I. INTRODUCTION

The fabrication of reliable far-infrared optoelectronic heterostructure devices requires development of suitable narrow gap semiconductors in which the band gap and lattice parameter can be independently controlled. A materials system satisfying these requirements is the quaternary IV–VI semiconductor, Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$. This solid solution pseudobinary alloy can be used as the active region in either detectors or lasers designed to operate in the 6–30 μm spectral range. Lattice-matched Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ quaternary layers have been grown on Pb$_{0.8}$Sn$_{0.2}$Te and PbSe substrates, and double heterostructure lasers fabricated from these materials have been demonstrated. Further device development, however, has been hindered by the limited availability, small size, and high cost of these IV–VI semiconductor substrates.

Liquid phase epitaxy growth of Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ alloys lattice matched with BaF$_2$ substrates have been grown on both bulk BaF$_2$ and BaF$_2$-coated silicon substrates, there are no reports of lattice-matched quaternary alloy growth on BaF$_2$. In our work, we are interested in fabricating far-infrared heterostructure devices using a new liquid phase epitaxy (LPE) process that has recently been used to grow PbSe$_{0.72}$Te$_{0.28}$ layers lattice matched with (100) BaF$_2$ substrates. Growth of smaller band gap Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ quaternary layers will enable, for example, fabrication of double heterostructure (DH) lasers. Accordingly, this article reports on the LPE growth and characterization of Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ quaternary alloys lattice matched with BaF$_2$ substrates.

II. Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ QUATERNARY ALLOYS

Employing a generalized version of Vegard’s law, the lattice parameter of Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ quaternary alloys can be expressed as

$$a = 6.126 + 0.334y - 0.123x - 0.009xsy.$$

The condition for lattice matching the 6.200 Å lattice parameter of BaF$_2$ is therefore

$$y_s = 0.334 - 0.009x_s.$$

The band gap of quaternary Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ at 77 K can be expressed as

$$E_g = 0.175 - 0.895x - 0.04y + 0.36xy.$$

In addition to composition dependence, the band gaps of Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ alloys are also very sensitive to temperature variations. IV–VI semiconductor lasers, therefore, have extremely wide temperature tuning ranges. For example, varying the heat sink temperature of a PbTe/Pb$_{0.78}$Sn$_{0.218}$Te/PbTe DH laser from 12 to 114 K varied the emission wavelength from 15.9 to 8.54 μm.
FIG. 1. Band gaps and corresponding cutoff wavelengths at 77 K plotted as a function of lattice parameter for various IV–VI semiconductors and BaF₂.

This property makes IV–VI semiconductor lasers useful for high resolution infrared spectroscopy applications.

IV–VI semiconductor alloys exhibit a distinctive band crossover phenomenon. As the tin content increases, the band gap decreases until, at a certain composition, the band gap becomes zero. Beyond this point, the band gap decreases with increasing temperature. This behavior has been observed in both Pb₁₋ₓSnₓSe (Ref. 10) and Pb₁₋ₓSnₓTe (Ref. 11) ternary alloys and is attributed to band inversion at the L point in the Brillouin zone.

We expect similar behavior in quaternary Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ alloys lattice matched with BaF₂ substrates where the band gap at 77 K can be approximated by substituting Eq. (2) into Eq. (3):

\[ E_g \approx 0.185 - 0.799 x_S + 0.133 x_T \]  \hspace{1cm} (4)

Negative band gap values for \( x_S > 24\% \) represent an inverted band structure. Figure 1 is a band gap versus lattice parameter plot for Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ alloys and BaF₂.

The quaternary alloy lattice matched with BaF₂ is indicated.

PbSe, PbTe, and SnTe all have NaCl-type crystal structures, but SnSe has an orthorhombic crystal structure. SnSe-rich compositions of Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ solid solutions will, therefore, exhibit a two-phase microstructure due to the immiscibility of SnSe in PbTe. The solid solubility limit of SnSe in PbSe has been reported to be 43 mole \% SnSe,\(^\text{12}\) while for alloys lattice matched with BaF₂ the two-phase region begins at a tin concentration of approximately 68%.\(^\text{13}\) This limit on the composition of Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ solid solutions lattice matched with BaF₂ nevertheless still allows a wide range of band gaps from 185 meV, through zero, to negative 300 meV at 77 K.

The first reported growth of quaternary Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ alloys was accomplished by melting stoichiometric quantities of the elements.\(^\text{14}\) In one series of experiments, Pb₁₋ₓSn₉Se₁₋₉Te₁₋₉ alloys were prepared by melting (1 – b) moles of PbSe and b moles of SnTe. Coincidentally, an alloy with the composition Pb₀.₉₄Sn₀.₋₄Se₀.₉₄Te₀.₉₄ had a measured lattice parameter of 6.195 Å, very close to that of BaF₂. Optical absorption studies were also performed, but only on alloys with SnTe concentrations up to 6%. The reported data do show that at 82 K the band gap decreases from 180 meV for PbSe to 160 meV for Pb₀.₉₄Sn₀.₋₄Se₀.₉₄Te₀.₉₄.

Historically, liquid phase epitaxy has been the primary growth technique for initial materials studies leading to the development of new heterostructure optoelectronic devices. This is due to the fact that LPE is an economical method for producing high quality material. LPE growth of Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ quaternary alloys having compositions that are lattice matched with BaF₂, however, will require knowledge of the relevant portion of the liquid-solid Pb-Sn-Se-Te phase diagram. Such data exist for growth of quaternary alloys lattice matched with Pb₀.₉₀Sn₀.₂₀Te (Ref. 1) and PbSe (Ref. 2) substrates, and data exist for growth of ternary PbSe₀.₇₅Te₀.₂₂ layers lattice matched with BaF₂ substrates.\(^\text{6}\) In the latter case, for example, liquid solutions of Pb₁₋ₓ(Se₀.₆₅Te₀.₃₅)ₓ, produce the desired lattice-matched alloy. In general, we would like to know what liquid solution compositions, \((Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ)_{1₋ₓ}(Se₁₋ₓTeₙ₋ₙ)ₓ\), produce solid Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ quaternary alloys that are lattice matched with BaF₂.

III. EXPERIMENTAL PROCEDURE

A standard sliding-substrate LPE graphite boat under a flowing hydrogen ambient was used to grow Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ quaternary alloys. Lead, tin, and polycrystalline pieces of the binaries PbTe and PbSe were weighed to yield various compositions of \((Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ)_{1₋ₓ}(Se₁₋ₓTeₙ₋ₙ)ₓ\) liquid solutions. The chalcogen content \( z \) was fixed at 1% which resulted in liquidus temperatures of around 530 °C. The liquidus temperature, which dictates the LPE growth initiation temperature, was measured by observing the surface of a slowly heated undercooled liquid growth solution and noting the temperature at which the last piece of solid dissolves. Our measured values are consistent with previously published data\(^\text{3}\) that show that \((Pb₁₋ₓSnₓSe₁₋ₓTeₙ₋ₙ)_{1₋ₓ}(Se₁₋ₓTeₙ₋ₙ)ₓ\) liquidus temperatures increase with \( z \). Cleaved (111)-oriented BaF₂ substrates were used for all growths. Growth was initiated 2° below the liquidus temperature by positioning the BaF₂ substrate under the growth solution. This growth proceeded for 10 min while the furnace cooled at 2° per minute. Growth was terminated by pulling the substrate out from under the growth solution.

Optical and scanning electron microscopic analyses,
see Fig. 2, of the grown material showed a trigonal pyramid crystallite morphology. This type of growth morphology has also been observed for PbSe growth on (111) BaF₂ at similar growth initiation temperatures. In both cases, the IV-VI semiconductor crystallites were oriented with the BaF₂ substrate. It is believed that this crystallite morphology is due to an incomplete epitaxy-enabling substrate surface reaction in which selenium and tellurium react with the BaF₂ substrate forming a (Se,Te) reaction product that catalyzes IV-VI semiconductor nucleation. Growth at higher temperatures, above 610 °C, where the reaction product completely covers the BaF₂ surface, has resulted in continuous PbSe (Ref. 15) and lattice-matched PbSe₀.₇₈Te₀.₂₂ epitaxial layers.

We have grown quaternary alloys from (Pb₀.₇₈Sn₀.₃₈Se₀.₆₀Te₀.₃₀)₀.₀₁liquid solutions with various tin contents x₁ up to 20%, tellurium contents y₁ of 60%, and a chalcogen content z of 3.5%. These growth solutions had liquidus temperatures in the range of 615 °C, and growth from them directly on BaF₂ has resulted in continuous epitaxial layers. We have chosen, though, to generate phase equilibria data in the 530 °C temperature range because this is the range over which active layers for DH lasers will be grown. The first layer for a DH laser structure will be a PbSe₀.₇₈Te₀.₂₂ cladding layer grown at a temperature above 610 °C. Subsequent LPE layers are then grown at lower temperatures to reduce interdiffusion of dopants across the heterojunction interfaces. As opposed to direct growth on BaF₂, Pb₁₋ₓSnₓSe₁₋ᵧₚ Teᵧₚ growth at 530 °C on chemically similar PbSe₀.₇₈Te₀.₂₂ is expected to yield continuous layers.

Lattice parameter mismatch between the BaF₂ substrate and the IV-VI semiconductor material. The lattice parameter of the IV-VI semiconductor alloy was calculated using the 6.200 Å lattice parameter of BaF₂ as an internal standard.

The x-ray data, Eq. (1), and previously determined liquid-solid phase equilibria data for the Pb₁₋ₓSnₓSe ternary alloys, that follow the relationship

$$x_s = 1.93x_L - 1.96x_L^2 + 1.03x_L,$$

were used to calculate the composition of the quaternary material. This method of calculating Pb₁₋ₓSnₓSe₁₋ᵧₚ Teᵧₚ solid composition assumes that the liquid-solid segregation coefficients for the metal (Pb and Sn) and nonmetal (Se and Te) atoms are independent. Pb₁₋ₓSnₓSe₁₋ᵧₚ Teᵧₚ compositions determined using Auger electron spectroscopy have agreed well with compositions calculated from x-ray data using the above assumption. These data and, moreover, work by Davarshvili et al. showing that the composition of the metal sublattice is, indeed, independent of the tellurium content in the liquid growth solution justify our assumption.

IV. RESULTS

Measured lattice parameters of the various IV-VI semiconductor alloys grown in this study are plotted as a function of tellurium content in the liquid solution y₁ for three different tin contents, x₁ = 20%, 40%, and 60%, in Figs. 4, 5, and 6, respectively. For each tin concentration, the lattice parameter increases as the tellurium concentration increases. The lattice-matching conditions with BaF₂...
Lattice matching with BaF$_2$ is at $y_L = 60\%$. Lattice matching with BaF$_2$ is at $y_L = 57\%$.

are $y_L = 60\%$, 58\%, and 57\%, respectively. Table I summarizes these data along with the previously determined condition for lattice matching the ternary PbSe$_{0.78}$Te$_{0.22}$ alloy with BaF$_2$. Values for tin and tellurium content in the liquid and solid are listed along with the calculated band gap energy and cutoff wavelength at 77 K for each composition.

The fourth alloy composition listed in Table I, Pb$_{0.67}$Sn$_{0.33}$Se$_{0.65}$Te$_{0.35}$, is similar to the composition, Pb$_{0.70}$Sn$_{0.30}$Se$_{0.70}$Te$_{0.30}$ of Ref. 14 that had a measured lattice parameter of 6.195 Å. Interpolating the data in Ref. 14, the composition with the same 6.200 Å as BaF$_2$ is Pb$_{0.66}$Sn$_{0.34}$Se$_{0.66}$Te$_{0.34}$ almost identical to that listed in Table I. This is further confirmation that our procedure for calculating solid composition is accurate and that the assumption of independent liquid-to-solid segregation coefficients for metal and nonmetal atoms is valid.

The relationship between tellurium content in the solid $y_S$ and tellurium content in the liquid $y_L$ is shown in Fig. 7. The $y_S$ values were calculated from the x-ray data using Eqs. (1) and (5). These data show that the liquid-to-solid segregation coefficient for tellurium is relatively small for $y_L$, less than 40\%.

V. DISCUSSION

The data listed in Table I show that tellurium content in the liquid growth solution $y_L$ decreases from 60\% to 57\%, while the tellurium content in the solid solution $y_S$ actually increases from 22.2\% to 34.6\%. Clearly, the role of tin content in the solid, which increases with the tellurium content according to Eq. (2), needs to be considered to account for this observation.

Since LPE growth takes place under near equilibrium conditions, we can say that tellurium's chemical potential in the solid solution alloy equals its chemical potential in the liquid growth solution,

$$\mu_{Te}^{S} = \mu_{Te}^{L}. \tag{6}$$

<table>
<thead>
<tr>
<th>$x_L$ (%)</th>
<th>$y_L$ (%)</th>
<th>$x_S$ (%)</th>
<th>$y_S$ (%)</th>
<th>$E_g$ (meV)</th>
<th>$\lambda$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60</td>
<td>0</td>
<td>22.2</td>
<td>185</td>
<td>6.72</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>14.3</td>
<td>27.5</td>
<td>73.5</td>
<td>16.9</td>
</tr>
<tr>
<td>40</td>
<td>58</td>
<td>22.2</td>
<td>30.5</td>
<td>14.2</td>
<td>87.5</td>
</tr>
<tr>
<td>60</td>
<td>57</td>
<td>32.9</td>
<td>34.6</td>
<td>-63.5</td>
<td>19.6</td>
</tr>
</tbody>
</table>

TABLE I. Compositions of liquid (Pb$_{1-x}$Sn$_x$)$_{0.99}$(Se$_{1-y}$Te$_y$)$_{0.01}$ solutions that yield Pb$_{1-x}$Sn$_x$Se$_{1-y}$Te$_y$ alloys lattice matched with BaF$_2$. Corresponding band gap energies and cutoff wavelengths at 77 K are also listed.
FIG. 7. Composition of group VI sublattice $y_S$ vs tellurium content in liquid growth solution $y_L$. A small, relative to selenium, liquid-to-solid segregation coefficient for tellurium is apparent for $y_L$, less than 40%.

If we assume that tellurium behaves ideally in the liquid growth solution, then the chemical potential of tellurium in the solid can be expressed as

$$\mu_{Te} = \mu_{Te}^0 + RT \ln y_L. \quad (7)$$

Equation (7) shows that the tellurium chemical potential in $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solutions decreases as the tellurium concentration in the liquid growth solution decreases. Since $y_S$ increases as $y_L$ decreases for $Pb_{1-x}Sn_xSe_{1-y}Te_y$ alloys lattice matched with $BaF_2$, we have a situation in which the chemical potential of tellurium actually decreases as its concentration in the solid increases.

Possible explanations for the highly nonideal behavior of $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solutions involve chemical bond energy and/or atomic size differences. Table II lists enthalpies of formation for $PbSe$, $PbTe$, $SnSe$, and $SnTe$. The selenides have higher bond energies than the tellurides, while the lead compounds have higher bond energies than the tin compounds. Table III lists ionic radii for $Pb$, $Sn$, $Se$, and $Te$ atoms showing that tellurium is larger than selenium, while tin is smaller than lead, size differences that are reflected in the lattice parameters of the binary compounds.

Figure 7 shows that $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solutions that have small tellurium concentrations are in equilibrium with liquid solutions that have relatively large tellurium concentrations. These alloys thus have relatively large tellurium chemical potentials according to Eq. (7). Both bond energy and atomic size effects can account for a high tellurium chemical potential in $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solutions. Tellurium, having lower bond energies than selenium with lead and tin, will have a smaller affinity for the solid. Also, the incorporation of large (relative to selenium) tellurium atoms in the growing solid can cost energy in the form of lattice strain. Relaxation of this lattice strain can, therefore, be a driving force for high tellurium chemical potential.

In the quaternary solid, tin atoms replace lead atoms on the group IV sublattice, thus changing the chemical environment for tellurium in the solid. Since tellurium is less strongly bound to tin than it is to lead, addition of tin would reduce the affinity that tellurium has for the $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid. In other words, if chemical effects alone were considered, an increasing tin concentration would increase the tellurium chemical potential. This is opposite of what is observed, suggesting that bond energy difference is not the dominant factor in determining tellurium chemical potential in $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solutions.

Substitution of lead atoms with relatively small tin atoms in the quaternary alloy creates more space on the group VI sublattice to accommodate relatively large tellurium atoms. Increasing the tin concentration in the quaternary alloy can thus reduce the amount of strain energy associated with the incorporation of tellurium into the growing solid. Reduction of this strain energy will tend to increase the affinity that tellurium has for the $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid. This is consistent with what is observed in that less tellurium is required in the liquid solution to achieve lattice matching, i.e., higher tellurium content in the solid, as the tin concentration is increased. We therefore conclude that composition dependent lattice strain is the dominant factor in determining tellurium chemical potential in $Pb_{1-x}Sn_xSe_{1-y}Te_y$ quaternary alloys that are lattice matched with $BaF_2$.

### VI. SUMMARY

A series of $Pb_{1-x}Sn_xSe_{1-y}Te_y$ solid solution IV–VI semiconductor alloys have been grown on $BaF_2$ substrates by liquid phase epitaxy. Liquid-solid phase equilibria data

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**Table II.** Enthalpy of formation at 298 K for binary IV–VI compounds.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\Delta H_{fus}$, 298 K (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe</td>
<td>-99.6$^a$</td>
</tr>
<tr>
<td>PbTe</td>
<td>-60.1$^a$</td>
</tr>
<tr>
<td>SnSe</td>
<td>-88.7$^a$</td>
</tr>
<tr>
<td>SnTe</td>
<td>-60.7$^a$</td>
</tr>
</tbody>
</table>

*See Ref. 18.

*See Ref. 19.

*See Ref. 20.

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**Table III.** Ionic radii of group IV and group VI elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Valence</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>+2</td>
<td>1.20</td>
</tr>
<tr>
<td>Sn</td>
<td>+2</td>
<td>0.93</td>
</tr>
<tr>
<td>Se</td>
<td>-2</td>
<td>1.91</td>
</tr>
<tr>
<td>Te</td>
<td>-2</td>
<td>2.11</td>
</tr>
</tbody>
</table>

*See Ref. 18.
show that, although tellurium content in the solid increases as the tin content increases, tellurium concentration in the \((\text{Pb}_{1-x} \text{Sn}_{x})_{0.99} (\text{Se}_{1-y} \text{Te}_y)_{0.01}\) liquid growth solution actually decreases slightly. A model has been proposed that explains this behavior in terms composition dependent lattice strain: an increasing tin concentration on the metal sublattice can reduce the lattice strain associated with tellurium incorporation, thus reducing a relatively large tellurium chemical potential in these alloys. These data can be used for LPE growth of lattice-matched IV–VI semiconductor heterostructures on \(\text{BaF}_2\) substrates. Such growth will facilitate development of novel far-infrared tunable diode lasers.

**ACKNOWLEDGMENTS**

This work was supported by grants from the Oklahoma Center for Advancement of Science and Technology and the National Science Foundation.