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N-type PbS and $PbS_{1-x}Se_x$ layers prepared by the hot-wall epitaxy

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The control of the sulphur compensation during growth of high quality n-type epitaxial lead-salt films is described. The experimentally observed degree of compensation cannot be explained by the phase diagram. Quantitatively it agrees well with the partial dissociation of the lead-salt molecules originating from the evaporation source. The carrier type of the films has been found to depend on the substrate material. Representative results for PbS, BaF_2 and NaCl substrates are summarized.

1. Introduction

Since the preparation of high quality monocrystalline binary and pseudobinary IV–VI compound films advanced continuously during the past few years [1–5] fabrication of novel optoelectronic devices became feasible. Infra-red sensitive photodetectors [6, 7] and infra-red emitting lasers [8, 9] comprising a wide range of the infra-red spectrum were constructed from these narrow gap semiconductors. Their wavelength can conveniently be adjusted by choosing a proper composition x, e.g. with $PbS_{1-x}Se_x$ the range from 4 to 7 μm can be covered at 77 K. This spectral range contains the absorption lines of some of the most important air polluting gases such as NO and CO, the detection of which has been carried out successfully using tunable lead-salt laser diodes [10, 11]. In order to improve the laser's operating performance, the use of double heterostructure (DH) configurations has become necessary. Production of those structures requires a method capable of depositing thin layers with controlled composition, high crystalline perfection, and well defined charge carrier distribution. The hot-wall epitaxy has become a valuable tool for this purpose [12]; up to now, however, no information is available about the fabrication of n-type PbS layers deposited by this method. Preparation and properties of such layers which are of great importance for high-efficient DH-injection lasers will be reported in this paper.

2. Deposition apparatus

Vacuum growth of thin monocrystalline layers has been carried out by means of a modified molecular beam epitaxy, the so called hot wall technique, the principle of which has already been described elsewhere [13, 14]. Two evaporation sources containing PbS and $PbS_{1-x}Se_x$, respectively, were mounted in an ultra-high vacuum chamber to allow heterostructure deposition without breaking the vacuum. Details of the evaporation sources are shown in Fig. 1. Some important details should be noted, e.g. the substrates are just placed over holes in the holder without any mechanical attachment, thus avoiding strains which can easily produce plastic deformation of the PbS seed crystals. Between the compensation source and the hot zones a capillary has been placed in order to reduce the flow of the compensating molecules. The knee in the connecting tube minimizes radiation heating from the high temperature regions. Additional cooling is provided for the vessel containing the compensation material. Special attention has been paid to the temperature control of this reservoir. According to our experience this has to be done with an accuracy of better than ± 0.5° C. Great care must be taken to maintain a continuously increasing temperature along the quartz tube connecting the compensation with the hot zone thus preventing any uncontrolled deposition in between.

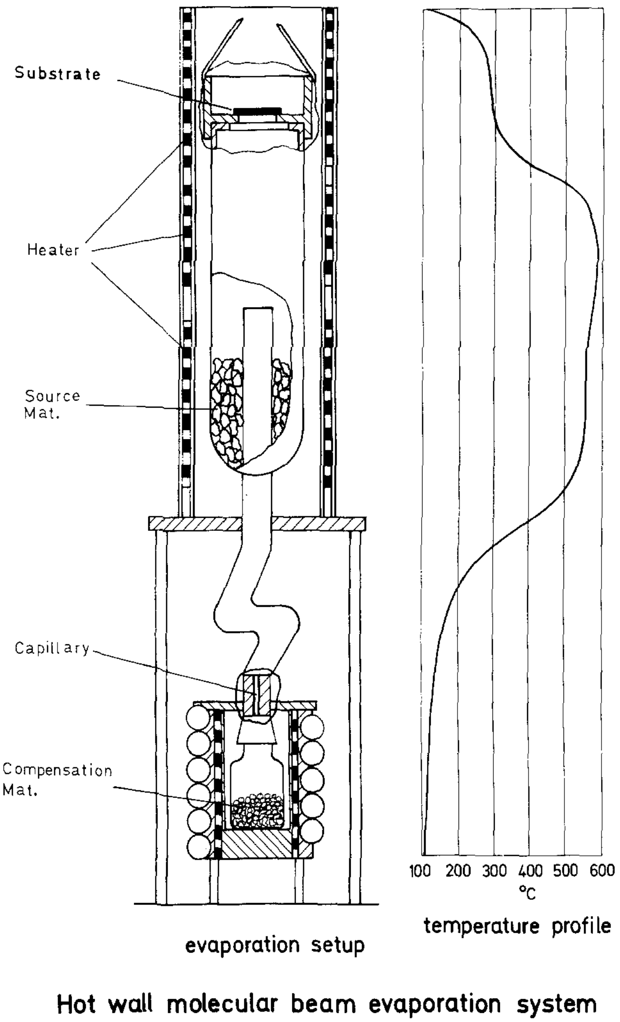

Figure 1 Schematic illustration of the evaporation apparatus together with the temperature profile.

3. Material and substrate preparation

Commercially available ultra high purity 6N elements were used as compensation materials without any further purification. For fabrication of the source materials the elements as well as the binary compounds were additionally purified [15]. The pseudobinary $PbS_{1-x}Se_x$ was alloyed by heating it to a temperature 50° C above its melting point and quenching it in water. The polycrystalline PbS and $PbS_{1-x}Se_x$ ingots were crushed into pieces with a grain size of a few mm. About 10 g were needed for each source.

Special care has been taken to keep the metal/chalcogen ratio of the source constant over a long operation period. This can be achieved if the material corresponds to the congruently subliming composition at the respective source temperature characterized by the minimum total vapour pressure in the phase diagram.

The desired composition is adjusted by a dynamic vacuum sublimation process during which the water-quenched material is transported from the hot end (850° C) of a long quartz ampoule to a region at a temperature corresponding to that of the epitaxial source. The cold end of the ampoule was thereby immersed in a dewar containing liquid nitrogen. This absorption pump maintained the dynamic vacuum and froze out the volatile pollutants such as O_2, CO_2 and CO.

As substrates served n- and p-type PbS wafers, which were about 0.8 mm thick and 1 x 1 cm^2 in area. They were wire sawn from large sublimation-grown crystals [16]. Mechanical polishing was done stepwise ending with 1 μm Al_2O_3 powder. The finish was achieved by a chemomechanical treatment on a Pellon cloth using a saturated iodine methanol solution diluted 1:100 with methanol. Immediately before putting the substrates into the growth apparatus their mirror-like surfaces were finally etched in an NaOH–H_2O–H_2O_2–ethyleneglycol solution and rinsed in diluted nitric acid. The results obtained by this technique proved to be superior to applying aqua regia which is known as a polishing etchant for PbS [17]. For Hall-effect measurements, freshly cleaved BaF_2 as well as NaCl crystals have been used as substrates.

4. Growth parameters

The substrate temperature was 320° C throughout all runs, a value sufficiently high for monocrystalline growth and low enough to minimize interdiffusion effects. The source temperature was 550° C yielding growth rates of about $3\,\mu m\,h^{-1}$. At this temperature, the congruently subliming PbS source material consists of a composition defined by a free electron density of about $4 \times 10^{18}\,cm^{-3}$ as can be obtained from the p–T–x phase diagram [18]. According to the x–T phase diagram [19] the vapour originating from such a source leads to an epitaxial deposit at the substrate temperature which lies outside the homogeneity range. For this reason an additional source which compensates the excess metal must be provided. If the temperature difference between source and seed were the only reason for making the compensation necessary, it should quantitatively amount to about 10^{-2}%. To verify this prediction experimentally we compensated films grown from a PbS source with selenium and measured the PbSe content in the epitaxial film. For n-type layers without metal precipitates we obtained a value of 4 ± 1%. The enormous discrepancy leads to the conclusion that another process is responsible for the Pb precipitates. It can be explained by the partial dissociation of the lead-salt molecules. Using the results of Colin and Drowart [20] who measured the partial vapour pressures of PbS, Pb and S_2 over solid PbS we obtain

$$\log p_{PbS} = 6.04 - 10.21 \times 10^3/T \qquad (1)$$

$$\log p_{Pb} = 4.33 - 9.6 \times 10^3/T \qquad (2)$$

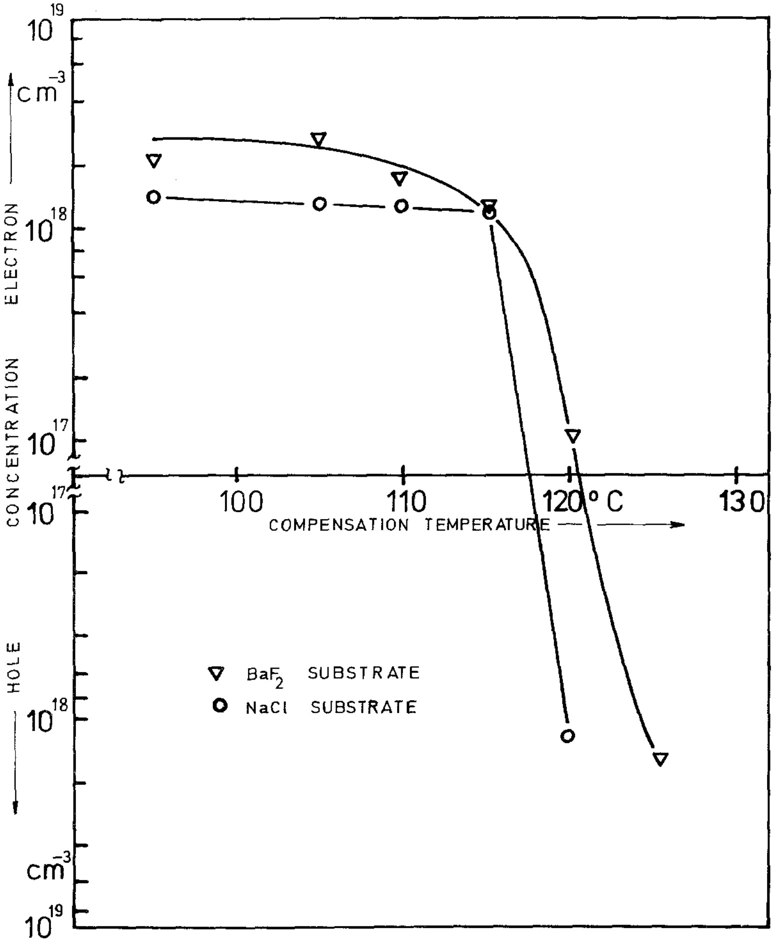

Figure 2 Charge carrier type and concentration of Se-compensated PbS films versus compensation temperature.

$$\log p_{S_2} = 2.3 - 8.3 \times 10^3/T \quad (3)$$

with the pressures in atm and the temperature in K. At our source temperature of 550° C about 10% of the evaporated PbS molecules are dissociated into Pb and S_2. Thus the observed depletion of chalcogen in the epilayers becomes evident if the sticking coefficient of the lead atoms is higher than that of the sulphur molecules. Assuming the same value for the sticking coefficient of S_2 and Se_2 molecules the above results indicate that the diatomic chalcogen compensation has to provide about one third of the vapour pressure of the dissociated molecules in order to balance the excess metal.

In the case of Se compensation, the selenium partial pressure varies with temperature [21] as

$$\log p_{Se_2} = 5.17 - 4.97 \times 10^3/T \quad (4)$$

which for this case requires an Se compensation temperature of 118° C. Fig. 2 demonstrates the agreement of this prediction with our experimental results, where we observed a change of the type of conductivity of the epilayers for exactly this compensation temperature.

Considering a sulphur-compensated evaporation system it is necessary to take into account the higher order S molecules originating from the sublimation of solid sulphur, with

$$\log p_{\Sigma S} = 8.85 - 5.2 \times 10^3/T \quad (5)$$

where ΣS consists mainly of S_8 molecules. Accordingly, the S compensation should be held at 30° C for growth of n-type films without precipitates. Because of inhomogeneous local heating due to radiation, the compensation temperature could not be controlled experimentally at this low value. To reduce the sulphur vapour pressure the capillary mentioned above was introduced. We were then able to work at reproducibly adjustable temperatures.

5. Layer properties

The carrier type of the films grown near the point of stoichiometric composition and under same conditions was different for the various substrates. Layers on BaF_2 revealed electron conduction. Those, however, deposited simultaneously on NaCl showed p-conductivity. Typical results for sulphur as well as for selenium-compensated PbS layers are summarized in Table I. In order to adjust the carrier concentration, no material other than the respective substrate material can be used for calibration of the compensation temperature concerned. Similar results have recently been found for PbTe [22].

The extremely crucial influence of the compensation temperature is demonstrated in Fig. 3. During growth of the layer shown in Fig. 3a and b, the temperature was too low, resulting in the formation of tiny lead droplets of about 1 μm diameter spread over the PbS surface. Scratches and cleavage steps were preferred, since their crystallographic deformation favours nucleation. The same sample has been overgrown at an elevated compensation temperature. This new layer was then covered with isolated cubes of about 1 μm^3 (Fig. 3c and d) which apparently grew at places where metal precipitates had previously been formed: as the sulphur vapour pressure was increased during the succeeding run it dissolved in the liquid lead and VLS-growth occurred at the islands.

TABLE I Electrical properties of Se- and S-compensated PbS layers deposited on different substrates

Substrate	Run no.	Compensation		Carrier		
		Material	Temperature (° C)	Type	Concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$, 300/77 K)
PbS	I/196	S	54*	p	(hot probe)	
BaF_2	I/196	S	54*	n	2.10^{17}	$660/2.3 \times 10^4$
NaCl	I/196	S	54*	p	10^{18}	$250/1.2 \times 10^3$
PbS	I/198	S	48*	n	(hot probe)	
BaF_2	I/198	S	48*	n	5.10^{17}	$370/6 \times 10^3$
NaCl	I/198	S	48*	p	9.10^{17}	$230/10^3$
PbS	I/217	Se	120	p	(hot probe)	
BaF_2	I/217	Se	120	n	10^{17}	$280/4 \times 10^3$
NaCl	I/217	Se	120	p	10^{18}	$300/1.4 \times 10^3$

* With capillary.

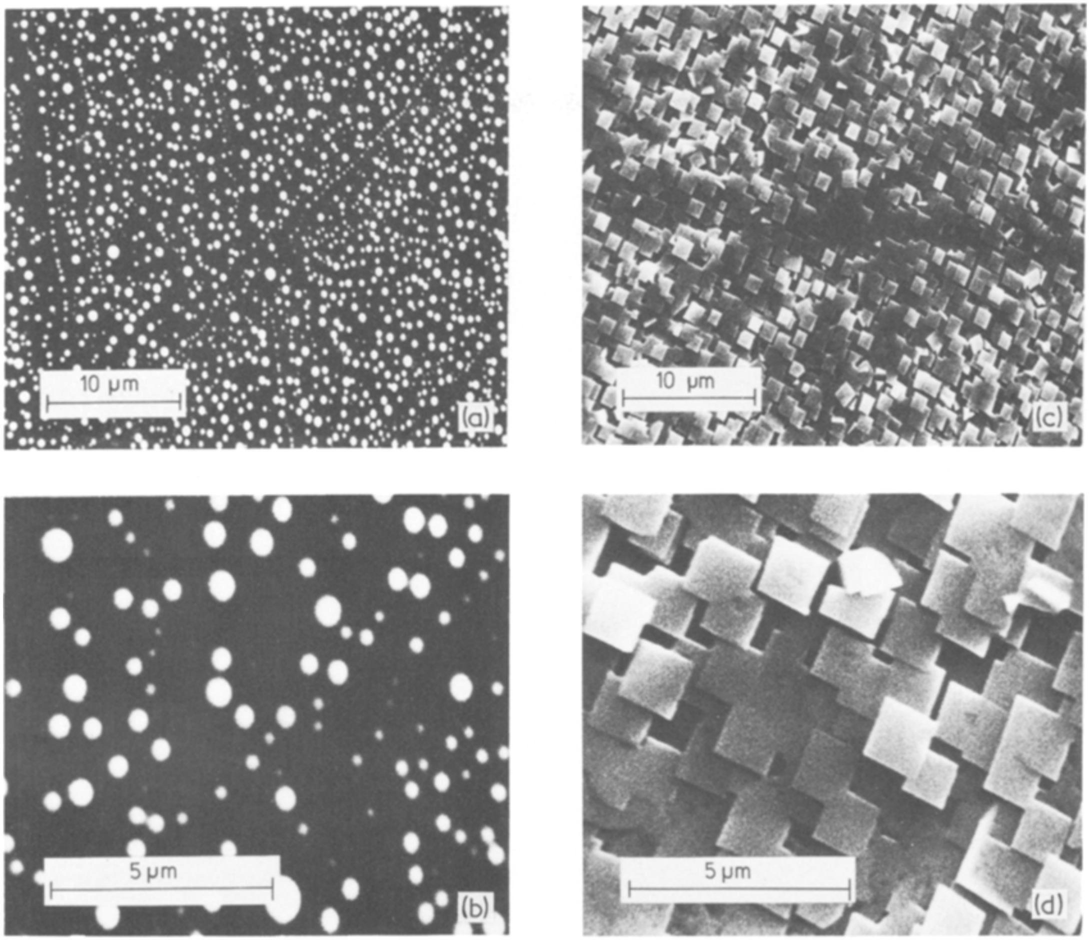

Figure 3 Surface morphology of PbS film: (a) and (b) compensation temperature too low. (c) and (d) same sample overgrown at a higher compensation temperature.

6. Conclusion

It has been demonstrated that the capillary acts as a suitable instrument for controlling the sulphur compensation. High quality n-type PbS films can be grown as an optically and electrically confining layer in lead salt DH-lasers by use of hot-wall epitaxy. Properties of these lasers have previously been reported [12].

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