

## 11-Surfaces, Interfaces and Thin Films

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**PS-11.01.13 DOPING OF Bi AND Cd DURING MOLECULAR BEAM EPITAXIAL GROWTH OF  $Pb_{1-x}Sn_xSe/CaF_2$ .** By Masanobu Suzuki\* and Torao Seki, Department of Electronics, Tohoku Institute of Technology, Yagiyamakasumi, Sendai 982, Japan, and Nobuo Miyamoto, Research Institute of Electrical Communication, Tohoku University, Katahira, Sendai 980, Japan.

Pseudobinary IV-VI compound semiconductors  $Pb_{1-x}Sn_xSe$  as well as  $Pb_{1-y}SnyTe$  are valuable as their applications to the infrared optoelectronic devices such as photovoltaic detectors and tunable laser diodes. It is because that they have small direct energy band gaps which can be widely changed in the infrared wavelength regions by the suitable choices of composition ( $x$  or  $y$ ) and temperature tuning. On the crystal growth of these materials, hot wall epitaxy (HWE) or molecular beam epitaxy (MBE) method has mainly been used, largely because the epitaxial films with good qualities can be produced and both the carrier type and densities of the films can be simultaneously controlled by either the adjustment of stoichiometric deviation or the incorporation of foreign impurity dopants during growth. The control of both the carrier type and densities in these materials by impurity doping at lower temperature is preferable to that by adjusting stoichiometric deviation because the excess lead tends to precipitate on the surface of epitaxial films and cause its retrograde qualities, while the chalcogen (Se or Te) reevaporates from the surface and does not fully incorporate into the film due to its high vapor pressure when the constituent elements lead or chalcogen are co-evaporated during HWE or MBE growth. There has been little exploration of impurity doping into  $Pb_{1-x}Sn_xSe$  except  $Pb_{1-y}SnyTe$  during MBE growth. We have already obtained unintentionally doped and as-grown p-type epitaxial films of  $Pb_{1-x}Sn_xSe$  grown by MBE (M. Suzuki and T. Seki, *Acta Crystallogr.* A43 (1987) Suppl. c120). In this paper, it was the object of study to prepare the intentionally doped n-type epitaxial films of  $Pb_{1-x}Sn_xSe$  ( $x=0$  and  $0.06$ ) by impurity incorporation during MBE growth, and also to make the control of carrier densities of the films possible in a wide range.

The binary compounds  $PbSe$  and/or  $SnSe$  were deposited from each pyrolytic BN Knudsen cell to grow  $PbSe$  and  $Pb_{0.94}Sn_{0.06}Se$  epitaxial films on  $CaF_2(111)$  substrates.  $PbSe$  and  $SnSe$  cell temperature were kept at  $705^\circ C$  and  $535^\circ C$ , respectively. The substrates were optically polished and chemically treated with diluted HF solutions, and prior to deposition, the thermal treatment of substrates was carried out at  $500^\circ C$  for 30 minutes in a vacuum of  $10^{-6}$  Pa.

The impurity materials such as Bi, Cd, and  $Bi_2Se_3$  were used as n-type dopants for comparison purposes. These materials were deposited additionally from the another separate cell during the film growth. The deposition fluxes were adjusted by varying the each cell temperature; Bi:  $200 \sim 600^\circ C$  and  $Bi_2Se_3$ :  $200 \sim 500^\circ C$  and Cd:  $100 \sim 250^\circ C$ . The relevant growth temperature,  $485^\circ C$ , was selected experimentally and the growth rate was about  $2 \mu m/h$ .

It was found that the electron carrier densities of  $Pb_{1-x}Sn_xSe$  epitaxial films could be controlled in the range of  $10^{13} \sim 10^{15} /cm^3$  at  $77K$  by Bi doping and up to  $10^{20} /cm^3$  by  $Bi_2Se_3$  doping, but the control of densities was limited to  $10^{16} /cm^3$  by Cd doping. Most Bi or Cd atoms appear to be incorporated substitutionally on Pb(Sn) sites, while in the case of  $Bi_2Se_3$  doping, BiSe may also substitute additionally for Pb(Sn)-Se in the crystal lattice, and these act as donors, although the mechanism of dopants incorporation during MBE growth could not be identified. The crystallines, surface morphologies, and electrical properties of these films were found to depend on the doping densities. The SIMS investigation indicated that the surface segregations of dopants or Pb(Sn) could not be observed even on the highly doped films with carrier densities of  $> 5 \times 10^{19} /cm^3$ .

**PS-11.01.14 SURFACE TOPOGRAPHY DUE TO GROWTH AND RELAXATION OF  $In_{1-x}Ga_xAs$  AND  $InGaP$  SINGLE HETEROEPITAXIAL LAYERS.** By H. Bluhm, U.D. Schwarz\*, G. Wagner, V. Gottschalch and P. Paufler\*\*, Inst. of Crystallography, Univ. of Leipzig, Germany. \*Inst. of Physics, Univ. of Basel, Switzerland, \*\*Inst. of Crystallography, Univ. of Dresden, Germany.

$In_{1-x}Ga_xAs$  and  $In_{1-x}Ga_xP$  single heteroepitaxial layers were grown by organometallic chemical vapour deposition on (001) oriented InP and GaAs substrates, respectively. The mechanical stress in the layer caused by the misfit of the lattice constants of layer and substrate can be varied by changing the composition of the layer. In our case the layers were grown under tensile stress conditions. The defect structure in the layers was investigated by transmission electron microscopy (TEM) (Wagner et al., *Z. Krist.*, 1989, 189, 269-292). Micromechanical processes during the relaxation of the strained layer lead to a characteristic topography on the (001) layer surface which can be observed by scanning force microscopy (SFM) in air. This technique allows surface imaging with a vertical and lateral resolution in the Angstrom region.

The (001)  $In_{1-x}Ga_xAs$  layer surface shows two characteristic features: straight grooves and steps parallel  $[1\bar{1}0]$  resulting from dislocation glide process on  $\{111\}$  planes and growth steps. Moreover, cracks parallel  $[110]$  were imaged. Relaxation takes place during the growth of the layer. The influence of the relaxation caused steps and grooves on the growing process and the location of the growing steps was investigated. Growing steps with a height of  $3.0 (\pm 0.3) \text{ \AA}$  were observed. This step height corresponds to half of the lattice constant of  $In_{1-x}Ga_xAs$ .

TEM-investigations on  $In_{1-x}Ga_xP$  layers have shown beside a dislocation structure like in the  $In_{1-x}Ga_xAs$  "ordering" of In and Ga atoms on  $\{111\}$  planes. The surface structure due to relaxation of the layer shows a strong dependence on the misorientation of the substrate surface and the sign and amount of the misfit. Layers grown on substrates with approximate exact orientation and a negative misfit (that means tensile strain of the layer) show higher surface steps than layers grown on substrates with misorientations of  $2^\circ$  or  $6^\circ$  and a positive sign of the misfit.

**PS-11.01.15 SLIP LINE RESOLUTION IN ATOMIC RANGE ON PLASTICALLY DEFORMED  $A_{III}B_V$  SEMICONDUCTOR SURFACE BY SCANNING FORCE MICROSCOPY.**

By K. Jurkschat, H. Bluhm, U.D. Schwarz\*, G. Klöß, and P. Paufler\*\*, Inst. of Crystallography, Univ. of Leipzig, Germany, \*Inst. of Physics, Univ. of Basel, Switzerland, \*\*Inst. of Crystallography, Univ. of Dresden, Germany.

During deformation of semiconductor-slices at elevated temperatures ( $400-600^\circ C$ ) slip lines raise at the (001) and (110) surface as traces of different  $\{111\}$  slip planes that can be detected by scanning force microscopy (SFM) with high resolution. We used a  $GaP:Te/(001)GaP$  homoepitaxial layer system (grown by VPE-technique) as a model substance because of its very smooth surface and the transparency of GaP in visible light. Deformation was carried out on a 4-point-bending stage adapted to a stereo microscope described elsewhere (B. Solcher et al., *Z. Krist.*, 1990, 192, 201-218). SFM allows the determination of differences in height on an atomic scale. Slip steps of these heights 0.2 - 0.6 nm which correspond to the movement of individual dislocations could be imaged by SFM for the first time. In addition the long range order distribution of glide steps is detected by interference microscopy.