Molecular Beam Epitaxy of $PbSe_{1-x}Te_x$ for Strain Engineering in IV-VI Semiconductor Heterostructures

A. Hallbauer, T. Schwarzl, R. T. Lechner and G. Springholz

Inst. of Semiconductor and Solid State Physics, Joh. Kepler Univ. Linz

Molecular beam epitaxy and the structural and electronic properties of ternary $PbSe_xTe_{1-x}$ layers on BaF_2 (111) for strain engineering of lattice-mismatched IV-VI semiconductor heterostructures is investigated. It is shown that although the ternary lattice constant exactly follows Vegard´s law, the energy band gap as a function of the ternary composition shows a substantial bowing behavior with a negative bowing parameter determined as –62 meV. Furthermore, the threading dislocation density in the layers is also found to depend drastically on the ternary composition due to alloy hardening that hinders the dislocation annihilation processes during strain relaxation. Nevertheless, very high quality layers are obtained for a selenium concentration of 78% for which the ternary compound is exactly lattice-matched to the BaF_2 substrate.

Introduction

The narrow band gap IV-VI semiconductors (PbSe, PbTe, PbS) have long been used for mid-infrared optoelectronic device applications [1]. These structures are usually grown on lattice-mismatched substrates such as BaF_2 or Si with appropriate fluoride buffer layers [1]. In heterostructures, band structure engineering is achieved by alloying with the wide band gap Eu or Sr chalcogenides for increasing the band gap, or with the Sn chalcogenides for reducing the band gap [1]. Because these compounds exhibit a lattice-mismatch of a few percent with respect to their lead salt counterparts, the lattice constants of the ternaries change with changing alloy composition. This can be compensated by admixtures of PbSe and PbTe, because the lattice constant of PbSeTe can be adjusted over a wide range due to the rather large difference of the PbSe and PbTe lattice constants (a_{PbTe} = 6.462Å, a_{PbSe} = 6.124Å). This can be utilized not only for achieving a lattice-matching to various substrate materials, but also for strain engineering in heterostructures as well as growth of high finesse epitaxial Bragg mirrors that are used for IV-VI compound vertical cavity surface emitting laser devices [2].

Experimental

In the present work, the growth behavior and the structural and electronic properties of $PbSe_xTe_{1-x}$ layers grown by molecular beam epitaxy onto (111) BaF_2 substrates was investigated. For this purpose a series of samples was grown at a temperature of 380 °C with ternary compositions adjusted in the range of x = 0 – 100% by controlling the flux rates from the PbTe and PbSe effusion cells. The alloy composition was determined precisely from beam flux rate measurements performed using a quartz crystal microbalance moved into the substrate position. These measurements were calibrated using several PbSe/PbSeTe and PbTe/PbSeTe superlattices in which the layer thicknesses were precisely determined by x-ray diffraction. Thus, a relative precision of the chemical composition of better than +2% could be achieved.

Results

All layers were characterized by high-resolution x-ray diffraction, Fourier transform infrared (FTIR) transmission, and atomic force microscopy (AFM) measurements. The ternary lattice constant was determined precisely from a detailed strain analysis using the asymmetric (264) Bragg reflection. In Fig. 1 (a) the resulting ternary lattice constant is plotted as a function of alloy composition. As indicated by the dashed line, it exactly follows Vegards law, i.e., corresponds exactly. The energy band gap of the ternaries was determined from the fitting of the FTIR spectra using a model dielectric function and the transfer matrix method as illustrated in the inset of Fig. 1 (b). The energy band gaps as a function of ternary composition (Fig. 1 (b)) are found to deviate significantly from a linear behavior, with only a minor change in the PbSeTe band gap as compared to the 325 meV PbTe band gap for Se concentrations up to about 50%. Above this composition, the band gap linearly decreases to the PbSe band gap of 180 meV at 300 K. This can be explained by the fact that the character of the conduction and valence bands of PbTe and PbSe are exchanged. With respect to the refractive index, a linear dependence of n versus x_{Se} was found.
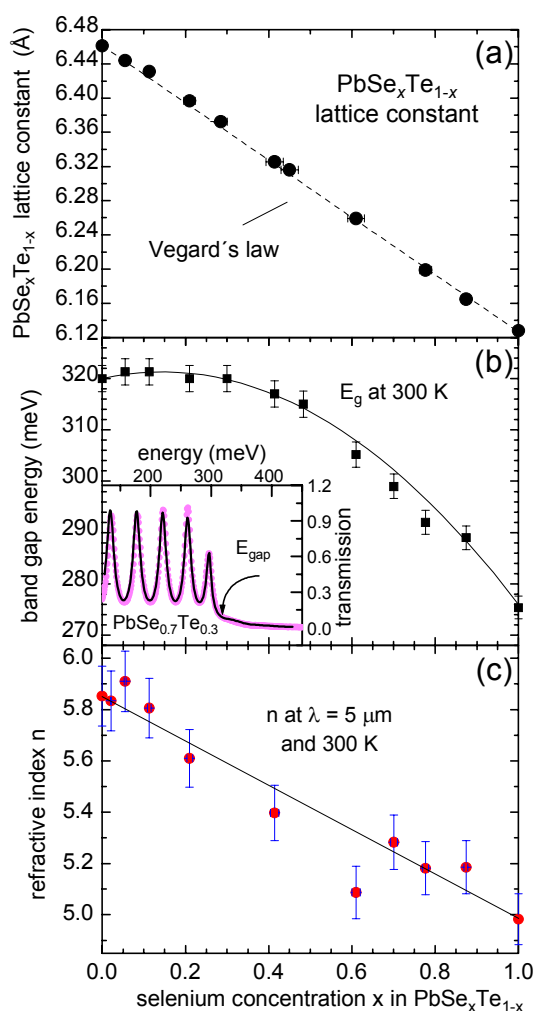

Fig. 1:   (a) Lattice constant of $PbSe_xTe_{1-x}$ as a function of Se concentration. The solid line corresponds to the linear interpolation between the PbTe and PbSe bulk lattice constants (Vegard´s law). (b) Energy band gap and (c) refractive index at $\lambda = 5$ µm of $PbSe_{1-x}Te_x$ as a function of Se concentration. The insert in (b) shows the FTIR transmission spectrum of a sample with $x_{se} = 70\%$.

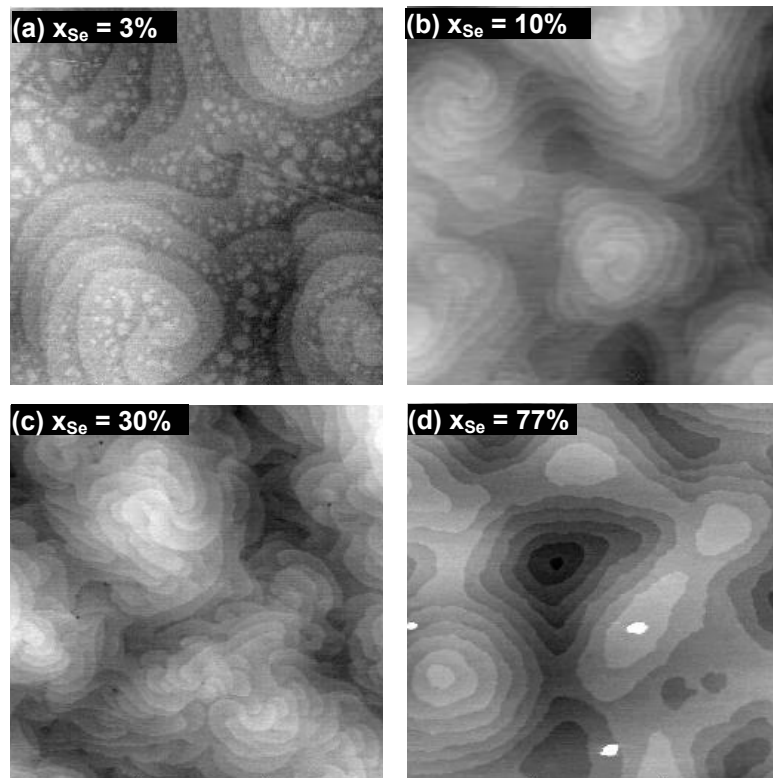Fig. 2: Atomic force microscopy images (3 x 3 μm^2) of 3 μm PbSe$_x$Te$_{1-x}$ layers on BaF$_2$ (111) with different Se concentration.

A particularly interesting effect was observed concerning the structural properties and threading dislocation density of the layers as determined from an analysis of large-scale atomic force microscopy images as shown in Fig. 2. For the pure PbSe and PbTe layers, rather low threading dislocation densities of around 10^7 cm^{-2} were found [3] as well as narrow x-ray rocking curve widths. With increasing alloy composition, however, both parameters drastically increase reaching a maximum for Se concentrations of ~50%. This is shown in detail in Fig. 3, where the threading dislocation density evaluated from the atomic force microscopy images is plotted as a function of the selenium concentration. With increasing selenium concentration, the threading dislocation density more or less increases linearly up to values of around 2 x 10^9 cm^{-2} for selenium concentrations in the range of 20 – 60%.

At higher selenium concentrations, the dislocation density decreases again because the ternary lattice constant approaches the lattice constant of 6.200 Å of the BaF$_2$ substrate. This is because much less misfit dislocations are required for strain relaxation due to the resulting decrease of the layer/substrate lattice-mismatch. For a selenium concentration of 78%, the ternary layer is exactly lattice-matched to BaF$_2$. As a result, no dislocations are formed during deposition, and the dislocation density drops by more than two orders of magnitude below 10^5 cm^{-2}. As the selenium concentration further increases, again a lattice-mismatch to the substrate builds up, and the threading dislocation density again increases. However, as the ternary composition approaches pure PbSe, the dislocation density drops again reaching a value of around 10^7 cm^{-2} for pure PbSe. This marked behavior is attributed to a strong alloy hardening effect of the ternary layers, which prevents an efficient relaxation of the layer/substrate lattice-mismatch by glide of dislocations. Therefore, the efficient dislocation annihilation processes known, *e.g.*, for pure PbTe are kinetically suppressed in the ternary layers.
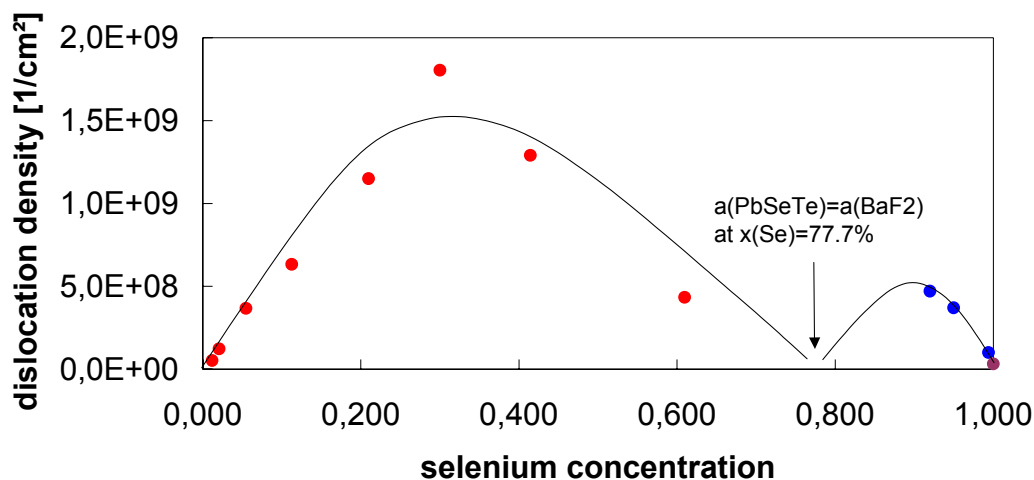
Fig. 3: Threading dislocation density of 2.7 μm $PbSe_{1-x}Te_x$ layers on BaF_2 (111) as a function of Se concentration. A minimal dislocation density is observed for x_{Se} = 78% because of the resulting layer/substrate lattice-match.

Conclusions

From investigation of ternary $PbSe_xTe_{1-x}$ layers grown by molecular beam epitaxy on BaF_2 (111) substrate it is shown that lattice constant exactly follows Vegard´s law, whereas the energy band gap as a function of the ternary composition shows a substantial bowing behavior. Although solution hardening effects in the ternary allows lead to a drastic increase of the threading dislocation density on the ternary composition, very high quality layers are obtained for a selenium concentration of 78% for which the ternary compound is exactly lattice-matched to the BaF_2 substrate. This opens promising perspectives for the growth of dislocation-free IV-VI based optoelectronic devices.

Acknowledgements

References

[1]   *see, e.g.,* G. Springholz, Z. Shi, and H. Zogg in "Thin Film Heteroepitaxial Systems" eds. W.K. Liu and M. B. Santos (World Scientific, Singapore, 1999) p. 621 – 688, and references therein.

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[3]   G. Springholz, A.Y. Ueta, N. Frank and G. Bauer, Appl. Phys. Lett. **69 (**1996) 2822 - 2824.