Investigations of PbSe layers after anodic electrochemical etching by scanning electron microscopy

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Investigations of the morphology of the surface of PbSe/CaF$_2$/Si(111) epitaxial structures after anodic electrochemical etching in a Norr electrolyte with anodizing current density of 2-8 mA/cm^2 and duration of 10-20 min were performed. Two possible morphology types of PbSe nanostructured surficial porous layers were distinguished. Agglomerated nanoislands with 80-400 nm lateral sizes and 70 nm average separating gaps were observed for the anodized films with initial flat terraced surface. It is shown that in this case it is possible to fabricate PbSe agglomerated nanoisland structures directly on silicon substrate. A double-layered porous structure was obtained for epitaxial PbSe films with initial granular surface. Top porous layer with a thickness of 75-100 nm presents a developed hierarchical porous network. Bottom layer is characterized with a presence of mesopores with 7-18 nm diameter propagating into the layer.

1 Introduction Porous semiconductors are currently widely studied, which is primarily due to the extremely valuable potential for semiconductor properties controlled modification allowing to implement novel practical applications. It was the discovery of a luminescence of porous silicon two decades ago [1] that opened a new field of porous semiconductors designed for optoelectronic applications, which is still promptly developing. Porous materials with high porosity and nanometer-sized pores are known to exhibit unique physical properties due to the extremely large surface to volume ratio and quantum confinement effects. Such properties open novel possibilities for the applications in optoelectronics, nanoelectronics, chemical and biochemical sensing. Among porous semiconductors, porous silicon naturally receives enormous attention and has been investigated most intensively. More recently, a development of other porous semiconductors, for example, the conventional II-VI, IV-IV, III-V compounds ([2-6] etc.), became a very fruitful field of research. However, it seems that IV-VI semiconductors were completely omitted from this tendency. These materials, and primarily lead chalcogenides PbX (X = Se, Te, S), are one of the most important for infrared optoelectronics. For instance, a mid-infrared vertical external cavity surface emitting laser based on epitaxial PbSe layer operating above room temperature has been recently realized [7]. Fabrication of nanostructured porous IV-VI semiconductors can be extremely promising from both fundamental and practical standpoints due to their outstanding physical properties [8]. PbSe quantum dots are very attractive for mid-infrared optoelectronics device applications, such as photon detectors [9]. An interesting prospective possibility is to use porous PbX layers as elements of gas analyzers with the extension of already existing technology with a fabrication of high surface to volume ratio of nanostructured material. We have recently developed and reported a technique for the porous structure fabrication based on anodic electrochemical etching of lead telluride epitaxial layers on silicon substrates in a potassium hydroxide based solution [10, 11]. The aim of the present work was to carry out anodic treatment for PbSe epitaxial layers under the same anodizing conditions as for PbTe and to compare the obtained results.

2 Experimental PbSe epitaxial films with n-type conductivity were grown with molecular beam epitaxy on silicon (111)-oriented substrates with 1000 Ohm·cm resistivity. CaF_2 buffer layers with 2 nm thickness were used in order to suppress lattice mismatch with the substrate [12]. Thickness of lead selenide films was from 2 to 3.5 μm. The films were divided into two groups depending on their initial surface morphology. While a part of the films had a flat surface with 2-3 nm high nanoterraces typical for PbX epitaxial films on Si(111) [12], another group had a developed granular surface morphology, which will be shown in more detail later. A vertical type electrochemical cell schematically shown in Fig. 1 was used, which allowed us to perform anodic electrochemical etching of heteroepitaxial multilayered $PbSe/CaF_2/Si(111)$ structures according to a technique that was previously elaborated and applied for the fabrication of porous PbTe layers [10, 11].
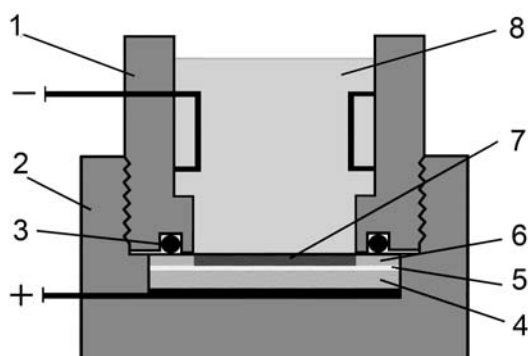

Figure 1 Schematic outline of electrochemical cell.

Prefabricated teflon base of the cell consists of two main parts: upper unit (1) with a circular platinum cathode and lower unit (2) with flat metallic anode. Experimental sample is placed directly on the anode and is pressed to it by elastic O-ring (3) to secure leak tightness. Experimental samples in our case consisted of silicon substrate (4), buffer layer (5), and epitaxial PbSe layer (6). Since lead chalcogenide films had 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 succesfully carry out anodic electrochemical etching of the PbSe layer. Porous (modified) area (7) was formed in the surficial area of epitaxial layer during anodic etching in electrolyte (8). A Norr solution (20 g potassium hydroxide, 45 ml distilled water, 35 ml glycerol, 20 ml ethanol) was used as an electrolyte [13]. This solution was originally proposed for the electrochemical polishing of PbTe [13] and PbSe [14] crystals with high current densities. 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. Anodizing current density was 2-8 mA/cm^2.

Treatment duration time for the main experiments was 10-20 min. All the experiments were carried out at room temperature. It was experimentally established that chemical reaction of the electrolyte with the material of the films was completely absent, and therefore the processes of the surface modification observed during anodic etching were purely electrochemical.

Morphological properties of the samples were studied by high-resolution scanning electron microscopy (SEM) using Zeiss Supra-40. Additional study was performed by atomic force microscopy (AFM) in tapping mode using NTEGRA Aura. Crystal structure of the samples was studied with x-ray diffractometry (DRON-3M, $\lambda = 1.54$ Å).

3 Results

3.1 Surface morphology modification of PbSe films with flat initial surface It should be foremost noted that the processes of electrochemical etching of PbSe in a Norr solution had their own special characteristics compared to previously studied PbTe films. An important feature of this process was the removal of a near-surface layer. Experimental measurements of the thickness of the removed film showed that the removal of the material depends linearly from the anodizing current density. For PbSe film samples anodized with $j_{an} = 2$ mA/cm^2 and $t = 10$ min a removed layer thickness was ~750 nm, and for the samples etched with 4 mA/cm^2 and $t = 10$ min it was ~1500 nm. These values are noticeably smaller than previously reported ones for PbSe crystals etched with high j_{an} values [14]. On the other hand, the obtained values of the removed lead selenide layer thickness were larger than for PbTe films treated under the same conditions.
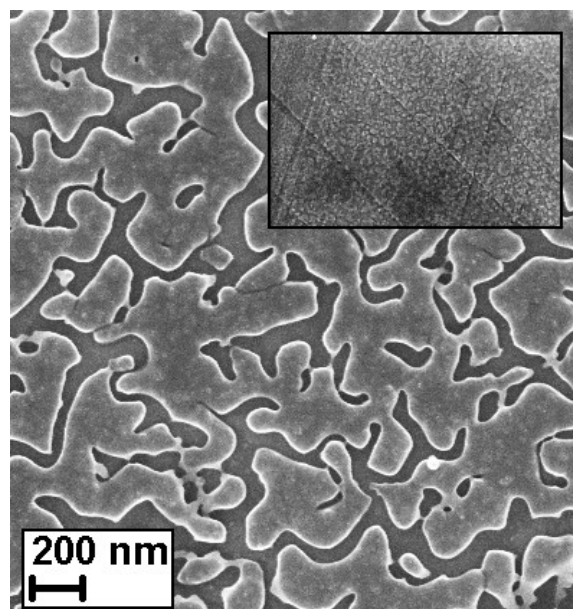

Figure 2 SEM normal plan-view of a surface of the anodized PbSe epitaxial film ($j_{an} = 2$ mA/cm^2, $t = 10$ min) with a flat initial surface morphology, which is shown in the insert with the same scale.

It was observed that during anodic treatment of PbSe films the results can be significantly different depending on the initial film surface morphology. A surface modification for the anodized PbSe films with initial flat surface resulted in a discontinuous surficial film morphology formation. Typical image of such film surface is shown in Fig. 2, while the insert in Fig. 2 displays the initial surface of the film with the same scale.
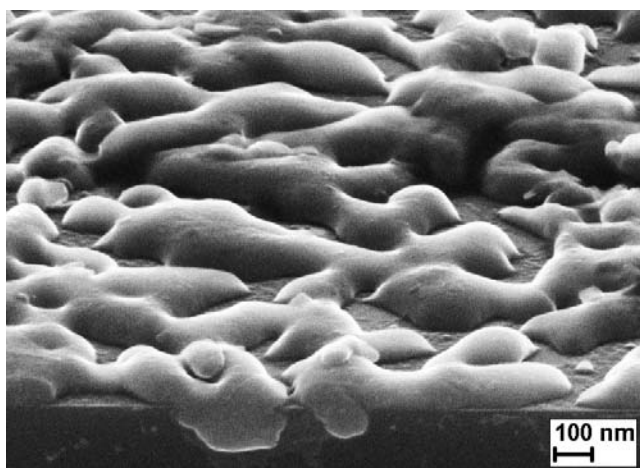

Figure 3 SEM tilt view at the angle of 70° of a surface of the anodized PbSe epitaxial film (j_{an} = 4 mA/cm^2, t = 20 min) with 2 μm initial thickness and a flat initial surface morphology.
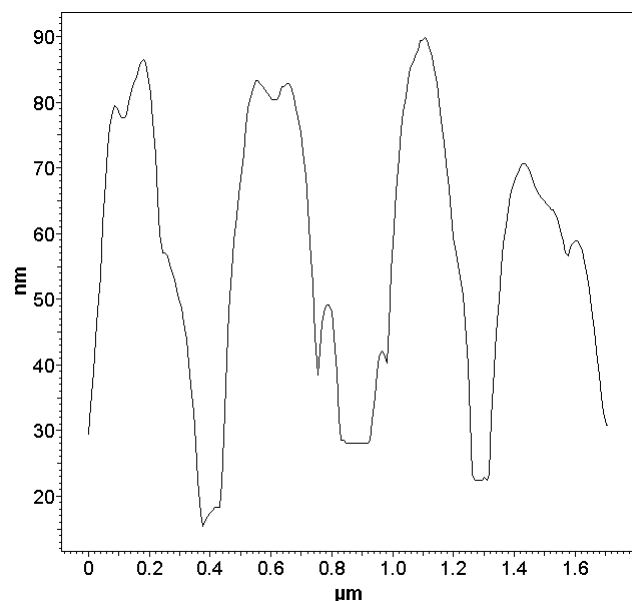

Figure 4 AFM profilogram of PbSe nanoislands on Si substrate (j_{an} = 4 mA/cm^2, t = 20 min, 2 μm initial thickness and a flat initial surface morphology of PbSe film).

Interconnected maze-like pattern was located on the surface of electrochemically etched PbSe film and consisted of agglomerated PbSe nanoislands with 80-400 nm lateral sizes and 70 nm average separating gaps. These na-

noislands had practically the same height of ~90 nm, which can be explained by the uniformity of the electrochemical etching process across the sample surface.

A possible practical application of such effect could be a fabrication of isolated PbSe nanoislands directly on Si substrate for thin initial films after anodizing for a sufficiently long period of time. This method proved to be successful and it was possible to fabricate such structures for the initial epitaxial films with the thickness of 2 μm and a longer treatment duration of 20 min. SEM tilt view image of an example of agglomerated PbSe nanoislands on Si is given in Fig. 3. Corresponding AFM profilogram of the nanoislands is given in Fig. 4.

3.2 Porous layer formation for PbSe films with granular initial surface For the films with an initial granular surface morphology a strong significantly different modification of a near-surface layer (~150-200 nm thickness) took place. A typical electron microscopy image of such layer surface is presented in Fig. 5, while the initial film surface is shown in the insert. The anodic electrochemical etching under given parameters allowed us to succesfully obtain double-layered porous structure for PbSe films. Remarkably, the films showed a strongly modified unique morphology significantly distinct from PbTe films treated under similar conditions [11]. While the overall picture can be described as macroporous, it is quite possible that the underlaying modified layer is mesoporous, as the exits of the pores with 7-18 nm diameter are clearly seen on certain surface areas. This observation is supported by cross-sections investigations, when an underlaying modified layer with 75-100 nm thickness was usually observed. Such morphology picture was found to be practically independent from current density in the interval of 2-8 mA/cm^2. Analysis of electron microscopy data shows that a network type porous morphology is obtained in this case. Fig. 6 shows a surface of the porous PbSe layer fabricated with current density of 8 mA/cm^2 and duration of 10 min. Hierarchical porous network with large open macropores (100-250 nm), on the walls of which a system of smaller secondary macropores (50-75 nm) and mesopores (15-20 nm) is observed. Alternatively, this morphology picture can be described as compiled with PbSe nanostructures as small as 30-50 nm, as well as larger clusters of 200-350 nm size, connected with 20-40 nm thin "suspension bridges". X-ray diffraction measurements showed that after the anodic etching the modified PbSe layers still had a distinctive (111) crystallographic orientation as the initial monocrystalline PbSe films on Si(111) and did not show any experimentally noticeable disorientation, amorphization or new phase segregation (Fig. 7). However, it is also worth mentioning that the formation of porous network structure and of an underlaying mesoporous layer takes place only in the near-surface region of the film with 150-200 nm overall thickness and does not depend on the film entire thickness and anodizing conditions.
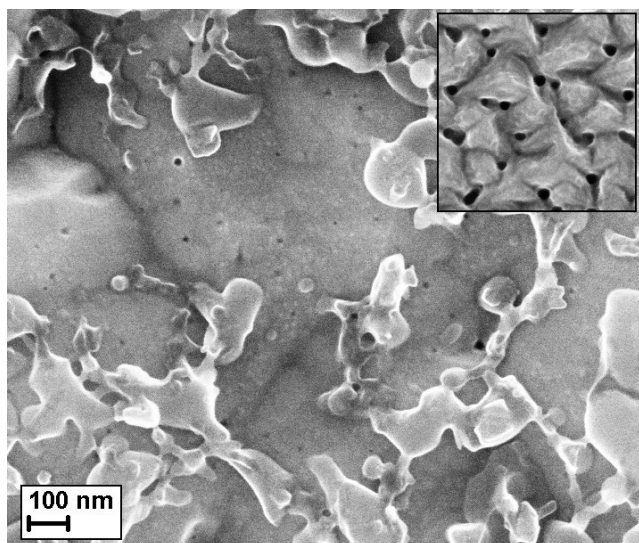
Figure 5 SEM normal plainview image of a surface of the anodized PbSe epitaxial film (j_{an} = 4 mA/cm^2, t = 10 min) with a granular initial surface morphology. The insert shows the initial PbSe film surface with the same scale.

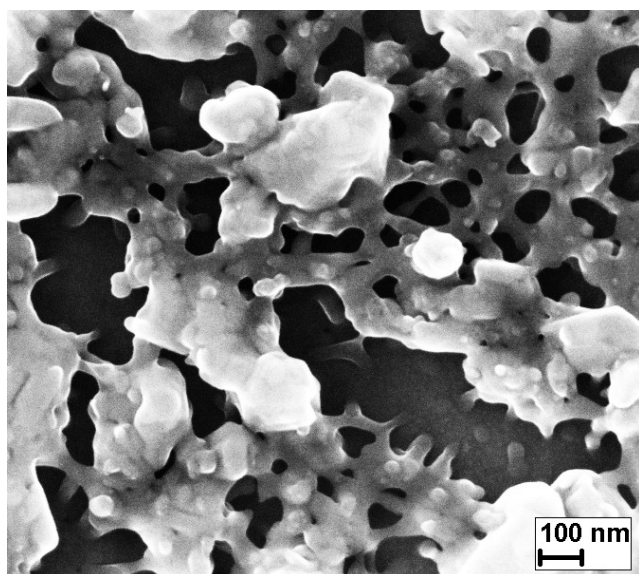**Figure 6** SEM normal plainview image of a porous network on the surface of the anodized PbSe epitaxial film (j_{an} = 8 mA/cm^2, t = 10 min) with a granular initial surface morphology.

The most possible reason of the observed pore formation in this case is the non-uniformity of the electrical field for the anodized films with prominent initial surface relief (see insert in Fig. 5). At low current densities the surface is preferrably etched at defects and surface irregularities. As widely known, PbX epitaxial monocrystalline films on sillicon substrates contain threading dislocations and a considerable amount of point defects, which strongly influence the anodic electrochemical etching process serving as nu-

cleations sites for the pores of the nanonetwork and the nanoislands depending on the condition of the initial surface in the respective cases.
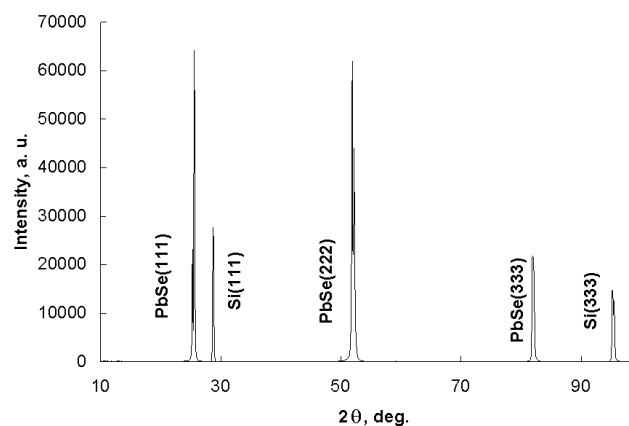

Figure 7 X-ray diffraction pattern for the anodized PbSe epitaxial film (j_{an} = 8 mA/cm^2, t = 10 min) with a surficial porous network.

4 Conclusions For the first time we have reported an approach to fabricate porous PbSe layers on silicon substrates based on anodic electrochemical etching in a Norr electrolyte. Morphological parameters of lead selenide porous structures are multiform and distinctly different from the results for porous lead telluride. High-resolution microscopy methods allowed us to precisely describe morphology of the resulting nanostructurized PbSe areas. Two types of morphology were observed for lead selenide epitaxial films with different surface morphology. The possibility to fabricate PbSe nanoislands directly on Si(111) substrate is presented. The mechanism of the modified layer formation is shown to be purely electrochemical. Obtained results are extremely promising and further experimental work is being carried out in order to completely understand the physics of IV-VI films modification during anodic electrochemical etching and to develop a reliable technique of PbX porous layers formation with desirable parameters for optoelectronic devices on silicon chips. The variety of the obtained PbSe porous structures shows that it is necessary to optimize conditions of the technological process for the fabrication of a defined pore morphology.

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