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(Invited)

Solution Growth of II-VI Compounds

M.Aoki, M.Washiyama, H.Nakamura, and K.Sakamoto
Depertment of Electronic Engineering, Faculty of Engineerng, University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

1. Introduction

Solution growth is one of the superior methods of crystal growth of semiconductors, which is widely applied to III-V compounds. However, only a few works have been done on the solution growth of II-VI compounds. From solution, single crystals are grown at relatively low temperatures, so we can obtain crystals with high purity and good crystallinity. In this review, the solution growth of some II-VI compounds, mainly ZnSe, using Te, Se, As-Se compounds as the solvents is reported.

2. Solution Growth (Free Growth in a Closed Tube)

2.1 Growth of some II-VI compounds using Te as the solvent[1]

Te was found to dissolve many Zn and Cd chalcogenides to appricable extents at elevated temperatures. Fig.1. shows the liquidus solubilities of them into Te. We succeeded in growing single crystals of ZnO, ZnS, ZnSe, CdS and CdSe from Te solution using the slow cooling method. Typical starting temperature and the cooling rate were 1000°C and 20°C/hour, respectively. The crystals thus obtained were mainly plate-like with a size of $3x3x0.5mm^3$ except for ZnO crystals which were needle-like. The solvent Te was inevitably incorporated in the grown crystals. The concentration of Te in ZnS and ZnSe were 0.1∿0.8at.% and 2∿5at.%, respectively.

2.2 Growth of ZnSe using Se and As_2Se_3 as the solvents.

ZnSe crystals grown from Te solution contain large amount of Te, so we consider them as mixed compounds, $ZnSe_{1-x}Te_x$. Fig.2. shows the Zn-Se-Te ternary phase diagram near the Te corner. Fig.2. indicates that the concentration of Te in ZnSe can be reduced by adding a small amount of excess Se to the Te solvent. We found that Se and As_2Se_3 can dissolve ZnSe and that the single crystals of ZnSe can be grown from these solutions using the solvent transport method. The solubility data are shown in fig.3. Typical growth temperature and temperature gradient were 850∿870°C and 6∿8°C/cm, respectively. We tried the doping of some kinds of impurity during the crystal growth and succeeded in growing the phosphorus doped ZnSe by using As_2Se_3 as the solvent.

3. Liquid-Phase Epitaxial Growth of ZnSe

3.1 Open-tube slide-boat method[2]

The epitaxial growth of ZnSe from Te solution was tried using the open-tube slide-boat method. Uniform and smooth epitaxial layers with the thickness of about

15μm were obtained on the (111)B oriented ZnS substrates. On the (111)B oriented ZnTe substrates ZnSe layers were also grown, the interface of ZnTe and ZnSe was however not so good due to the melt-back of the ZnTe substrates.

3.2 Closed-tube Nelson method

Uniform ZnSe layers were grown epitaxially on ZnTe substrates using Te(97at.%)+Se(3at.%) as the solvent. At the growth closed-tube Nelson method was used because of the high vapor pressure of Se at the growth temperature. By adding excess Se to the solvent, the melt-back of the substrates was hardly observed.

4. Evaluation of the Grown Crystals by Photoluminescence

The ZnSe crystals grown from the Te solution ($ZnSe_{0.9}Te_{0.1}$) show strong green photoluminescence at 77K. The peak was at about 2.4eV with a wide half width of about 0.16eV. The origin of this peak is not clear. The ZnSe crystals grown from Se solution and As_2Se_3 solution show sharp I_1 exciton lines in the photoluminescence spectra at 4.2K, indicating the high purity and the good crystallinity of them. Photoluminescence at 4.2K of the phosphorus doped ZnSe grown from As_2Se_3+P solution has DA pair emission bands due to the P acceptor. The depth of the P acceptor was found to be very shallow (about 84meV).

5. Possibility of the Application to Devices

The interesting properties of the solution grown crystals and well-controlled LPE technique will bring us some new devices. For example, ZnSe crystals grown from Te solution were found to be highly photoconductive, which suggests that n-ZnSe/p-ZnTe heterostructure can be applied to the solar cells of spectrum-divided type for the higher energy part. Our preliminary experiment showed the open-circuit voltage and the energy conversion efficiency of this structure cells to be about 1.0V and about 1%, respectively. Furthermore, we believe the LPE of pure or acceptor doped ZnSe has a possibility to realize the blue LED's with MIS or pn junction structures.

References (1). M.Washiyama et.al.: Jpn.J.Appl.Phys. 18 (1979) 869.

(2). H.Nakamura et.al. : Jpn.J.Appl.Phys. 20 (1981) 11.

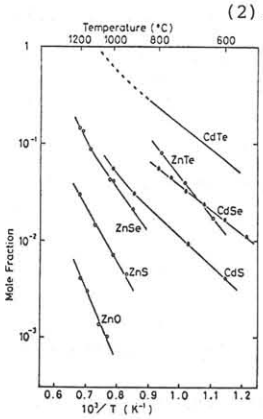

Fig.1.

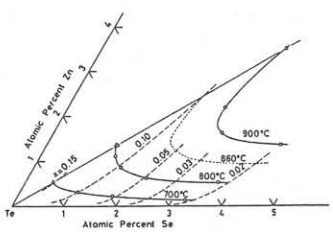

Fig.2.

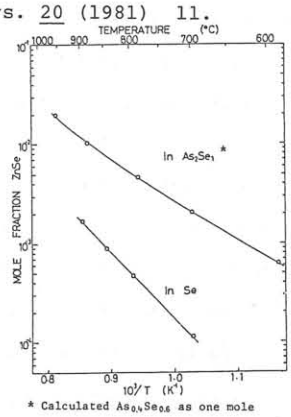

Fig.3.