Variations of the parameters of PbSe nanolayers with change of their technology

A Pashaev1, O Davarashvili2, M Enukashvili2, Z Akhvlediani2,3, R Gulyaev2 and M A Dzagania2

1National Aviation Academy, Bina 25km, Baku AZ-1045, Azerbaijan
2Iv. Javakhishvili Tbilisi State University, Chavchavadze 1, Tbilisi 0128, Georgia
3E. Andronikashvili Institute of Physics, Tamarashvili 6, Tbilisi 0186, Georgia

E-mail: omardavar@yahoo.com

Abstract. For designing IR photodetectors based on strained PbSe layers, the optimization of the technology of molecular epitaxy with a “hot-wall” has been performed with the aim of fabrication of the layers with combining high values of residual deformation and thickness. By investigating the characteristics of layers such as the thickness, tangential lattice constant, deformation and x-ray diffraction line halfwidth, the best conditions for growing the layers of optimal thickness of 50-80nm and the highest deformation 1·10⁻² were obtained. The width of the forbidden gap in the obtained layers increased by 0.15eV at T=300K as compared with unstrained PbSe layers.

1. Introduction
Recently we have proposed to use the strained layers of PbSe grown on KCl substrates with a great lattice constant for designing the high-sensitivity high-temperature IR photodetectors [1]. This objective can be achieved through the realization of effective “negative” pressure in PbSe layers when the forbidden gap width increases in them and, when doped with impurities Cr, In and Yb having variable valency, then levels of impurities shift into the depth of the forbidden gap. In this case, the impurities can significantly compensate electrically active nonstoichiometric defects. So the concentration of current carriers in the PbSe layers can be decreased by a factor of 4 or 5 [2]. The optimal thickness of epitaxial PbSe layers for sufficient absorption of IR radiation, from one hand, and for the shift of the levels of the impurities in the forbidden gap, on the other hand, is estimated as 50-80nm [3]. Formation, structure of other IV-VI semiconductor nanolayers and their possible applications were discussed in [4-6].

Hence, it is important to establish the process conditions for fabrication of epitaxial PbSe layers for realization in them the maximum residual deformation at the layer thickness of 50-80nm.

2. Variations of experimental conditions
For fabrication of epitaxial PbSe layers by molecular epitaxy a “hot-wall”, the source of epitaxy, polycrystalline PbSe, was placed at the bottom of the quartz ampoule. Colliding with the hot wall, the evaporated molecules reached the KCl (100) substrate placed on a stainless mask at the open end of the
quartz ampoule practically without losses. Optimal process conditions were established by varying the following conditions: growth temperature (temperature of the KCl substrate), and the growth rate and duration, and analyzing the obtained parameters: layer thickness, tangential lattice constant, deformation and x-ray diffraction line halfwidth. The growth rate, the rate of bringing the evaporated molecules to the substrate, was varied by varying the source temperature and the distance between the mask with the substrate and the open end of the quartz ampoule. Three cases were studied: 1) the distance between the substrate and the end of the ampoule was 12nm at the epitaxy source temperature 470°C; 2) the distance between the substrate and the end of the ampoule was 2.5mm at the epitaxy source temperature of 470°C; 3) the distance between the substrate and the end of the ampoule was 1.0mm at the epitaxy source temperature of 510°C.

### Table 1. Data on the conditions of growth, tangential lattice constants and deformation of epitaxial PbSe layers on KCl substrates.

| No. | Layer | Epitaxy source temperature, °C | Substrate temperature, °C | Growth duration, s | Layer thickness, μm | Overall growth rate, V, nm/s | Growth rate stage, nm/s | Tangential lattice constant, a, Å | Deformation, ε = (a - aPbSe) / aPbSe · 10^6 | X-ray diffraction line halfwidth, Δ, mm |
|-----|-------|-------------------------------|--------------------------|-------------------|---------------------|-----------------------------|------------------------|--------------------------------|---------------------------------|--------------------------------|
| 1   | SL-537| 470                           | 280                      | 90                | 159                 | 1.8                         | 5.0                    | 6.142(1)                         | 0.27                            | 21                             |
| 2   | SL-541| 470                           | 300                      | 80                | 95                  | 1.2                         | 4.3                    | 6.162(0)                         | 0.59                            | 19                             |
| 3   | SL-555| 470                           | 300                      | 75                | 73                  | 1.0                         | 4.9                    | 6.177(4)                         | 0.83                            | 20                             |
| 4   | SL-562| 470                           | 300                      | 67                | 56                  | 0.8                         | 6.0                    | 6.188(5)                         | 1.00                            | 20                             |
| 5   | SL-577| 470                           | 240                      | 30                | 182                 | 6.0                         | 7.8                    | 6.149(9)                         | 0.37                            | 22                             |
| 6   | SL-581| 470                           | 240                      | 10                | 35                  | 3.5                         | 12.5                   | 6.210(1)                         | 1.38                            | 26                             |
| 7   | SL-602| 510                           | 240                      | 12                | 226                 | 19                          | 22.6                   | 6.139(2)                         | 0.20                            | 31                             |
| 8   | SL-605| 510                           | 240                      | 20                | 440                 | 22                          | 23.9                   | 6.132(6)                         | 0.10                            | 36                             |

### 3. Results and discussion

In all cases, the “delay” of epitaxy was observed: this was the first stage of formation and merging of islands, proceeding at low rate. The thickness of layers was close to the sensitivity of its detection by the x-ray method and made up 5-10nm. At the second stage, the two-dimensional growth continued at a higher rate. The “delay” in the first case made up 60s, the second case – 8s, and the third case – 2s [7].

Table 1. Data on the conditions of growth, tangential lattice constants and deformation of epitaxial PbSe layers on KCl substrates.

In the Table 1 are listed the data on the layers selected for illustration of the abovementioned cases. The layers thickness was measured by the x-ray method by measuring the radiation from two reflecting planes - from a clean substrate and a substrate with a deposited layer.
The tangential lattice constant of the layer was determined by a symmetrical circuit and by diffraction patterns of $\theta$ -2$\theta$ scanning at the reflection from plane (400). Radiation $\text{CuK}_\alpha$ ($\lambda = 1789\text{Å}$) was investigated. Deformation $\varepsilon$ was determined as $\varepsilon = (a_l - a_{\text{PbSe}}) / a_{\text{PbSe}}$ in respect to a nonstrained PbSe layer (monocrystal). The halfwidth of the x-ray diffraction line was also determined by diffraction patterns at reflection from plane (400).

In Fig.1 is shown the relationship among the thickness, the growth rate and the tangential lattice constant of layers.

Based on the data given in the Table and Fig.1, we can draw the first general conclusions. The tangential lattice constant of the layers increase with decreasing thickness. The lattice constant range from 6.140 to 6.190Å was achieved at the growth rate 4-8nm/s (the region between dotted lines in Fig.1) and corresponding layers thickness from 55 to 180nm. The lattice constant range from 6.126 to 6.140Å was realized at the layers, thickness from 200 to 450nm and more at the growth rate of 20-25nm/s. The lattice constant 6.210Å was realized at the layers thickness of 35nm and the rate of cooling 12.5nm/s.
According to works [8,9], in addition to these data, the sizes of subgrains in the layers, their number and the disorientation among them, and also the critical thickness at which the number of dislocations grows and they were accelerated were assessed. For the layers thickness 55-180nm, the size subgrains made up 50-70nm, their average disorientation was \((1.2 \cdot 10^{-3})\)' their number was equal, to \(2 \cdot 10^4\), and the corresponding critical thickness was \(\sim 70nm\). For the layers thickness from 200 to 450nm, the size of subgrains was \(\geq 100nm\), their average disorientation was \((3.6 \cdot 10^{-4})\)' the corresponding critical thickness being \(\sim 15nm\). For the layer 35nm thick, the critical thickness was 80nm at the average disorientation of subgrains \((8 \cdot 10^{-6})\)' - their number making up \(3 \cdot 10^4\). The value of deformation \(\varepsilon\) of the layer 35nm thick was equal to \(1.38 \cdot 10^{-2}\).

By concrete examples, it is seen how the growth duration of layers affects their parameters (Fig. 2). First of all, this effect was revealed in the row of layers 1-4 (Table) when the lattice constant increased from 6.142 to 6.188\(\AA\) after, the growth time decreased from 30 to 7' and at close growth rates of 1-2nm/s at the first stage. The obtained lattice constants can be explained by that, at the epitaxy temperature of 300\(^\circ\)C, nonstochiometric defects managed to migrate with the growth process and, the shorter the growth duration, more efficiently they accommodated, or more precisely being annihilated, in dislocation nuclei, they impeded the energy transfer of elastic energy of the layers to deformations.

The growth duration determines the level of parameters of the layers in the case of different growth rates both the overall and at the second stage, the lattice constant of layer SL-577 was higher than that of layer SL-537. In this case, the growth rate for the latter layer made up 22s, while for the latter one -30s higher.
Fig. 3. Dependence of the halfwidth of x-ray diffraction pattern (reflecting plane (400)) on the growth rate of epitaxial PbSe layers.

At higher growth rate than that of the lattice constant of 6.210 Å was achieved for layer SL-581 at short growth duration -2s. This means that, despite low temperature of epitaxy (240°C), for layers SL-577 and SL-581, high lattice constants were achieved at short growth duration. Despite that, for layers SL-602 and SL-605, at the second stage the growth duration made up 10 and 18s, respectively, at the growth rate ≥ 20nm/s and the thickness of layers 220 and 440nm, respectively larger subgrains ≥ 100nm with higher disorientation (3·10^{-4}) were formed. At critical thickness ~15nm, relaxation of strain at subgrain boundaries increased, and hence the lattice constants were not high. As is shown in Fig.3, in this case, the halfwidth of the x-ray diffraction line was equal to 31' and 36', respectively, which exceeded those for SL-577 and SL-562 (26' and 20', respectively).

Fig. 4. Deformation ε = \frac{a_l-a_{PbSe}}{a_{PbSn}} \cdot 10^2 of epitaxial PbSe layers dependence at their thickness

Thus, the high growth rate causes additional relaxation of strain, which is due to an increase in the elastic energy of layers at high values of thickness as well.
On the other hand, in layers SL-541 and SL-577, at close growth duration at the second stage, 20 and 22s, respectively, and comparable x-ray diffraction line halfwidth of 19 and 22', respectively, the constant lattice of layer SL-541 (6.162Å) was higher than that of layer SL-577 (6.149Å). This can be explained by lower growth temperature of layer SL-577 and by close critical thickness of these layers ~70nm, i.e. by low tendency to relaxation of strain at subgrain boundaries. In Fig.4 is shown the thickness dependence of deformation in PbSe layers. in the thickness range from 55 to 80nm, the deformation made up 0.7·10^{-2} -1·10^{-2}. Under such deformation in the layers, the forbidden gap width increased by 0.15eV as compared to the unstrained layer [10, 11]. The epitaxial PbSe layers with 50-80nm thick with the lattice constant 6.140-6.190Å and the deformation of the level to 1·10^{-2} can serve as the basis for designing of IR photodetectors and lasers.

4. Conclusions

If we follow the character of relaxation of strain with decreasing lattice constant as a whole, we will see that, in the case of layer with the lattice constant 6.210Å, critical thickness >100nm and significantly finer subgrains (30nm), the substrate – layer interface. For layers 1-5 (Table) with the lattice constant 6.140 – 6.190Å, the size of subgrains 40-70nm and critical thickness 50-70nm, only minor part of the relaxation of strain takes place at subgrain boundaries, and it generally occurs at the substrate – layer interface as well. For the layers with lattice constants 6.140 – 6.190Å, and the size of subgrains >100nm and the critical thickness 15nm, major part of the relaxation of strain occurs at the subgrain boundaries. Solid solutions PbSnSe have considerable reserves for realization of the dielectric state when the levels of impurities shift deeply into the forbidden gap and the concentration of current carriers can decrease by at least a factor of 7. Without a doubt, this opens up new possibilities for designing high – sensitivity high –temperature IR photodetectors.

References

[1] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Gulyaev R, Bychkova L and Zlomanov V 2013 Nano Studies 8 253
[2] Pashaev A, Davarashvili O, Enukashvili M, Bychkova L, Dzagania M and Zlomanov 2014 Herald Azer.Eng. Acad. 6 49
[3] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Gulyaev R and Zlomanov V 2013 Bull Azer. Nat. Acad. Sci. 33 31
[4] Prabahar S, Suryanaraynan N, Rajasekar K and Srikanth S 2009 Chalcogenide Zett. 6 203
[5] Abbas N, Al-Fawade E and Alatya S 2013 J.Mat. Sci. Eng. A3 82
[6] Cruz S, Tellez G, Rosas U, Perez R, Merino R, Lima L and Moreno O 2013 J.Mat.Sci.Eng. A3 621
[7] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Gulyaev R, Bychkova L and Zlomanov V 2013 J.Mat. Sci. and Eng. A3 235
[8] Pashaev A, Davarashvili O, Enukashvili M and Dzagania M 2014 Bull Azer. Nat. Acad. Sci. 38 31
[9] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Gulyaev R and Zlomanov V 2013 J.Mat. Sci. and Eng. A3 117
[10] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Gulyaev R and Zlomanov V 2014 IJEIT 3, 318
[11] Pashaev A, Davarashvili O, Enukashvili M, Akhvlediani Z, Bychkova L and Gulyaev R 2014 Advanced Materials Research 1025 831