Growth Mechanism and Characterization of PbTe_{0.5}Se_{0.5} Thin Films Used by Closed-Space Vapor Transport in a Vertical Reactor

Yanuar Hamzah¹), Jimmi Copriady²) and Ariswan³)

¹) Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Riau
Kampus Bina Widya, Pekanbaru 28293, Indonesia
²) Department of Chemical Education, FKIP Universitas Riau
Kampus Bina Widya, Pekanbaru 28293, Indonesia
³) Department of Physics Education, Faculty of Mathematics and Natural Sciences,
Universitas Negeri Yogyakarta
Jalan Colombo No.1, Karang Malang, Yogyakarta 55281, Indonesia

*) Corresponding author: yanuar.hamzah@gmail.com

(Received: September 30, 2018 Accepted: March 31, 2019)

Abstract

A simple method for growing thin film of semiconductor material PbTe_{0.5}Se_{0.5} has been designed using the vapor transport (CSVT) method in a vertical reactor. The objectivity of this method is to study thin film growth formation due to chemical reactions during the deposition process in the reactor. In this study will describe some formations the vapor transport mechanism of PbTe_{0.5}Se_{0.5} semiconductor material using iodine gas (I₂) to accelerate the etching reaction on the substrate surface. Next, we will describe how the mechanism of the reaction in the reactor zone for growing thin films on the substrate. The thin films were characterized by structural, morphology properties and its composition. The film structure is a cubic structure with the maximum diffraction intensity at peak (222). The surface morphology of the thin film has a microcubes shape with a grain size~10 to 20 μm.

Keywords: etching reaction; micro-cube; PbTe_{0.5}Se_{0.5}; close-spaced vapor transport

How to Cite This Article: Hamzah, Y., Copriady, J. and Ariswan. (2019), Growth Mechanism and Characterization of PbTe{0.5}Se{0.5} Thin Films Used by Closed-Space Vapor Transport in a Vertical Reactor, Reaktor, 19(1), 11-17, http://dx.doi.org/10.14710/reaktor.19.01.11-17.

INTRODUCTION

The CSVT method using horizontal reactors was first used to grow semiconductor crystals in the 1980s. This model can grow semiconductor material for III-V GaAs elements that were published in 1983 (Chávez et al., 1983), other researchers have examined the equilibrium and the growth rate of thin films of As₂ and As₄, Ga₂O₃. (Cote et al., 1986). Yanuar et al., 2018 using the CSVT in a vertical reactor method have succeeded in growing thin layers of group I-III-VI² elements CuIn(S,Se)₂. GaAs photovoltaic devices from group III-V elements have been fabricated using steam transportation methods in the form of GaAs
powder material in a horizontal reactor developed by Ritenou et al., 2015.

Naemullah et al., 2014 has reported that material semiconductor PbS, PbSe and PbTe have energy gap 0.41 to PbS, PbSe and 0.3 to 0.28 for PbTe. Synthesis of PbSeTe nanocubes has been reported Quan, et al., (2011). PbTe0.5Se0.5 material is one of the ternary lead chalcogenides functional materials, this material is extensively studied for applications as thermo-electric materials (Korkosz et al., 2014), infrared photoelectric detection (Song et al., 2018) and solar cell (Leschikies et al., 2009). Furthermore, this material is very prospective for infrared light emitting diodes (Yan et al., 2015), and the optical properties are very effective in mid-infrared regimes. The application of lead chalcogenides material has also been reported by Yamini et al., 2014 as a functional material for infrared detectors, light emission devices, infrared lasers in optical fibers and thermoelectric materials.

The technique for growing PbTe, PbSe thin films have been used many researchers in the last decade is vacuum evaporation (Kumar et al., 2003), alternative techniques such as thermal evaporation PbTe and PbSe condensation (Fedorov et al., 1999), physical vapor deposition (Arivazhagan, et al., 2012), RF magnetron sputtering (Song et al., 2018 and Feng et al., 2015). Strelsov et al., 1997 grew a thin layer of PbS, PbSe and PbTe alloys using a cathodic electro-deposition technique. According to Smith et al., 2011, there are still few publications on the development of the high-quality synthesis of PbSe-PbTe alloy material available in published publications, perhaps because of the tendency of alloys of lead chalcogenides compound to diffuse through mixed boundaries in the pseudo-binary phase of PbSe-PbTe compounds. Today, the researchers are considered the most effective method for preparation PbSeTe including low cost, low vacuum, large area, and high-quality thin film products. The CSVT also provides a simple method to grow the metal chalcogenide elements to results in the proper structure and crystal properties. In this study, we present the CSVT in a vertical reactor use to study of PbTe0.5Se0.5 thin films grow and mechanism of the formation reaction that occurs during the deposition process. The deposition parameters such as source temperature (Tsource) material alloy and substrate temperature (Tsub) plays an important role in the mechanism of the reaction in the reactor. The influence of different temperature deposition on the structural and morphology properties has been investigated. Thin films of PbTe0.5Se0.5 obtained are characterized.

METHOD EXPERIMENT
Preparation of PbTe0.5Se0.5 ternary alloy

The PbTe0.5Se0.5 (nPb: nSe: nTe = 50:25:25) ternary alloy source material (99.99 % purity Sigma Aldrich) from a mixture of stoichiometric proportion were grown by Bridgman Horizontal Furnace method in evacuated (10–5 Torr) quartz tube. The ampoule was placed in a horizontal furnace through a temperature of 900°C for 24 hours the procedure has been described in the literature (Yanuar et al., 2018). The PbTe0.5Se0.5 polycrystalline ingots (black metallic in color) was crushed using a mortar to powder form and then compressed with a pressure of 300 kg/cm² using a hydraulic press with a diameter of 1.8 mm and a thickness of 0.5 mm. The PbTe0.5Se0.5 pellet is ready to be used as source material for deposition processes in the CSVT.

Design of CSVT in a Vertical Reactor

CSVT is fast and simple processes for deposition semiconductor materials. They do not require a very high vacuum; the equipment is not complicated and low cost. The reactor used for PbTe0.5Se0.5 thin films deposition is shown in Figure 1. Yanuar et al., 2018 has been reported the CSVT consist of a quartz tube 20 cm high and 20 mm in diameter. The reactor tube is connected to a diffusion pump (10–5–10–4 Torr) to vacuumed before the thin film deposition. The PbTe0.5Se0.5 pellet is carried out in the reactor where the material source of PbTe0.5Se0.5 and substrate are placed facing each other at the base of the tube which is separated by a spacer made of quartz glass with a distance (d) which can be varied from 0.3 to 1 mm. Solid iodine (I2) as a reagent is placed at the upper part of the reactor to accelerate the reaction for deposition (closed under vacuum by a valve). Finally, the reactor tube is placed above a heating element of silicon carbide (SiC) material. In this deposition, a slide glass microscope was used as the substrate.

Before the deposition process, the substrate was heated using a substrate heater (heating coil) with a temperature interval of 60-90°C for 10 minutes.

Figure 1. Schematic diagram of CSVT vertical reactor
The PbTe$_{0.5}$Se$_{0.50}$ source material and substrate temperature were measured by sensors put inaccessible point (out of the reactor tube deposition zone). Because the distance between the substrate and the source is very close (d=1 mm) to accept sensor, the sensor for the source is placed under the reactor and above the substrate.

In this study, two samples were grown with the following labeled: sample 380/320 with the temperature deposition ($T_w=380^\circ$C; $T_a=320^\circ$C) and sample 650/560 ($T_w=650^\circ$C; $T_a=560^\circ$C). The temperature gradient between the source material and the substrate separated by spacers 1 mm which is the driving force for transporting the source material in the growth of PbTe$_{0.5}$Se$_{0.50}$ thin films. The deposition time for the growth of source material on substrates in the reactor is 10 minutes. When deposition is finished, vacuum pumps are closed. Finally, the reactor cooled by opening the lid of the reactor. A PbTe$_{0.5}$Se$_{0.50}$ thin film as samples is characterized to observe structural, morphology properties and their composition.

Characterization

Characterization of the structure source material PbTe$_{0.5}$Se$_{0.50}$ as powder and thin films of the sample used x-ray diffraction (XRD), Shimadzu XRD-700 Japan with radiation sources CuK$_\alpha$=0.15406 nm. Morphology and elemental composition of the sample using a scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS), SEM, JEOL JSM-6360 LA, Japan (the energy of the electrons is 15 keV).

RESULTS AND DISCUSSION
The Mechanism of Growth PbTe$_{0.5}$Se$_{0.50}$ thin films

A scheme in Figure 2 describes the mechanism of the growth of PbSe$_{0.5}$Te$_{0.5}$ thin film in the reaction zone CSVT in vertical reactor method. The iodine gaseous species reacts between two zones (source-substrate) will be produced PbI$_2$ gaseous by diffusion.

In the reaction zone is divided into two regions i.e the region between the source ($T_w$) and the substrate temperature ($T_a$) is not very large, the formation of the material are transported only by diffusion reaction between the two regions.

Characterization of thin films PbTe$_{0.5}$Se$_{0.50}$

For source PbSe$_{0.5}$Te$_{0.5}$ polycrystal sample, the XRD shows that the compound is composed completely of PbSeTe. Another phase is not detected.
The source PbSe$_{0.5}$Te$_{0.5}$ sample has an orientation along a direction (200) at the angle of reflection 20$\approx$28.4° between 20$\approx$27.5° for PbTe and 20$\approx$29.1° for PbSe standard reference, presented in dot green line (Figure 4b) and additional reflection from (111), (220), (311), (222), (400) and (422). These results are in good agreement between PbTe (JCPDS No. 06-0354) in Figure 4a and PbSe (JCPDS No. 08-0028) in Figure 4c and XRD standard reference as shown in Table 1. Table 1 shows the XRD measurement for PbSe$_{0.5}$Te$_{0.5}$ source material with the comparison to PbTe and PbSe standard XRD reference.

Figure 5 (a) shows the XRD patterns of a reference standard PbI$_2$ (JCPDS-07-0235). The 380/320 sample has an orientation along a direction (002), (003) and (004) with very high relative intensities (Figure 5b). These results are in good agreement in the reference (JCPDS-07-0235).

![Figure 4. XRD pattern of PbSe$_{0.5}$Te$_{0.5}$ polycrystal for source material deposition comparison with reference PbSe (JCPDS No. 08-0028) and PbTe (JCPDS No. 06-0354)](image)

Table 1. XRD data for PbSe$_{0.5}$Te$_{0.5}$ source material

<table>
<thead>
<tr>
<th>PbTe ref.</th>
<th>PbSe$<em>{0.5}$Te$</em>{0.5}$</th>
<th>PbSe ref.</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>20</td>
<td>I</td>
</tr>
<tr>
<td>23.7</td>
<td>10</td>
<td>24.4</td>
<td>20</td>
</tr>
<tr>
<td>27.5</td>
<td>100</td>
<td>28.4</td>
<td>100</td>
</tr>
<tr>
<td>39.4</td>
<td>80</td>
<td>40.6</td>
<td>40</td>
</tr>
<tr>
<td>46.9</td>
<td>10</td>
<td>47.8</td>
<td>16</td>
</tr>
<tr>
<td>48.9</td>
<td>30</td>
<td>50.1</td>
<td>20</td>
</tr>
<tr>
<td>57.2</td>
<td>20</td>
<td>58.9</td>
<td>19</td>
</tr>
<tr>
<td>64.5</td>
<td>50</td>
<td>66.2</td>
<td>23</td>
</tr>
<tr>
<td>71.7</td>
<td>40</td>
<td>73.7</td>
<td>18</td>
</tr>
</tbody>
</table>

Ref.=reference; 20°=degree; I=Intensity of XRD reflection

Experimental results confirm that this temperature CSVT method in the source and substrate temperature is very low to deposit a thin film PbSe$_{0.5}$Te$_{0.5}$. It shows the reaction mechanism between metal Pb and iodine gas and the formation of PbI$_2$ grown on a substrate. This can be described that the diffusion reaction between Se$_2$ and Te$_2$ gas with Pb does not occur if the source material and substrate at the low-temperature deposition.

![Figure 5. XRD pattern of (a) reference PbI$_2$ (JCPDS-07-0235), (b) sample thin film of 380/320, and (c) 650/560](image)

Table 2. XRD data for PbI$_2$ standard reference, sample 380/320 and 650/560

<table>
<thead>
<tr>
<th>PbI$_2$ ref.</th>
<th>PbI$_2$ film (380/320)</th>
<th>PbSe$<em>{0.5}$Te$</em>{0.5}$ film (650/560)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>20</td>
<td>I</td>
</tr>
<tr>
<td>25.5</td>
<td>6</td>
<td>25.4</td>
<td>11</td>
</tr>
<tr>
<td>38.6</td>
<td>6</td>
<td>38.7</td>
<td>67</td>
</tr>
<tr>
<td>52.3</td>
<td>6</td>
<td>52.4</td>
<td>62</td>
</tr>
<tr>
<td>24.5</td>
<td>30</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>28.4</td>
<td>27</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>40.6</td>
<td>7</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>50.3</td>
<td>100</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>59.7</td>
<td>15</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>

Ref.=reference; 20°=degree; I=Intensity of XRD reflection
Shifting the angle of reflection led to the expansion of the lattice parameter \( a=6.459 \, \text{Å} \) for source material into \( a=6.286 \, \text{Å} \) for thin film. These relative structural parameters in accordance with the model are calculated using the approach of generalized gradient approximation via first-principles calculations obtained \( a=6.27 \, \text{Å} \) (Naemullah et al., 2015). Strelsov et al., 1998 has been observing that thin film amorphous PbSeTеМ \( x \) by cathodic electrodeposition method where the maximum of angle reflection \( 20=31° \) cubic lattice structure with lattice parameter \( a=6.241 \, \text{Å} \).

Accordingly (Yamini et al., 2017) in Figure 6 shows the comparison of our lattice parameter \( a \) and energy gap (\( E_g \)) as a function of composition \( x=0.5 \) with previous studies of lead chalcogenides (PbQ, Q=Te, Se, S) alloys. In these studies show that the lattice parameters \( a \) decrease as a function of composition \( x \) and nonlinear variation of the energy band gap (\( E_g \)). Although the differences in our PbSe0.5Te0.5 thin film lattice parameter \( a=6.286 \, \text{Å} \) from linear Vegard’s law value for composition \( x=0.5 \) is small \( (a=6.290 \, \text{Å}) \). Vegard’s law describes that the relationship between lattice parameter PbSe and PbTe correspond to the linear interpolation as seen a solid line in Figure 6.

In this work, we did not measure the optical properties of the PbSe0.5Te0.5 thin film, using the data (Yamini et. al., 2017) for the energy gap at 300K obtained is 0.295 eV compared to these reference the energy gap is 0.299 eV a slightly different of 0.004 eV as seen the empty circle and red square in Figure 6. The relation between lattice parameters and energy gap as a function of the lead chalcogenide alloys composition \( (x) \) can be perspectives for tuning the band gap energy in the optical application.

Figure 7(a) shows the foto thin film and source material of PbSe0.5Te0.5 polycrystal. Figure 7(b) and (c) SEM micrographs of the surface and cross-section of PbSe0.5Te0.5 film (sample 650/560) on the slide glass microscope substrate, respectively.

![Figure 6](image6.png)

**Figure 6.** The relationship between the lattice parameter \( a \) and energy gap (\( E_g \)) as a function of composition \( x \) in literature data for \( \text{PbSe}_x\text{PbTe}_{1-x} \) (Yamini et. al., 2017) with the comparison to our work.

![Figure 7](image7.png)

**Figure 7.** (a) Foto of thin film and PbSe0.5Te0.5 polycrystal, (b) SEM micrographs of sample 650/560 morphology, and (c) cross-section view.

Microcubes grains with a size of about 10-20 \( \mu \text{m} \) are observed homogenous on the surface. The trigonal shapes grains are non-homogeneous and distributed on the PbSe0.5Te0.5 surface with a grains size of 5-15 \( \mu \text{m} \) as shown by the black arrow in this micrograph. The cross-sectional micrograph observation of the PbSe0.5Te0.5 film shows that the columnar grains grow on the substrate with the thickness of about 20 \( \mu \text{m} \). Trigonal grains that have covered the surface PbSe0.5Te0.5 film because of excess Te (see Table 3) which has a trigonal crystal structure \( (a=b=0.4457 \, \text{Å} \) and \( c=0.5929 \, \text{Å} \) in the space group P3121 (Li et al., 2015). Te excess plays an important role as doping to improve conductivity in the thermoelectric material application.

Table 3 shows the comparison of composition measurements the source material and thin films samples by EDS. It is observed that the source material of PbSe0.5Te0.5 polycrystal is near-stoichiometric with a composition \( x=(\text{Te}+\text{Se})/2=0.51 \) with slightly excess Te. For sample 380/320 shows a thin film obtained is PbI2 with composition Pb=33.61% and I=66.39%. The absence of elements of Se and Te in source temperature \( (T_{\text{source}}=380^\circ \text{C}) \) in the reaction zone of the deposition mechanism of etching only. Mixing and decomposition reactions has not occurred to deposit metallic Pb gas compounds with chalcogen Te2 and Se2 gas to substrate at the temperature of 320°C.
Sample 650/560 composition of thin film deposition has shown that in the source temperature (T_{sub} = 650°C) occurs deposition mixing between PbI2 gas with chalcogen Se, and Te on the substrate. This indication is shown from the results of the compositional elements of Pb=50.24%; Te=25.72%; Se=24.24%; a composition x= (Te/Te+Se) = 0.52 and Pb/(Te+Se) ratio = 1.01. The composition of the Se increases from source material PbSe0.5Te0.5 polycrystal 23.98% to 24.04% in thin film sample 650/560 due to the increase in gas diffusion Se2 on the substrate. Excess Te on thin films that have been deposited relatively easier for the decomposition of PbTe compared PbSe where there is always a small percentage of elements Te at both the source material and cause a thin film of excess Pb.

Table 3. EDS analyses of source material, sample 380/320 and 650/560

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental composition (% atomic)</th>
<th>Pb</th>
<th>Te</th>
<th>Se</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric</td>
<td></td>
<td>50.00</td>
<td>25.00</td>
<td>25.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Source material</td>
<td></td>
<td>50.39</td>
<td>25.63</td>
<td>23.98</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample-380/320</td>
<td></td>
<td>33.61</td>
<td>0.00</td>
<td>0.00</td>
<td>66.39</td>
</tr>
<tr>
<td>Sample-650/560</td>
<td></td>
<td>50.24</td>
<td>25.72</td>
<td>24.04</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Although the time of deposition PbSe0.5Te0.5 thin film is 10 minutes, excess Pb exists due to the temperature of the source material (T_{sub}) is higher than the temperature of the substrate (T_{sub}) in CSVT method. The study of thermodynamic models in CSVT method for growing thin film alloys metal chalcogenides M=Sn,Pb; X=S,Se,Te very interesting to study further.

CONCLUSION

In summary, we have deposited the microcubes PbSe0.5Te0.5 film on slide glass microscope substrates by using CSVT in a vertical reactor method. The reaction mechanism of thin film growth using this method in the reaction zone is dominated by surface etching reaction, mixing reaction and decomposition reaction of metal (Pb) with chalcogenide gaseous Te2 and Se2. The thin film of PbSe0.5Te0.5 is a cubic structure with the morphology of grain size varying between 10-20 μm. The composition of this film is near stoichiometric (Pb-excess) with a ratio of metal-chalcogenides is 1:0.1, without iodide. The CSVT a in vertical reactor method can grow a PbSe0.5Te0.5 thin film in a short time and produce a high-quality film. These findings can develop to further devices in tuning the composition (x) ternary PbSe1-xTe1-x lattice parameters (a) and the optical band gap (Eg) for optoelectronic applications.

REFERENCES


