# Domain configuration in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> ferroelectrics-semiconductors

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## 1. Introduction

Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals belong to the class of sulfide ferroelectrics with noticeable semiconductor properties. They are proper uniaxial ferroelectrics of the monoclinic symmetry, which undergo second order phase transition 2/m - m at the temperature 337 K. These crystals exhibit high photoconductivity and photorefractive properties in red and IR spectral region, large electro-optic, pyroelectric and piezoelectric coefficients [1-3]. Due to these characteristics  $Sn_2P_2S_6$ crystals are shown to be very promising materials for optical applications such as electro-optics, image processing, laser beam correction etc. In the most parts of applications a single domain state of the sample is required, so the problems of the crystal poling, domain switching, single-domain state fixing and unipolarity controlling are of interest from the both fundamental and practical viewpoints.

The present work is devoted to studies of the static domain structure of the  $Sn_2P_2S_6$  ferroelectrics by using the chemical etching and atomic force microscopy (AFM), as well us to the reconstruction of the domain topology.

## 2. Experimental

The studied  $Sn_2P_2S_6$  single crystals were grown by a vapor transport method. The samples were cut out along the main X, Y, Z axes in a form of parallelepipeds with linear sizes ~4 mm, and their sides were optically polished. The coordinate system used here is typical for monoclinic crystals, when the Y-axis coincides with a normal to the m mirror plane, and the X-axis corresponds to [100] crystallographic direction in the unit cell chosen as in [1]. The spontaneous polarization vector  $P_s$  lies in the (010) plane, and, as it was shown in previous investigations [4], deviates on an angle  $\varphi$  about 14° from [100] direction. In this case one can expect to reveal (for instance, by etching) different surface charge states corresponding to the anti-parallel domains on the X- and Z-cuts, whereas the Y-cut is electrically neutral. The typical sample configuration, coordinate system and polar vector direction are depicted in Fig. 1.

Elaborating the etching mixture, we found that most typical acid-based solutions are ineffective for  $Sn_2P_2S_6$ . As more efficient the alkaline mixtures contained NaOH, KOH and NH<sub>4</sub>OH were used. These optimized solids provide the fast enough (10-30 min) surface etching of the  $Sn_2P_2S_6$  samples at ambient temperature, revealing the both defect and domain structures. To verify an origin of the obtained patters, we compared the etching patterns of the poled and annealed crystals. All the pictures attributed with the domains are found to be absent in the poled samples. The etching figures were fixed with a CCD camera and an opti-

cal microscope (Fig. 2).

From the analysis of the typical etching figure one can conclude that the equilibrium domain patterns are formed by two kinds of the walls: first ones, inclined relative to spontaneous polarization vector on an angle about 10 degrees (that should correspond to the charged walls), and second one, which are parallel to the symmetry plane. Really, as it is seen in Fig. 2, the typical etching figure on the Z-cut are the wedges oriented along X, with the angle apex near 22-27° (bordered by two charged walls) or half of this value (when one of the walls is neutral, i.e. parallel to the mirror plane). Besides, the narrow needle-like domains enlarged along Y-axis are also distinguished (Fig. 2.a). Another picture is observed on the X-face of the crystal, which is close to the polar cut (Fig. 2,b). It is seen that the typical figures here are triangles with the vertex angle near 30°. The basis of the isosceles triangles is typically parallel to the mirror plane, i.e. correspond to the neutral domain walls.

The presence of the charged walls is well confirmed by studies of the AFM method. This technique requires the perfect quality of the sample surface. On this reason the natural (110) natural face of the  $Sn_2P_2S_6$  sample (marked by dots in Fig. 1) was examined. The topology of this crystal surface obtained in the amplitude mode is shown on Fig. 3. The typical pattern here is the rhombus-like figures with the sharp angle near 20-25°, and their characteristic dimensions are about several micrometers. This well corresponds to the data obtained by etching. Evidently, the observed lines are not parallel to the polar axis, so they should also correspond to the charged walls.

The possibility of the existence of the charged domain walls in an equilibrium state is explained by its screening by movable charge carriers. In this case the orientations of the domain walls are defined mainly by the minimum of the elastic contributions to the total wall energy. From other side, such domain wall is surrounded by the screening charge, localized within a layer with thickness in order of Debye length (~1  $\mu$ m in case of Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>). This non-uniform charge produces a static electric field, which change the local values of the refractive index due to electro-optic effect. In results it becomes possible to observe the light reflection on these layers, which are formed around the charged domain walls between opposing domains.

This effect was found by first in [5] and named as "directional light scattering". When the light beams propagated along some definite directions inside the  $Sn_2P_2S_6$ crystal being in the polydomain state, a bright light scattering along the entire beam was clearly seen at direct angle to the beam direction within rather narrow space angle. It was verified [6] that this scattering is definitely connected with domains, because the effect was absent as in the poled sample, as in the paraelectric phase [5].

The effect of the directional light scattering by domain walls permits to found an orientation of the light reflecting planes inside the sample. For example, when the light beam is directed along Y axis, the maximal scattering is seen at the angle of 8° in the XZ mirror plane. This permits to conclude that the walls are inclined on 4° in this plane, as it shown in Fig. 1. It was also established experimentally that the P<sub>s</sub> vector is turned off in the opposite side (Fig. 1).

## 3. Discussion

Basing on the above data, one can propose the following configuration of the most typical domains in the studied crystals (Fig. 1). There are two types of domain walls in the crystal bulk (shown by dashed lines): two charged ones, symmetrical relative to the (010) mirror plane (i.e. ADda and DCcd figures in Fig. 1), and neutral, coinciding with this plane (GEeg). According to the previous examinations of the light scattering anisotropy, the charged walls are turned off on  $\sim 4^{\circ}$  in the XZ plane from the X direction in the opposite side from the polar vector (Fig. 1,  $\angle Ddb$ ). Geometrical consideration shown in Fig. 1 gives the parameters of the cross-section figures which can be obtained on the X- and Z-cuts of the crystal. For example, admitting the angle between the mirror-symmetrical charged walls to be equal 30°, we obtain the vertex angles on the etching figures on the Z-cut ( $\angle NQR$ ) equal to 29°, 30° - on the X-cut ( $\angle BCD$ ), as well as 24° on the (110) plane, tested by AFM method ( $\angle B'C'D'$ ). These angles correlate well with experimentally obtained ones (Fig. 2,3).



Fig. 1. The reconstruction of the ferroelctric domains in the bulk of the  $Sn_2P_2S_6$  crystals (dashed lines) and their cross-sections by X, Z and (110) cuts. Here *ABCD* and *GEF* correspond to the etching figures obtained on the X-cut, *KLM* and *NQR* – on the Z-cut, and *A'B'C'D'* – AFM picture obtained on the (110) natural face.



Fig.2. The etching figures obtained on the Z-cut (a) and X-cut (b) of the  $Sn_2P_2S_6$  crystals. The depicted area is  $15 \times 15 \ \mu m$ .



Fig. 3. The AFM (amplitude mode) picture obtained on the (110) natural face of the  $Sn_2P_2S_6$  crystal. The aria is  $30\times30$  µm.

#### 3. Conclusions

A presence of the charged domain wall in the  $Sn_2P_2S_6$ ferroelectric crystals is confirmed by using the chemical etching and the AFM studies. In addition, the walls, parallel to the symmetry plane, are also observed. These data well correlate with the light reflection by domain walls described earlier. Using all these data, the domain configuration in the bulk of this crystal is proposed.

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