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Influence of the structure of the near-surface region on the characteristics of low-energy cathodoluminescence of lithium niobate

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Abstract. The influence of the changes in the structure of near-surface region of a lithium niobate *Z*-cut single crystal grown from a congruent melt on the characteristics of the low-energy cathodoluminescence has been investigated. It is shown that radiation spectra strongly depend on the structure of the near-surface region. The luminescent properties of the crystal annealed in air at 950 °C in contrast with those of the polished crystal are found to be stable against the bombardment of the crystal by electrons with energy at least up to 1.3 keV. The effect of electron bombardment of the crystal face on the radiation spectra taken from the opposite face was observed.

1. Introduction

Investigations of the near-surface region (NSR) of ferroelectric crystals are of interest in both pure scientific fields, e.g. phase transitions at the crystal surface, and screening of spontaneous polarisation, and applied fields, e.g. integrated optical elements, and devices based on applications of surface acoustic waves. In numerous papers dealing with such investigations, polished crystals were used. The NSR of these crystals contains disturbance as a result of the mechanical treatment layer, the characteristic thickness of which for example in lithium niobate (LN) is of the order of 100 Å [1]. It is evident that one should take into consideration the existence of the disturbed layer (DL) in the cases in which the characteristic thickness of the probing layer is less than or comparable with that of the DL. Such a situation takes place when one examines the photoelectron emission (escape depth of photoelectrons, about 10 Å or less [2]), the optical and luminescent properties at frequencies at which the damping length of the wave is comparable with the thickness of the DL, e.g. in the case of LN these are frequencies of about 5 eV or more [3, 4], and the low-energy cathodoluminescence (CL) [5, 6]. However, the existence of the DL which can lead to a deviation in the properties measured from those in the volume part of the crystal other than the deviation arising from the presence of the crystal surface itself, to our knowledge, have not been taken into account so far. In the present paper the influence of the changes in structure of the NSR on the characteristics of the low-energy CL of LN is demonstrated.

2. Experimental method

Experiments were carried out in a metal apparatus under vacuum conditions not worse than 1.5×10^{-10} Torr. The sample was in the form of a plate with dimensions $6 \text{ mm} \times 10 \text{ mm}$ and thickness 0.4 mm cut perpendicular to the optical axis from an undoped† single-domain LN crystal grown from a congruent melt by the Czochralski technique. Crystal faces were polished using in the final stage $1 \mu\text{m}$ diamond powder. The crystal with polished faces further is called the 'polished crystal' in contrast with the 'annealed crystal', the state of the same crystal after subsequent annealing. To restore the crystalline structure of the DL crystal, it was annealed in air at 950°C for 4 h. The annealing procedure used was as in [1] in which the workers having used RHEED, showed that the structure of the NSR of the crystal subjected to such annealing corresponds to that of the volume. The sample was placed in a wire frame so that the opposite faces were free. The polarity of the face was determined by the dynamic pyroeffect method.

Luminescence was excited by a beam of electrons with energy in the range 100–1300 eV, the beam current being up to 0.1 mA (the cross section of the electron spot at the sample surface was $1 \text{ mm} \times 3 \text{ mm}$). To control the heating action of the beam, the sample temperature in the vicinity of the electron spot was measured with a thermocouple. The temperature rise does not exceed several degrees Celsius under conditions of maximum current and electron energy $E = 400 \text{ eV}$. The angles of incidence and observation of radiation were 45° and 0° , respectively. CL spectra were measured in the wavelength range 200–700 nm by an automatic device operating in the photon-counting regime. The calibration procedure of the optical system was the same as in [7]. The composition of the surface examined was controlled by Auger electron spectroscopy (AES); the energies of the primary electrons were 1 keV and 3 keV, and the current densities $1 \mu\text{A mm}^{-2}$ and $0.15 \mu\text{A mm}^{-2}$, respectively.

3. Results

The CL spectra taken from the positive face (the direction of the outward normal coincides with that of spontaneous polarization) of the polished crystal, hereafter called the 'initial spectra', are shown in figure 1. The pronounced bands centred at about 450 and 590 nm, which have not been observed earlier in the low-energy CL spectra of LN [6], are characteristic of these spectra. The CL spectra taken from the negative face of the polished crystal are shown in figure 2. The distinguishing feature of the spectra compared with those in figure 1 is the absence of the bands near 450 and 590 nm. After bombardment of the *negative* face by electrons with $E = 400 \text{ eV}$ for 5–6 h (current density, $30 \mu\text{A mm}^{-2}$) the spectra of the *positive* face changed and became almost indistinguishable from those of the negative face shown in figure 2 and similar to the CL spectra obtained in [6]. Later these modified spectra of the positive face were unchanged (hereafter they are called the 'final spectra'). Auger spectroscopy investigations made in parallel with CL measurements showed the cleaning of both faces from carbon-containing compounds and a significant increase in the conductivity caused by bombardment of the faces by electrons with $E = 400 \text{ eV}$ for several hours. The increase in the conductivity follows from the disappearance of the surface charging under the AES beam. The Auger spectra obtained are similar to those published earlier [6].

† X-ray analysis showed presence of Mn, Fe and Cr atoms in quantities not larger than 0.001–0.004 at. %.

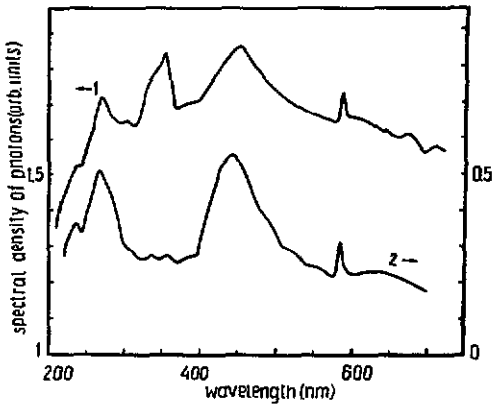


Figure 1. CL spectra taken from the positive face of the polished crystal ('initial spectra'). The spectra were obtained with $E = 400$ eV (curve 1) and $E = 100$ eV (curve 2).

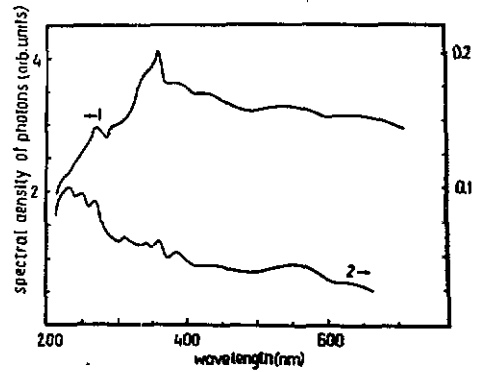


Figure 2. CL spectra taken from the negative face of the polished crystal. The spectra were obtained with $E = 400$ eV (curve 1) and $E = 100$ eV (curve 2).

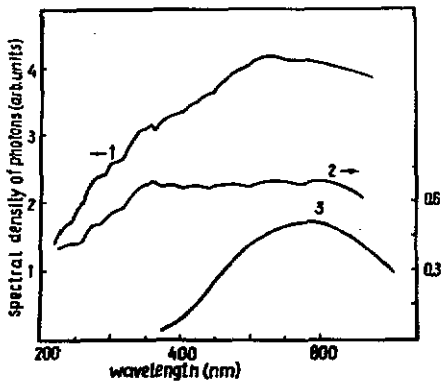


Figure 3. CL spectra of the annealed crystal obtained with $E = 400$ eV (curve 1) and $E = 170$ eV (curve 2). Curve 3 shows the difference between the CL spectrum of the annealed crystal and the final spectrum of the polished crystal; both spectra were obtained with $E = 400$ eV.

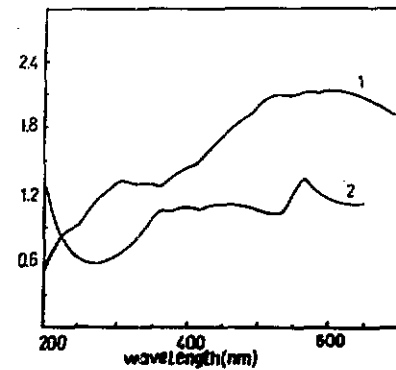


Figure 4. Ratios of the CL spectra obtained with $E = 400$ eV. Curve 1 shows the ratio of the spectrum of the annealed crystal to final spectrum of the polished crystal. Curve 2 shows the ratio of the spectrum of the polished crystal taken before annealing to that taken after annealing in a pure oxygen atmosphere.

The CL spectra of both faces of the annealed crystal are identical and are shown by curves 1 and 2 in figure 3 (the threshold energy above which the radiation appears is about 170 eV). One should note that, after annealing, the surface resistance significantly increased, e.g. for $E = 1$ keV the shift of the Auger lines was about 100 eV in comparison with that of about 10 eV in the case of unbombarded faces before annealing. Bombardment for many hours of the annealed crystal in contrast with the polished crystal did not lead to either cleaning of the faces from carbon-containing compounds nor to an increase in the conductivity, and the luminescent properties proved stable against bombardment up to an electron energy of at least 1.3 keV.

4. Discussion

Let us consider the possible reasons for the differences existing between the CL spectra of the annealed and polished crystals (see curves 1 in figures 2 and 3). Evidently these differences could result not only from modification of the structure of the NSR because of its recrystallization but also from absorption by the crystal of the oxygen and other components of the annealing atmosphere. Auger analysis of the annealed crystal did not show the appearance of any new impurities at the surface after annealing. Hydrogen, which is not detected by AES, can be incorporated into LN during annealing. Incorporation of the hydrogen results in the creation of the optically active centres whose frequencies are in the infrared [8] and not in the range investigated in the present work. Modifications of the CL spectra of LN caused by absorption of the oxygen were studied in [6]. In figure 4, two curves presenting the ratios of the CL spectra taken before and after different annealing procedures are shown. Curve 1 is the ratio of the CL spectrum of the annealed crystal to the final spectrum of the polished crystal (the annealing procedure has been mentioned above). The ratio of the CL spectrum of the polished crystal, whose NSR before annealing had an oxygen deficiency caused by electron bombardment at $E = 1$ keV, taken after annealing to that taken before annealing in a pure oxygen atmosphere is shown by curve 2. Curve 2 was obtained on the basis of the CL spectra measured in [6] in which oxidation has been performed at 650 °C when according to [1] no essential changes in the structure of the NSR occur. The significant differences that exist between two curves in figure 4 indicate that oxygen absorption which can take place during annealing is not the main reason for the changes in the CL spectra caused by annealing. The thin film of the carbon-containing compounds present at the surface of the annealed crystal also cannot be the main reason for the spectral changes. This results from the fact that CL spectra of the polished crystal ($E = 400$ eV) measured before and after removal of the film are similar and the thicknesses of the carbon-containing coverage at the surfaces of the polished and annealed crystals according to Auger spectra were about the same. Taking these arguments into account we believe that the origin of the changes in the CL spectra, caused by annealing, is modification of the structure of the NSR because of its recrystallization.

The main difference between the CL spectra of the polished (final spectrum) and annealed crystals is the relative intensity of the band centred at about 570 nm (figure 3, curve 3). Consequently the degree of perfection of the NSR of a Z-cut congruent LN crystal can be indirectly estimated according to the relative intensity of this band in the low-energy CL spectra. The shape of the band considered is similar to that of the band centred at about 550 nm observed earlier [6]. One should also note that, as the characteristic depth of the excitation of radiation in the energy range examined does not exceed a value of the order of 100 Å [6] and the thickness of the DL is of the same order, therefore the low-energy CL spectra of the polished crystals mainly reflect the properties of DL which differ from those of the annealed crystals where the DL is absent.

Now let us mention some observed features whose study was not the aim of the present work but which in our opinion are of interest. In the initial spectra of the polished crystal the pronounced band centred at about 450 nm as well as relatively narrow band centred at about 590 nm (see figure 1) were observed. These bands were not determined previously in low-energy CL spectra of LN. The band with its maximum near 450 nm and approximately the same half-width as in our spectra was observed earlier in photoluminescent spectra of undoped LN [9]. Klose *et al* [9] have suggested that radiative recombination of a free or bounded electron with the hole captured at the recombination

centre is the probable origin of the band. The band near 450 nm (and also 590 nm) observed in our spectra has the following properties

(i) The relative contribution of the band increases with decrease in the electron energy from 400 to 100 eV (cf curves 1 and 2 in figure 1), which also results in a decrease in the electron penetration depth by several times [2].

(ii) The band was observed only in the CL spectra taken from positive face of the crystal†.

(iii) The band was almost completely suppressed (and was no longer observed) after bombardment of the *opposite* negative face by electrons with $E = 400$ eV for several hours‡.

Although these properties do not allow one to establish definitely the origin of the bands considered but emphasize the substantial role of the surface region in the mechanism which is responsible for the existence of the bands as well as in the participation of the mobile carriers. The last statement follows from the observed influence of the bombardment of the opposite face on CL spectra. In fact, in the absence of heating of the crystal, whose thickness is larger than the penetration depth of the bombarding electrons by some orders of magnitude, the effect of the bombardment of the opposite face on the CL spectrum evidently must result only from the action of the electric field. This field, induced by surface charging (which also results in the observed shift of Auger lines), is almost homogeneous across the crystal as the characteristic size of the electron spot at the sample surface (about a millimetre) is larger than the crystal thickness. The field can redistribute the charges near the opposite face, thus affecting the CL spectra.

It is necessary to note that the reasons for the absence of the surface cleaning and increase in the conductivity as well as the stability of the luminescent properties of the annealed crystal against its bombardment by electrons are still unclear. The absence of the characteristic changes in CL spectra such as those observed with the polished crystal in [6] and resulting from the oxygen escape, induced by bombardment of the crystal by electrons with medium energies [10], allows one to assume that oxygen escape from the annealed crystal is impeded. This assumption can also explain the fact that there is no change in the conductivity because it is known to increase with decrease in the oxygen content in the LN lattice. However, further investigations are necessary in order to establish the detailed mechanism for these effects.

Acknowledgment

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† The disappearance of the bands in CL spectra taken from the *positive* face after bombardment of the *negative* face as well as bombardment of the positive face, which resulted in an increase in the conductivity and disappearance of the charging of the positive face under the beam, *prior* to CL measurements from the negative face do not allow one to affirm that in CL spectra of the negative face these bands are absent in principle.

‡ This unexpected (for us) effect has not been specially investigated in the present work which deals with the influence of the changes in structure of NSR on the CL characteristics. Despite the fact that the effect was observed only once in contrast with the other results reported, we mention it here. In future we intend to examine it in detail.

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