Dynamic Stability of Metal-Nanocluster Composites Based on LiNbO$_3$ Under Heavy-Ion Bombardment

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Dynamic Stability of Metal-Nanocluster Composites Based on LiNbO₃ Under Heavy-Ion Bombardment

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In-situ optical measurements during implantation of 60 keV Cu− ions, aimed at fabrication of metal nanoparticles embedded in LiNbO₃ single crystals, enable us to determine conditions of stability of metal nanocomposites and, accordingly, to represent evolution of nanocomposites with the help of non-equilibrium phase diagrams. The observed saturation behavior of optical absorption of nanocomposites was attributed to formation of the structures which were dynamically stable under ion bombardment. Unlike radiation resistant substrates, such as SiO₂ or Al₂O₃, in LiNbO₃ formation of the dynamically stable structures is accompanied by surface patterning.

Keywords  Lithium niobate; metal nanoparticles; nanocomposite; ion implantation; optical absorption

1. Introduction

Metal-nanoparticle composites (MNC) based on LiNbO₃ are promising for ultra-fast optical devices [1,2]. Heavy-ion implantation is a versatile tool for fabrication of embedded metal nanoparticles and for modification of domain structures of ferroelectrics [3]. In particular, heavy-ion implantation has an advantage, because the injected elements are immiscible. Fabrication of nanocomposites is easily controlled via variation of the ion energy and particle flux and fluence. Furthermore, formation of metal nanoparticles can be monitored by means of in-situ measurements of: (a) optical absorption in the region of the surface-plasmon-resonance (SPR) and (b) ion-induced photon emission (IIPE) [4].

Since high-flux ion implantation is very attractive, stability of nanocomposites under ion bombardment becomes an important issue [5]. In this paper, we study conditions of stability of metal nanocomposites during ion implantation of LiNbO₃. We apply in-situ optical measurements to monitor nanocomposite formation. Such optical measurements have been already used [4] for the investigation of MNC stability during heavy-ion implantation of silica glasses (SiO₂), which is not as complicated material as LiNbO₃ single crystals.

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compare the results obtained for SiO$_2$ and LiNbO$_3$, the first of which is a radiation resistant material and the second has a soft non-linear matrix.

2. Experiment

Disk-shaped samples of LiNbO$_3$ (z-cut, 15 mm diameter, 0.5 mm thick) polished to optical grade were irradiated by 60 keV Cu$^-$ ions at ion fluxes ranged from 1 to 50 $\mu$A/cm$^2$ ($6 \times 10^{12}$–$3 \times 10^{14}$ ions/cm$^2$s) up to a fluence of $2 \times 10^{17}$ ions/cm$^2$. The Xe lamp was used for illumination of the sample back surfaces through a hole in the holder. Intensified CCD cameras collected spectra of optical transmission and ion-induced photon emission in the range of photon energies from 1.3 to 6.2 eV.

The optical transmission and reflection data measured ex-situ in irradiated samples by a dual beam spectrometer was used for the calculation of the optical absorption. Such measurements allow us to reveal typical SPR peaks at 2 eV, which indicate the formation of Cu nanoparticles.

The surfaces of as-implanted samples were examined by AFM in the tapping mode. Distribution of implants was estimated with the TRIM and TRIDYN simulation codes within the linear cascade approximation [6–7].

3. Results and Discussion

A typical fluence dependence of optical loss of SPR measured during implantation of 60 keV Cu$^-$ ions into LiNbO$_3$ at a constant ion flux [8] is shown in Fig. 1. The onset of metallization of Cu nanoparticles is determined as the fluence at which the SPR peak appears. Accordingly, Cu atoms precipitate at fluences lower than $6 \times 10^{15}$ ions/cm$^2$. At higher fluences an increase of the concentration of Cu nanoparticles manifests itself as the increase of the SPR peak, which demonstrates eventually the distinct saturation behavior. It is worth noting that similar fluence dependencies have been obtained during implantation of 60 keV Cu$^-$ ions into SiO$_2$ [4].

Flux-dependent evolution of nanocomposites in LiNbO$_3$ is demonstrated on the nonequilibrium phase diagram in Fig. 2. Unlike conventional equilibrium phase diagrams, component concentration is replaced by the ion fluence, whereas the ion flux plays a role of a fictitious temperature. The phase diagram consisted of three regions. A similar phase diagram for SiO$_2$, also consisting of three regions, was presented in Ref. [5]. The following

![Figure 1. Fluoence dependence of optical loss in the range of SPR measured for LiNbO$_3$ implanted by 60 keV Cu$^-$ ions at an ion flux of 30 $\mu$A/cm$^2$.](image-url)
interpretation of this phase diagram for SiO$_2$ was proposed. The first region, at low fluences, could be considered as corresponding approximately to the region of the existence of a single phase. Namely, the region of the existence of a solid solution of Cu atoms in the matrix (SiO$_2$): no SPR is observed and the IIPE band of Cu$^+$-solute increases with increasing of the fluence. The second region, at intermediate fluences, corresponds to accumulation of Cu atoms in nanoparticles: the SPR peak gradually increases and the intensity of the Cu$^+$-solute IIPE band does not vary with the fluence. Two phases (metal nanoparticles and a solid solution) coexist in this region and the Cu solute concentration remains almost constant at a constant ion flux [9]. The third region, at high fluences, corresponds to saturation of nanocomposites: almost no variation of the SPR peak is observed and the Cu$^+$-solute IIPE band increases with the fluence until a new steady-state concentration of Cu solutes is achieved. In this two-phase region, Cu concentration of nanoparticles and, consequently, Cu concentration of nanocomposite as a whole are constant at a constant ion flux. While discussing the presented non-equilibrium phase diagrams, we must note that the ion flux does not explicitly represent the dose rate, since the chemical composition and structure of nanocomposites vary with the ion fluence. Cu concentration of nanocomposite is not proportional to the fluence, for example, due to the saturation effect.

Ion implantation gave rise to the oxygen deficiency of the silica glass matrix, in which Cu nanoparticles tend to form quasi-two-dimensional distributions [2]. Unlike the situation observed in SiO$_2$, ion implantation of LiNbO$_3$ resulted in formation of complex nanocomposites consisting of metal Cu nanoparticles distributed among nanoregions of the host medium [10]. Spatial distributions of the Cu nanoparticles and nanoregions in the implanted region are not correlated with each other. Besides oxygen deficient, lithium-depleted regions are created in the substrates and concentration of Nb ions increases [11]. Also, no luminescence due to Cu solutes was found out in implanted LiNbO$_3$ substrates, and the concentration of unprecipitated Cu could not be monitored. Nevertheless, the considerations applied for explanation of SiO$_2$ behavior are also valid to some extent for LiNbO$_3$. In particular, the saturation behavior is a common feature for both materials, and it is an evidence of the formation of dynamically stable structures under ion bombardment [5]. Formation of dynamically stable structures: (a) minimizes variations of the chemical and phase composition of nanocomposites with the ion fluence and (b) diminishes the efficiency of ion implantation reducing the implants capability to assemble into nanoparticles.

The saturation behavior is supposed to stem from competition between accumulation of implants and surface recession due to sputtering. In this case, saturation time is roughly equal
to the ratio $R_p/SF$ of the projectile range of ions $R_p$ to the rate of surface recession $SF$. For chemical composition change, TRIDYN calculations predicted saturation at ion fluences above $1 \times 10^{17}$ ions/cm$^2$. Saturation behavior of SPR was observed both in Cu-implanted SiO$_2$ and in LiNbO$_3$, however, it was flux-dependent [4,8]. It should be noted that while the post-collision processes (radiation-induced diffusion, phase transitions, etc.) play essential role in nanocomposite formation, they are not considered in TRIDYN calculations.

In contrast to the surface recession, radiation-induced diffusion may enhance the efficiency of nanocomposite formation. If the diffusion and sputtering are considered simultaneously, the time evolution of the implant concentration profile can be expressed by the following equation:

$$\frac{\partial N}{\partial t} = G(x) + SF \frac{\partial N}{\partial x} + D \frac{\partial^2 N}{\partial x^2},$$  

(1)

where $N$ is the implant concentration, $G(x)$ is the generation rate, $F$ is an ion flux, $S$ is a differential surface recession (change of thickness per unit ion fluence), $D$ is a diffusion coefficient.

Competition between the second (surface recession) and the third (diffusion) terms on the right-hand side of Equation 1 determines the saturation behaviors, namely, the steady-state concentration profiles. Concentration profiles obtained during ion implantation depend on the ratio $D/R_pSF$. For LiNbO$_3$ implanted by 60 keV Cu$^-$ ions, the value of $R_pS$, calculated with the help of the TRIDYN code, is about 1 nm$^4$/ion and is smaller than that for SiO$_2$ (1.5 nm$^4$/ion). This presents an advantage for efficient formation of nanocomposites.

The saturation behavior of SPR can also depend on non-uniform deposition of incoming-ion energy, namely, preferential energy absorption by metal nanoparticles, as compared to the substrate. The energy losses can be compared for a multilayer structure by using TRIM calculations [5]. Within this approach, a layer of closely packed nanoparticles is approximated by a continuous metal layer situated inside the insulator matrix. The estimations show that the preferential process of energy absorption during ion bombardment is due to the recoils occurring in the Cu film. For example, the total energy absorbed by the films, 2 to 10 nm thick, located at a depth from 20 to 50 nm, is twice larger than the energy absorbed by SiO$_2$ matrix. When such a dense nanocomposite is irradiated by the high ion flux, the nanoparticles are destroyed so frequently that further implantation becomes inefficient. It is obvious that frequent destruction of nanoparticles should also result in an increase of the steady-state concentration of Cu solutes during implantation. In LiNbO$_3$, the selective energy absorption is less significant, as compared to SiO$_2$ [5].

It was found that MNC sometimes experience drastic transformations prior to the saturation behavior. For example, the pronounced rearrangement is observed during implantation of 60 keV Au$^-$ ions into SiO$_2$ [5]. During this transformation, both the position and height of the SPR peak as the functions of the ion fluence demonstrate $\lambda$-type dependencies. It was proposed that the MNC underwent the rearrangement of the structure to adjust to the ion bombardment. As a result, the size/depth distribution of nanoparticles and chemical composition of the MNC after the transformation become dynamically stable under ion irradiation. The knowledge of the bulk properties of above discussed dynamically stable structures is necessary for understanding the radiation-induced processes during ion bombardment. Experiments carried out in LiNbO$_3$ allowed us to observe rearrangements on the surface as well. After 60 keV Cu$^-$ ion implantation of SiO$_2$ the investigated samples were smooth. In contrast, under such ion implantation conditions the uniformly distributed hillocks on the surfaces were observed in LiNbO$_3$ (Fig. 3). The mean
height of hillocks varied with the ion fluence, as it is shown in Fig. 4 for a series of the samples implanted at different ion fluences. The fluence dependence of height presented in Fig. 4 suggests that the surface of MNC experiences the rearrangement in order to adjust to the ion bombardment. This rearrangement precedes the formation of dynamically stable surface structure.

Experiments on the domain kinetics during cyclic switching in LiNbO$_3$ with surface layer modified by Cu ion implantation by direct method demonstrates two qualitative distinctions as compared to conventional LiNbO$_3$. First, pinning of the domain walls leads to appearance of the residual domains at the wall rest positions which played the role of domain growth centers for subsequent backswitching. Second, cyclic switching results in essential fatigue effect which represents formation and growth of the regions occupied by frozen domains with charged domain walls [11]. Similar behavior observed in conventional LiNbO$_3$ with sputtered electrodes was attributed to stabilization of the charged domain walls by charge injection. Thus, it is reasonable to consider that implanted nano-clusters of Cu represent a source of bulk screening charge.

Figure 4. Fluence dependence of the mean hillock height at the surface of LiNbO$_3$ implanted with 60 keV Cu$^-$ ions at an ion current of 5 $\mu$A/cm$^2$, measured by AFM.
4. Conclusion

Optical transmission of LiNbO$_3$ was measured during implantation of 60 keV Cu$^-$ ions. In-situ optical measurements enable us to determine conditions of stability of metal nanocomposites. The evolution of nanocomposites was illustrated with the help of non-equilibrium phase diagrams.

During heavy-ion implantation of LiNbO$_3$ single crystals, competition between the ion implantation and the surface recession due to sputtering results in formation of metal-nanocluster composites with dynamically stable structures, i.e. with depth profiles (concentrations, sizes) independent on the ion fluence. Unlike radiation resistant substrates, such as SiO$_2$, formation of the dynamically stable structures in LiNbO$_3$ is accompanied by surface patterning (formation of dynamically stable surface structures).

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