Fabrication and study of porous PbTe layers on silicon substrates

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Fabrication of porous PbTe layers on Si substrates using a developed technique based on anodic electrochemical etching of PbTe/CaF$_2$/Si(111) heteroepitaxial structures in a Norr electrolyte with anodizing current density 2-4 mA/cm^2 is reported. The structural and morphological parameters of such layers are investigated with x-ray reflectometry and diffractometry methods and with high-resolution scanning electron microscopy. The influence of anodizing conditions on the parameters of the layers is discussed, as well as the morphological peculiarities of the anodized structures. The presence of cylindrical mesopores with diameter of 7-26 nm inclined at the angle of ~35° to the surface normal is shown. The value of the porosity for the near-surface layer of lead telluride films is in the interval of 41-68% and depends on the anodic electrochemical treatment conditions.

1 Introduction One of the most fascinating fields of modern semiconductor technology is the formation of local porous areas with modified physical parameters. The most comprehensive research was obviously carried out for porous silicon [1], especially after the discovered photoluminescence from porous layers with Si nanocrystallites. More recently, a new porous semiconductor materials, such as germanium, IV-IV, II-VI, III-V semiconductors ([2, 3] etc.), were fabricated and studied. However, IV-VI semiconductors still are not reported to be succesfully obtained in a porous form. These materials, especially binary and ternary lead chalcogenide solutions, are widely used in infrared optoelectronics and are exceptionally promising for the emerging nanodot-based devices on silicon chips [4]. Mid-infrared vertical external cavity surface emitting lasers with the active medium of a one wavelength thick PbTe layer grown by molecular beam epitaxy on a Si substrate were recently realized [5]. Hence, the study of the structural and optical properties of porous networks of such materials is rather significant too, and has not been reported up to now in the literature. There is only one publication in this field [6], which, unfortunately, does not fully describe the morphological picture of the porous layers, their physical properties and geometrical parameters of the pores. Considering that lead chalcogenide semiconductors are already widely used for optoelectronic applications, the study of their modified porous form with nm-sized pores is of primary importance. Taking into account the compatibility of anodic electrochemical etching with available technologies, since it is a promising and reliable method, fabrication of IV-VI semiconductor nanopore networks is extremely promising for practical applications, such as light emitting layers, microthermogenerators on Si chips. These open possibilities for the development of a variety of new devices. In our recent work [7] we have developed a novel method of lead chalcogenide anodizing based on a treatment of PbTe/CaF$_2$/Si(111) structures in a Norr solution [8]. The purpose of the present work was to study porous structure that is formed using this method in lead telluride films at low anodizing current densities compared to conditions used in [7].

2 Experimental PbTe films with n-type conductivity grown by molecular beam epitaxy on Si(111) substrates

with 2 nm thin CaF_2 buffer layers were used for the porous layers fabrication. The thickness of the initial epitaxial PbTe films was 2.3 μm. The films had [111] orientation along the growth direction as confirmed with x-ray diffractometry measurements [9]. The films were treated with anodic electrochemical etching in a Norr solution. It is based on the aqueous solution of potassium hydroxide, glycerol and ethanol and was originally proposed for a wet polishing of PbTe crystals. A number of experiments was carried out in order to determine an optimal solution composition for the anodic etching and as a result a classical solution as described in [8] was used. Treatment was carried out in a vertical type electrochemical cell. The cell had a teflon base containing a circular platinum cathode in its upper part and a flat metallic anode at the bottom. Experimental samples $PbTe/CaF_2/Si(111)$ were placed directly on the anode and the cell was filled with electrolyte. Electrochemical anodic etching was carried out by applying direct current between anode and cathode. Local porous area was subsequently formed in the epitaxial layer during anodic treatment in electrolyte. The main parameters of the anodic electrochemical etching process are treatment duration t and anodizing current density j_{an}, which is calculated as a ratio of current strength for the current stabilization process to the contact area surface of the sample with electrolyte. A technological peculiarity of this work was the use of low current densities of 2-4 mA/cm^2 (Table 1), that were not studied before. During such anodizing process the electrical breakdown of a 2 nm thin insulating CaF_2 layer did not take place and anodizing was performed rather uniformly across the sample surface exposed to the electrolyte.

The structural parameters of the samples were investigated with x-ray reflectometry and diffractometry methods (using high-precision custom-made x-ray system with BSV-27 x-ray tube with copper anode and a BDS-6 scintillation detector). Morphology of the samples was studied using high-resolution scanning electron microscopy (Zeiss Supra-40).

3 Results and discussion The porosity values of the samples were calculated using high-resolution x-ray reflectometry based on the measurement of reflective capability of x-ray radiation in the angle interval of total external reflection. Porosity value (P) was estimated from the comparison of integral curves of x-ray reflectometry before and after anodizing. From the corresponding critical angles θ_{cna} and θ_{ca} (angular position of a total external reflection curve point with a half-height intensity in a decrease curve area) P was calculated according to equation [10]:

$$P = 1 - (\theta_{ca}/\theta_{cna})^2. \tag{1}$$

It was established that it is possible to vary porosity value in a sufficiently wide interval of 41-68%. The maximum porosity corresponds to the longer anodizing durations (Table 2). It is important to note that for the larger current densities (~6-8 mA/cm^2) the porosity value starts to diminish. It should be also mentioned that x-ray reflecto-

metry method provides information on the porosity only for the thin near-surface layer (~100 nm).

Table 1 Conditions of anodizing for PbTe films on Si substrates after anodic electrochemical etching.

No.	Anodizing current density j_{an}, mA/cm^2	Anodizing duration t, min
1	2	10
2	2	20
3	4	10
4	4	18

Next, average pore size in a lateral and vertical directions was evaluated from a triple crystal x-ray diffractometry curves within a framework of a kinematic approach [7, 11]. It is based on the diffractometry curves measuring with a sample rotation at a small deviation angle from the precise Bragg position. Distribution on intensity around the reciprocal lattice node represents a Fourier-image of the form-factor of the dissipating object (a single pore). The intensity is therefore defined by the geometrical dimensions of the pores. The values of the full pore size in a lateral direction were calculated from the diffuse peak width according to equation [11]:

$$L_x \approx \lambda/2\Delta\theta_x \sin\theta_B, \tag{2}$$

where $\lambda = 1.54$ Å (X-ray $CuK_{\alpha 1}$ radiation wavelength), $\Delta\theta_x$ is a width of a diffuse peak for a scanning along axis x, θ_B is the Bragg angle. Average dimension of the pores in depth (along axis z) is given by:

$$L_z \approx \lambda/2\Delta\theta_z \cos\theta_B. \tag{3}$$

Thus the average pore dimensions (values L_x, L_z) were calculated for PbTe porous areas. The results are shown in Table 2.

Table 2 Pore parameters calculated from x-ray measurements for PbTe films on Si after anodic electrochemical etching.

No.	Porosity, %	Pore size interval in a lateral direction L_x, nm	Average pore size in a vertical direction L_z, nm
1	41	58-80	180
2	52	50-60	160
3	45	48-59	150
4	68	40-47	140

Also of note, the triple crystal x-ray diffractometry curves were almost symmetrical for all the experimental samples, indicating an absence of deformation of near-surface layers, which presence is usually typical for porous silicon [1]. There were no additional maxima of diffuse scattering, which evidences the absence of short range ordering in the pore distribution. For all the samples, values of L_z are larger than L_x, which points out that the pores are elongated in the vertical direction. The noticeable interval

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of L_x values indicates that the pores are inclined to the surface normal. X-ray reflectometry and diffractometry experimental results allowed us to conclude that investigated PbTe layers are indeed porous with a nanosized mesopores that have a columnar-like shape and are inclined to the surface normal. However, it is important to note that the determination of the precise angle of the pore inclination from the triple crystal x-ray diffraction data would not be reliable, due to the approximate results of calculations using (2) and (3), and due to the statistical averaging of data from all the pores for all the directions in the film. The direct measurement of the pore propagation angle will be performed with scanning electron microscopy immediate observation, as described below.

The next stage of our investigations was to perform high-resolution scanning electron microscopy investigations of the anodized PbTe layers and to compare these results to the porosity parameters obtained from the x-ray measurements. Figure 1 shows a typical morphology of the surface of PbTe film after anodic electrochemical etching. A similar granular-like domain morphology is observed for all of the investigated samples. The lateral dimensions of such domains are 40-300 nm with an average value of 130 nm and their density is $\sim 1 \cdot 10^{10}$ cm^{-2}. Any striking dependence on the anodizing conditions for the series of PbTe samples was not observed. On the surface of each large domain there are visible exits of the pores (Fig. 1), which seem to propagate at a certain angle to the surface normal due to the (111) orientation of the lead telluride epitaxial films.
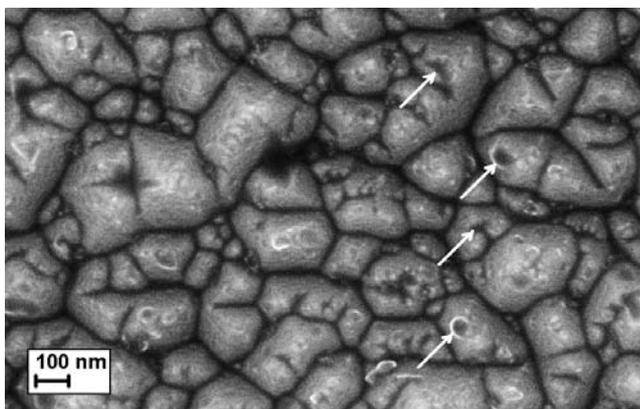
Figure 1 Scanning electron microscopy image of a surface of the anodized PbTe epitaxial film (for $j_{an} = 4$ mA/cm^2 and $t = 18$ min). Some of the pore exits on the surface are shown with arrows.

Figure 2 shows a typical cross-section of PbTe layer obtained with a cleavage of substrate along natural direction [110]. For all the samples columnar mesopores inclined to the surface at the angle of $\sim 35°$ (as determined from the cross-sections taking into account the tilt view angle) with a pore diameter varying from 7 to 26 nm were observed. It is important to note that the average pore depth was in excellent agreement with L_z values obtained from x-ray investigations (Table 2). The L_x values, which correspond to the full pore dimension along axis x, for the inclined pores describe the average distance along the surface between the beginning and the end points of a single pore. These values are also in agreement with the electron microscopy data.
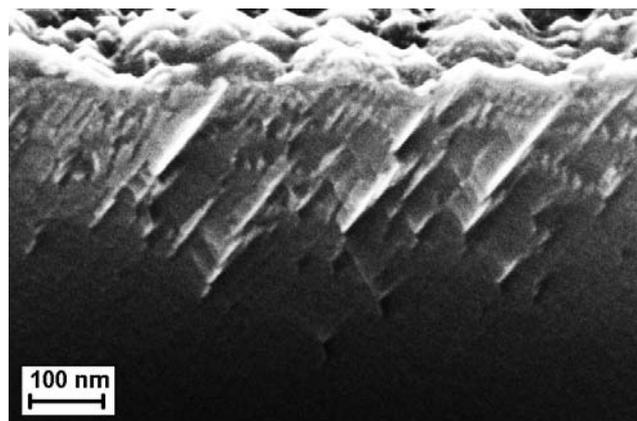
Figure 2 Scanning electron microscopy tilt view at the angle of 70° of the cross-section of the anodized porous PbTe epitaxial layer (for $j_{an} = 4$ mA/cm^2 and $t = 10$ min) with visible crystallographically oriented mesopores.

Another important feature of the anodic etching of PbTe films was the reduction of the film thickness during treatment (surficial material removal). For the applied anodizing conditions the thickness of the removed layer was of order of magnitude of hundreds of nanometers. Hence, it is possible to acquire a situation when by decreasing the film thickness due to the higher anodizing current density and longer anodizing duration a completely porous layer would be obtained. Such structure was actually observed for the samples with anodizing duration of 18 min, when the remained after anodic treatment PbTe layer with ~ 300 nm thickness was completely porous, as shown in Fig. 3.

The results related to the nanodomain structure formation on the surface of porous layers are significantly different from a classical porous silicon situation. We have to note that the characteristic property of epitaxial lead chalcogenide films on Si(111) is the presence of the threading dislocations with $1 \times 10^7 - 4 \times 10^8$ cm^{-2} density, as well as the terraced initial surface and a large amount of point defects. The process of the fragmentation of the epitaxial films into nanodomains during anodic treatment is influenced by these structural inhomogeneities. Besides, an important role can be possibly played by the processes of a relaxation of a tensile strain in lead telluride films on silicon during anodic electrochemical etching of these epitaxial films.
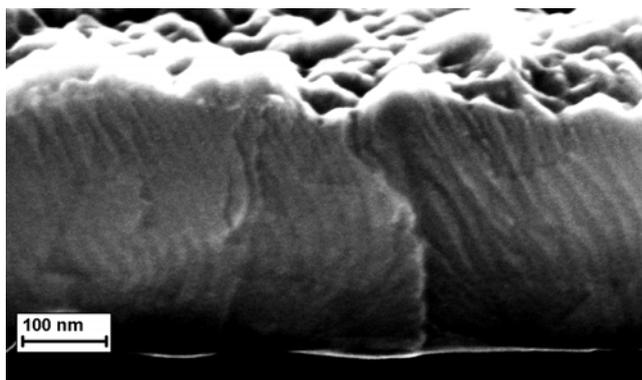
Figure 3 Scanning electron microscopy image of a cross-section of the anodized PbTe epitaxial layer (for j_{an} = 4 mA/cm^2 and t = 18 min). Dark stripe at the bottom of the image is the Si substrate.

Analysis of the crystallographic orientation of the pores in PbTe porous layers is extremely interesting. As was observed, on the surface of each domain there are several pits that are identified as inclined pore exits from the surface electron microscopy images (comparing Fig. 1 and Fig. 2). The pores propagate at the angle of ~35° to the surface normal. It is well known that the threading dislocations in lead chalcogenide (111)-oriented films have about the same propagation angle of 36° [12] (angle between [111] and [101] directions). A conducted evaluations show that the density of the pores is on several orders of magnitude higher than the density of dislocations in the lead telluride films and therefore the observed picture (Fig. 2) can not be identified with the threading dislocations in the film. It is widely reported [13] that in (111)-oriented semiconductors preferential pore propagation corresponds to two main directions: <100> or <113>. In former case the inclination angle from the surface normal of the pore array is 35°, while in latter case – 29°. Considering the close obtained value of the pore growth vector angle for the studied PbTe anodized films, we can assume that the crystallographic <100> directions play a major role in the pore propagation in PbTe films on Si(111) substrates. Another key feature of a pore formation mechanism (for low current densities range) is the penetration of the pores at the depth of 150-180 nm and the simultaneous removal of the surficial layer. As a result, the mesoporous layer thickness is virtually independent from the treatment duration.

4 Conclusions In this work we have studied structural and morphological properties of PbTe porous layers after anodic electrochemical etching in a Norr electrolyte under varied treatment conditions with low anodizing current density (2-4 mA/cm^2). X-ray measurements yielded porosity values in the interval of 41-68%, with the porosity increasing with etching duration. A specific "granular" nanostructurization took place on the surface of PbTe films. The pore preferential propagation angle of ~35° was estimated. The cylindrical pore diameter is 7-26 nm and the depth of the pores is 150-180 nm as determined with x-ray and electron microscopy investigations. We have to notice an overall good agreement in an overall porosity network morpohology and pore geometrical parameters as determined with x-ray and electron microscopy investigations. It is shown that for the longer treatment durations it is possible to obtain fully mesoporous thin layers with a thickness of 150-200 nm. For the first time the pore morphology was visualized for PbTe porous layers and the fundamental features of the pore formation in PbTe were determined. Concluding, the most important and incontestable practical result of the work is a fabrication of porous PbTe layers with crystallographically oriented nm-sized pores. The applied fabrication technique upon necessary optimization should be applicable for the formation of local nanostructured porous areas of IV-VI semiconductors on Si for various practical applications.

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