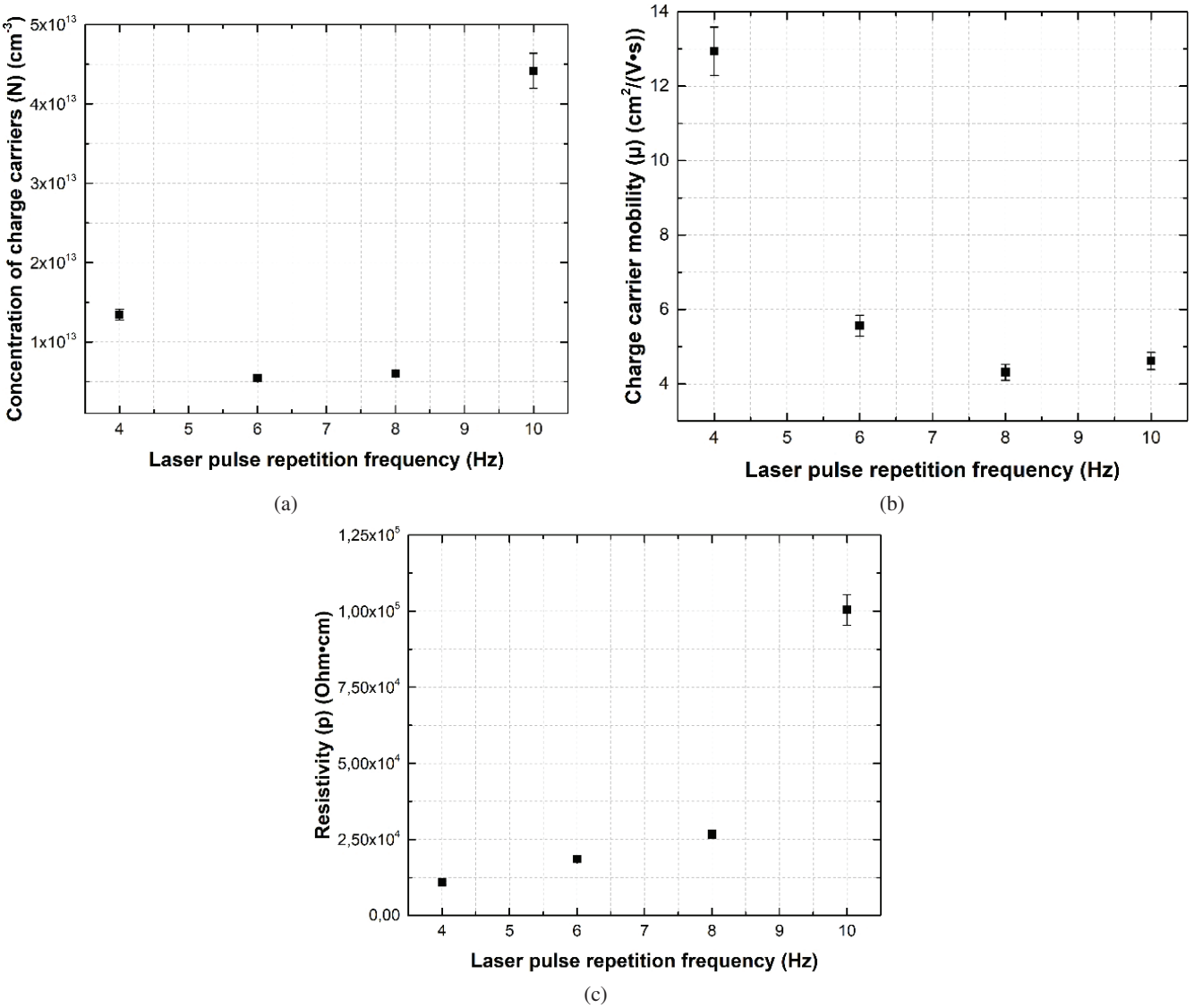



Fig. 6. Dependences of $N$ (a) and $\mu$ (b) of charge carriers, as well as $\rho$ (c) of nanocrystalline $LiNbO_3$ films on the laser pulse repetition frequency.

mobility of charge carriers negatively affect the piezoelectric effect.[37] Thus, $LiNbO_3$ films obtained at laser pulse repetition frequency of 8 Hz to 10 Hz are the most suitable for piezoelectric energy harvesters.

## 4. Conclusion

Based on the obtained results, films fabricated at a laser pulse repetition frequency of 4 Hz are formed according to the island mechanism, whereas increasing the laser pulse repetition frequency to 10 Hz, the growth mechanism changes to a more complex one. Obtained results are in line with Ref. 34.

It was found that changing the repetition frequency of laser pulses from 4 Hz to 10 Hz make it possible to control the nucleation process during PLD, and films fabricated at a laser pulse repetition frequency of 10 Hz can be used as part of a piezoelectric converter of mechanical energy.[38] Obtained results allow fabricating $LiNbO_3$ films, which can be used in cutting-edge lead-free transducers for alternative energy devices and energy harvesters.

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