Fabrication of porous nanostructured lead chalcogenide semiconductors for modern

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Abstract. Porous structures of lead chalcogenides with porosities of 20-68% and pore dimensions as small as 7-20 nm were fabricated using an anodic electrochemical etching technique applied to epitaxial PbTe and PbSe films on Si. Anodized lead selenide demonstrated two basic types of porous morphology: quasiporous noncontinuous layers and hierarchical porous layers. Lead telluride had a more typical mesoporous morphology, with pores propagating at an angle of 35° to surface, which corresponds to the <100> directions in the epitaxial films and is promising for the fabrication of photonic crystals with Yablonovite-like structure. The sizes of PbTe nanocrystallites in porous layers with high porosity were calculated to be 26 nm, which indicates that quantum confinement conditions are realized in this material. Such low-dimensional morphology of porous lead telluride is prospective for the fabrication of microscale thermoelectric devices with high *ZT*.

1. Intoduction

The processes of pore formation in solids present a unique and diverse approach to the fabrication of novel nanomaterials with improved properties. As of late, the top-down anodic electrochemical etching process resurged as an extremely promising technique for porous modification on nanoscale. Porous materials with high porosity and nanometer-sized pores are known to exhibit unique physical properties due to specific and rather complex nanostructured morphologies, which result in an extremely large surface to volume ratio and the quantum confinement effects. The possibility to employ new properties of high-porosity materials, which take place due to the quantum-size effects, is widely studied for porous silicon and an array of other semiconductor materials. However, one glaring omission is the study of the binary compounds of lead chalcogenides PbX (X = Te, Se, S). The main attractive property of PbX materials is the large value of exciton Bohr radius (20-50 nm), which gives a unique opportunity for the fabrication of the nanostructured materials with outstanding properties [1]. Currently there are two major fields of the practical application of lead chalcogenides: infrared

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optoelectronic devices (quantum dot lasers, detectors, superlattice-based Bragg mirrors) [2], and thermoelectric devices (microcoolers, microthermogenerators) [3]. PbTe is one of the most studied and widely used intermediate temperature (450-800 K) thermoelectric materials. It is well known, that the modern development of thermoelectric devices strongly requires an increase in the value of the thermoelectric figure of merit ZT so that it exceeds 1 at 300 K. A scientific approach to solving this problem exists and it is associated with the creation of low-dimensional systems on the basis of existing thermoelectric materials. From a physical point of view this is to be expected from the reducing of thermal conductivity by suppressing the phonon thermal conductivity due to the scattering of phonons at the nanoscale boundaries and inhomogeneities. PbTe is currently receiving a significant amount of attention due to the demonstration of $ZT > 1$ by employing nanogranular powder materials or creating nanosized inclusions in bulk crystalline material [3-6]. For example, for thin film systems with PbTe quantum dots in a PbSe matrix $ZT = 2.5$ at 550 K was reported [5]. A completely novel approach for thermoelectric devices fabrication is to employ porous materials with a nanometer-scaled morphology. Application of nanostructured porous lead chalcogenide materials can lead to a remarkable improvements and new devices, such as monolithically integrated cooling systems for IR-detectors and microprocessors, microrefrigerators, microthermogenerators, which seem to become more and more in demand considering the new alternative energy sources. Therefore, it is extremely important to fabricate, investigate and apply new nanostructured porous PbX materials. In our work we present our latest results in porous lead chalcogenide layers study based on the recently developed method of PbX anodic etching in a Norr solution [7].

2. Experimental details

In this work we have applied a traditional anodic electrochemical etching widely used for porous material fabrication for lead chalcogenide film structures. Initial samples were PbTe and PbSe epitaxial films with 2-3.5 µm thickness grown with molecular beam epitaxy on Si(111) wafer substrates with 2 nm thin CaF$_2$ buffer layers.
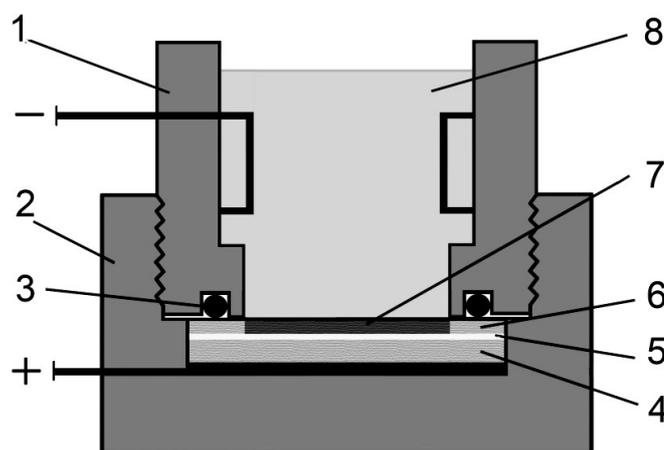

Figure 1. Schematic image of electrochemical cell. 1 - upper cell unit with a circular Pt cathode, 2 – lower cell unit with flat anode, 3 – elastic O-ring, 4 – sample's silicon substrate, 5 – sample's buffer layer, 6 – sample's epitaxial PbX film, 7 - modified area of the PbX film, 8 – electrolyte.

A vertical type teflon electrochemical cell with a circular platinum cathode and a flat metallic anode was used to perform anodic electrochemical etching of PbX/CaF$_2$/Si(111) structures. A schematic of the cell is given in figure 1. The prefabricated teflon base of the cell consisted of two main parts: upper unit with a circular platinum cathode and lower unit with flat metallic anode. Experimental samples were placed directly on the anode and were pressed to it by elastic O-ring to ensure no leaks. Since lead chalcogenides have a significantly lower resistivity (~0.1 Ohm × cm) than Si substrate (1000 Ohm × cm), there was no necessity to create a highly doped layer at the bottom of the Si substrate in order to successfully carry out anodic electrochemical etching of the PbX layers. Anodic etching of lead chalcogenides was carried out in a potassium hydroxide based Norr electrolyte

[7, 8]. Anodizing current density j_{an} was in the range of 2-8 mA/cm^2. The etching duration time t_{an} was 10-20 min. Morphological properties of the PbX samples were studied by high-resolution scanning electron microscopy (SEM) using Zeiss Supra-40, the structural parameters of the porous samples were investigated with the specifically developed x-ray reflectometry and triple crystal diffractometry methods [9].

3. Results and discussions

3.1. *Anodic electrochemical etching of lead selenide films*

Lead selenide films were divided into two groups depending on their initial surface morphology. While some films had a flat surface with 2-3 nm high nanoterraces typical for PbX epitaxial films on Si(111) [10], another group had a developed faceted surface morphology. During anodic electrochemical etching a strong surface modification took place for PbSe films in both cases. For the PbSe/CaF$_2$/Si(111) structures with an initial flat nanoterraced PbSe surface, anodic etching in a Norr electrolyte resulted in a non-continuous surficial film morphology formation, when interconnected maze-like pattern consisted of structures with 80-400 nm lateral sizes and 90-100 nm thickness. The formation of such porous network structures took place only in the near-surface region of the film and did not depend on the film's entire thickness and anodizing conditions. This allowed us to fabricate isolated PbSe nanoislands directly on the Si substrate for the initial epitaxial films with lower thickness using higher current densities [11]. On the other hand, for the PbSe films with a developed faceted initial surface a developed hierarchical surficial porous network layer formation was observed after anodic etching (figure 2). Characteristics of the porous nanostructured morphology were as following: large open macropores (100-250 nm), smaller secondary macropores (50-75 nm), and mesopores (15-20 nm).
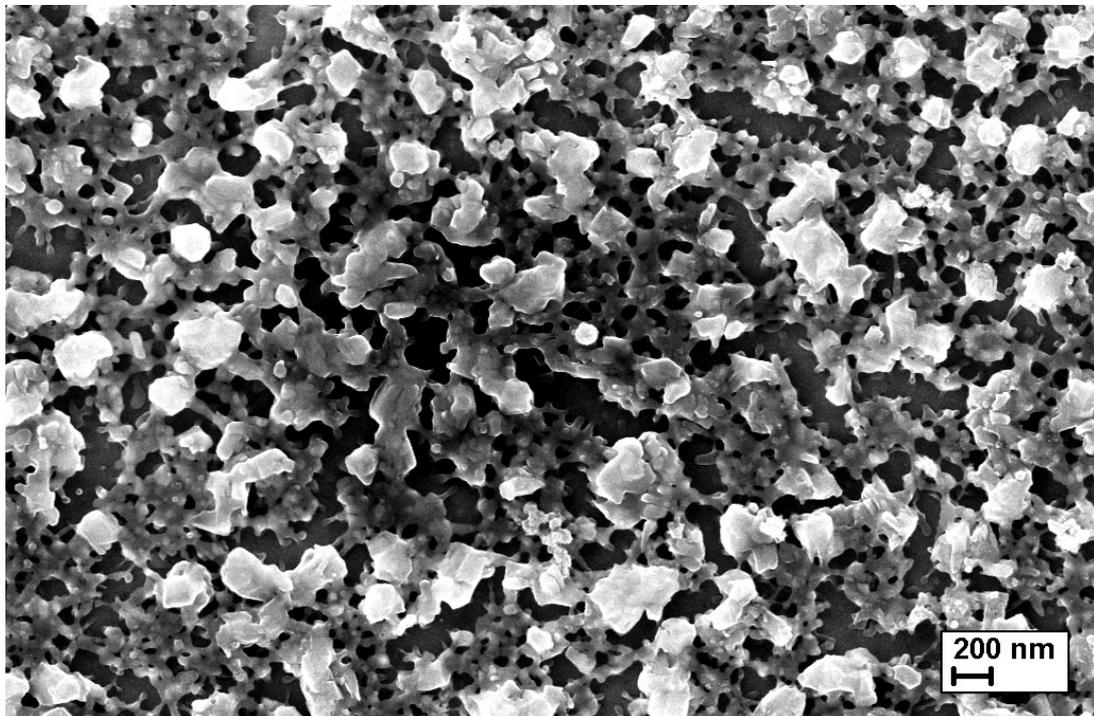

Figure 2. SEM image of the surface of the anodized porous PbSe epitaxial layer (j_{an} = 8 mA/cm^2 and t_{an} = 10 min) with hierarchical porous surficial layer.

The most possible reason for the observed complex pore formation in this case is the non-uniformity of the electrical field for the anodized films with prominent initial faceted surface relief. At applied low current densities the surface is preferably etched at defects and surface irregularities, and facet boundaries serve as nucleation sites for the pores of the nanonetwork. Hence, the mechanism of the modified layer formation, which results in the variety of the obtained PbSe porous structures, is purely electrochemical. Therefore, during subsequent research it is necessary to optimize conditions of the anodic etching process (firstly, by varying the electrolyte solution) for the fabrication of a defined pore morphology in PbSe samples.

3.2. *Anodic electrochemical etching of lead telluride films*

The processes of the modification of PbTe layers during anodic etching were significantly different from previously described PbSe layers. The first unique feature of the anodized PbSe/CaF$_2$/Si(111) structures was the presence of a domain-like surface morphology with inclined exits of the pores clearly visible on the surface (the initial surface was flat with nanoterraces [10]). The lateral dimensions of the domains were 40-300 nm with an average value of 130 nm and their density was ~1 $\times 10^{10}$ cm^{-2}. Any striking dependence for their geometrical parameters versus the anodizing conditions for the series of PbTe samples was not observed. On the surface of each large domain there were exits of the pores seemingly propagating at a certain angle to the surface due to the (111) orientation of the lead telluride epitaxial films [12]. Cross-sections of the anodized PbTe films obtained with a cleavage of substrate along natural direction [110] displayed uniform arrays of columnar mesopores inclined to the surface at an angle of 35° with a pore diameter of 7-26 nm (figure 3). Remarkably, the porous layer occupies only the top region (150-180 nm) for all the anodized PbTe films. Just like for PbSe, an important feature of the anodic etching of PbTe films was the surficial material removal. Hence, we were able to develop a technique to fabricate completely mesoporous PbTe layers with 150-300 nm thickness on Si [12].
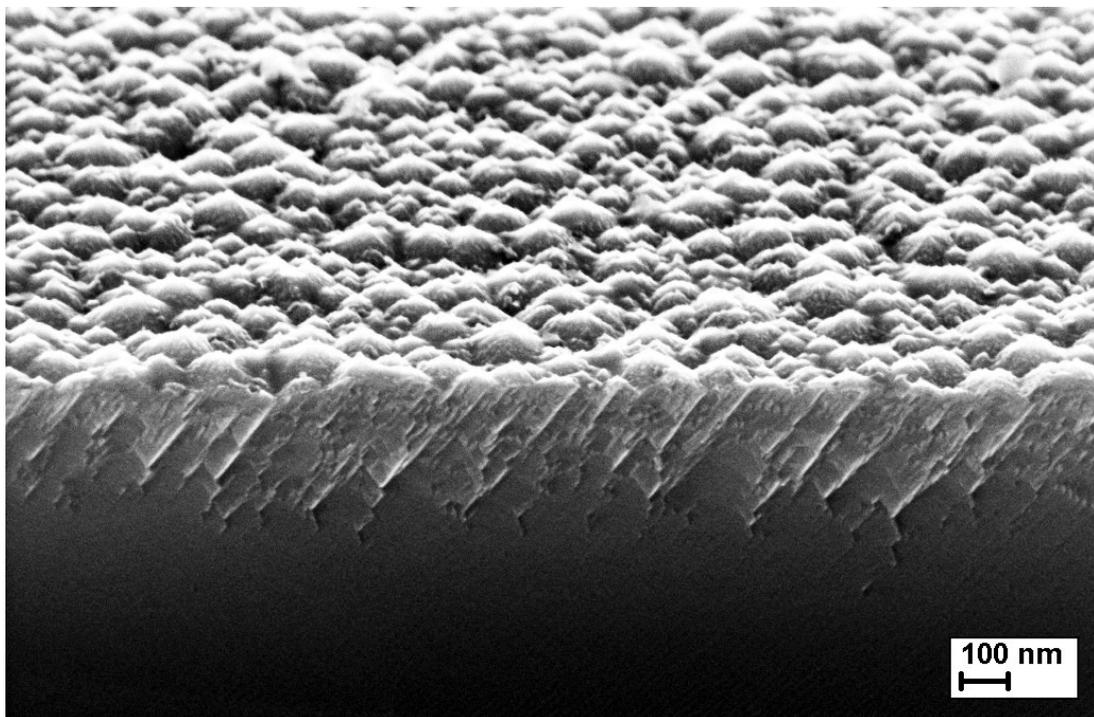

Figure 3. SEM image of the cross-section of the anodized porous PbTe epitaxial layer ($j_{an} = 4$ mA/cm^2 and $t_{an} = 10$ min) with 35° inclined mesopores (SEM tilt view at the angle of 70°).

In order to analyze the physics of the specific porous morphology formation in epitaxial (111)-oriented PbTe films we have to contemplate that the characteristic property of the epitaxial lead chalcogenide films on Si(111) is the presence of the threading dislocations and of a large amount of point defects. The process of the fragmentation of the epitaxial films into domains during anodic etching is therefore influenced by these structural inhomogeneities. It is well known [13] that the threading dislocations in lead chalcogenide (111)-oriented films have about the same propagation angle of 36° (angle between [111] and [101] directions). Evaluations showed 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 can not be identified with the threading dislocations in the film. It is widely known that in (111)-oriented semiconductors preferential pore propagation corresponds to two main directions: <100> or <113> [14]. In the former case the inclination angle from the surface normal of the pore array is 35°, while in the 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 determining role in the pore propagation in PbTe films on Si(111) substrates.

Average pore sizes in a lateral and vertical directions calculated from a triple crystal x-ray diffractometry measurements [9] were in a perfect correspondence with the SEM data. The porosity values (P) calculated using high-resolution x-ray reflectometry in the angle interval of total external reflection for anodized PbTe films were $P = 41$-68% with the highest porosity values corresponding to the longer anodizing durations [9, 12]. It is very important that using our etching technique the high porosity values can be relatively easily achieved.

In order to investigate the modification of the optical properties of PbTe films during pore formation we have measured the transmission spectra of PbTe/CaF$_2$/Si(111) structures before and after electrochemical treatment using Perkin Elmer 16PC Fourier transform spectrometer in the wavelength range of 2.2-16.7 micron. Before and after anodic etching the spectra had the classic form of interference associated with the phenomenon of interference in the film system. As a result of the anodic electrochemical etching of the PbTe films with high porosity $P = 65\%$ an increase of energy gap value from 0.31 to 0.34 eV took place. This result indicates the formation of low-dimensional structures in the sample. To estimate the size of the nanoparticles the hyperbolic model [15] was used, which has recently been widely applied for the PbTe nanoparticles of spherical shape. The exact form of nanoparticles in our case is unknown, but we would assume that PbTe nanocrystallites have a spherical shape, as is generally the case for other mesoporous semiconductors. For the anodized PbTe material with the nanoparticles with a spherical shape the energy gap E_g^{an} can be calculated according to the following equation:

$$E_g^{an} = \sqrt{E_g^2 + E_g \frac{\pi h}{m^* R^2}}\ ,\tag{1}$$

where E_g is the band gap of bulk monocrystalline PbTe, h – the Planck constant, R – average radius of a nanoparticle, m^* – effective exciton mass. According to the isotropic model [16]

$$\left.\begin{aligned}\frac{1}{m_e^*} &= \frac{1}{3}\left(\frac{2}{m_{et}} + \frac{1}{m_{el}}\right)\\[2mm]\frac{1}{m_h^*} &= \frac{1}{3}\left(\frac{2}{m_{ht}} + \frac{1}{m_{hl}}\right)\end{aligned}\right\}\tag{2}$$

where m_{et} and m_{ht} are transverse and m_{el} and m_{hl} are longitudinal effective masses of electrons and holes in PbTe. Using data from [16], at 300 K $m_0/m_{et} = 11.6$, $m_0/m_{ht} = 10$, $m_0/m_{el} = 1.2$, and $m_0/m_{hl} = 0.7$, where m_0 is electron rest mass. Using equation (1), we have determined that for $E_g^{an} = 0.34$ eV, the radius of nanoparticles is 13 nm. Therefore, in nanostructured porous PbTe films with high porosity, the conditions of strong quantum confinement effects take place, when the particle size becomes smaller than the exciton Bohr radius (50 nm for PbTe). These results indicate that it is extremely promising to apply the method of nanostructured porous lead telluride layers fabrication for the

practical aims. The nanoscale morphology is known to result in a strong phonon scattering and consecutive *ZT* gain, which is why PbTe porous layers with high porosity can be used for thermoelectric devices. An important positive attribute of our results is the capability of PbX modified layers formation directly on silicon substrates, providing an effective way for the fabrication of Si chip integrated devices. The mesopore propagation angle of 35°, on the other hand, is promising for the fabrication of photonic crystals with Yablonovite-like structure.

4. Conclusions

In summary, porous nanostructured lead telluride and lead selenide layers on silicon substrates were fabricated. SEM investigations showed the formation of material specific porous morphology. For PbSe layers two types of modified layers were distinguished, one of them being a complex hierarchical porous layer. For PbTe layers inclined mesopore ensemble formation was observed. Energy gap value increase for lead telluride with high porosity, determined from transmission spectra, allowed us to calculate the nanocrystallite radius confirming the presence of quantum size effects in nanostructured samples.

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