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STRUCTURAL PROPERTIES OF $Pb_{1-x}Mn_xTe$ ALLOYS

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Abstract

$Pb_{1-x}Mn_xTe$ crystals were grown by Bridgman method and by molecular beam epitaxy (MBE). Structural properties of bulk crystals were studied both by optical microscopy after chemical polishing and etching, and by X-ray powder diffraction. For chemical polishing the solution of 5 vol.% Br_2 in HBr at the room temperature after exposure for 2 minutes was determined A solution of 20g KOH in 1 ml H_2O_2, 2ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at the room temperature after exposure for 6 minutes was found to be a suitable etching solution. The lattice parameters of samples obtained on different way (Bridgman and MBE) were determined.

1. Introduction

The pseudobinary alloys PbTe-MnTe, or $Pb_{1-x}Mn_xTe$, with a rock salt structure, are narrow band gap semiconductors [1-3]. $Pb_{1-x}Mn_xTe$ crystals have possibility to be used as an infrared detector (an epilayer grown on Si substrate) [4] or as a substrate for the growth of $Hg_{1-x}Cd_xTe$ [5]. $Pb_{1-x}Mn_xTe$ crystals take part as low-dimensional thermoelectric materials in two-dimensioned (2D) quantum well system [6], in investigations of the effect of negative magnetoresistance and long-term non-equilibrium process [7], or as materials for analysis the nature of phonon dispersion relation anomalies of IV-VI compounds in the high symmetry phase [8]. The aim of our work was to investigate the structural properties of $Pb_{1-x}Mn_xTe$ alloys as a necessary component for the better understanding these promising materials.

2. Experimental

The $Pb_{1-x}Mn_xTe$ ($x \leq 10$ at.%) crystals were grown by the Bridgman method with the lowering speed of 1 mm/h. The ingots had diameters 10 mm and length about 50 mm. The chemical composition of our sample was checked by an electron microprobe, which revealed the good chemical homogeneity of the material.

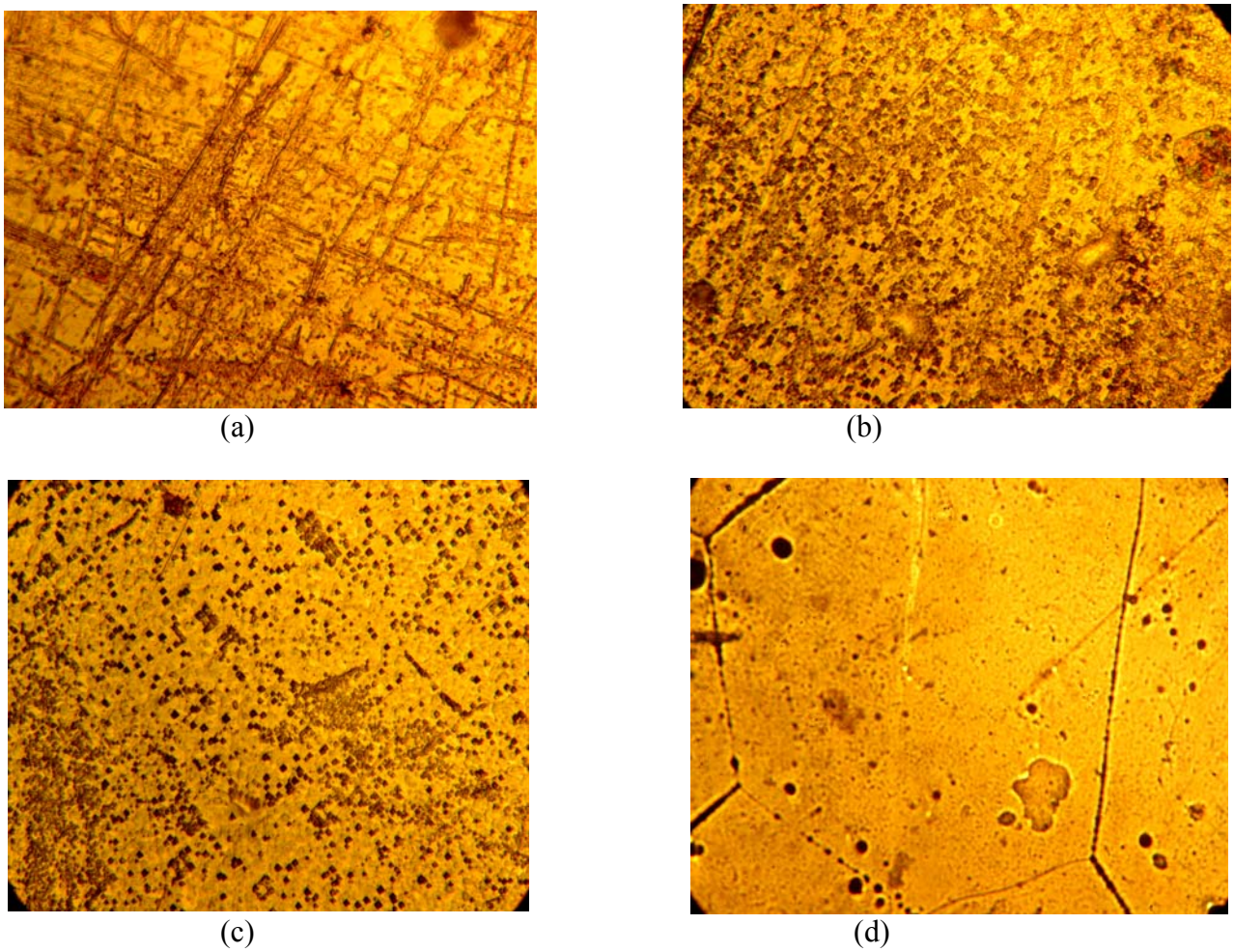
The specimens were cut parallel to (100) (the cleavage plane) with an inner blade diamond cutter and then mechanically polished. Chemical polishing was carried out in solutions of 3 vol.% Br_2 or 5 vol.% Br_2 in HBr at the room temperature after exposure for 2 minutes. Two etchants gave suitable etch-pits for optical investigations. A solution of 20g KOH in 1 ml H_2O_2, 2ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at the room temperature after exposure for 6 minutes, and a mixture of KOH saturated aqueous solution, ethylene glycol, and H_2O_2 after exposure for one minute. The present of low-angle boundaries were observed by means of microscopic examination on chemically etched samples.

The chemical compositions of the products were determined by the XRD powder technique. The bulk samples were examined under the same conditions, using a Philips PW 1729 X-ray generator, a Philips 1710 diffractometer and the original APD software.

$Pb_{1-x}Mn_xTe$ layers were deposited on BaF_2 or KCl substrates. Prior to the $Pb_{1-x}Mn_xTe$ growth cleaved (111) surface of BaF_2 or (100) surface of KCl has been covered by a 0.1 – 0.3 μm thick PbTe buffer layer. The manganese mole fraction x was determined (after the process) for individual layer by energy dispersive X-ray fluorescence analysis. The thickness of layers were between 0.3 and 4 μm. These samples we used only for the comparation of lattice parameter data.

3. Results and discussion

The widely known etch-pit technique is very suitable for the study of crystalline solids. For such studies, cleavage planes are often preferred to the maturely surface, because the former are free from the usual growth features and the characteristic surface marking which affect the each patterns produced. It was found [9] that a mixture of 25 ml KOH saturated aqueous solution, 25 ml



(a) (b) (c) (d)

Figure 1: The picture of etch-pits for $Pb_{1-x}Mn_xTe$ bulk samples with 0.002 (a), 0.2 (b), 2 (c) and 10%Mn (d). Magnification 500x, except (d) where is 100x.

ethylene glycol and 1 ml H_2O_2 is suitable etching solution (etchant) for $Pb_{1-x}Sn_xTe$ crystals. As we did not find in literature etchant for $Pb_{1-x}Mn_xTe$ crystals, we used the same. This etchant produced sizable pits with characteristics shape for (100) plane in about 1 minute at room temperature. The microscopic observation of chemically etched (100) surfaces was also showed the other structural characteristics. It was confirmed that obtained $Pb_{1-x}Mn_xTe$ were single crystals in the cases of 0.002, 0.02, 0.2 and 2% Mn and low-angle grain boundary free crystals. In the case of 10% Mn polycrystal was obtained. Also, no cellular structure and metal inclusions were observed. Dislocation density was estimated to be about 10^{-4} cm^{-2}, which is lower than cited in literature. We used another etchant [10], also formulated for $Pb_{1-x}Sn_xTe$, a solution of 20g KOH in 1 ml H_2O_2, 2ml

glycerol ($C_3H_8O_3$), and 20 ml H_2O at the room temperature, and find that after exposure for 6 minutes it can be seen well developed etch pits. Square pits with characteristic shape for (100) plane were clearly seen. Figure 1 shows etch pits at $Pb_{1-x}Mn_xTe$ samples with 0.002 (a), 0.2 (b), 2 (c) and 10% (d), respectively. The sample with 10% Mn is polycrystal and on Fig.1 (d) it can be clearly seen boundaries between three grains. Estimated dislocation densities were about 10^6 cm^{-2} what is accordance with literature.

Prior the chemical etching, the samples were chemical polished to remove surface damage using solutions of 3% Br_2 or 5% Br_2 in HBr. The best results were obtained in solution of 5% Br_2 in HBr at room temperature after exposure time of 2 minutes. The powdered samples structural properties were obtained using X-ray diffraction analysis. A Philips PW 1710 diffractometer was used in the 2θ ranges from 10° to 100°. The unit cell of $Pb_{1-x}Mn_xTe$ was calculated by the least square method. All the reflections correspond to PbTe crystals and gave the parameter of the cubic unit cell a = 0.6459 (5) nm and V = 0.26946 nm^3 [11]. Some divergence from the compared results can be explained by the fact that X-ray powder diffraction analysis give a statistical result and that Mn atoms entered into unit cell produced some contractions the Mn atom is smaller than Pb atom. Also could be noticed that obtained $Pb_{1-x}Mn_xTe$ single crystals were confirmed by X-ray diffraction.

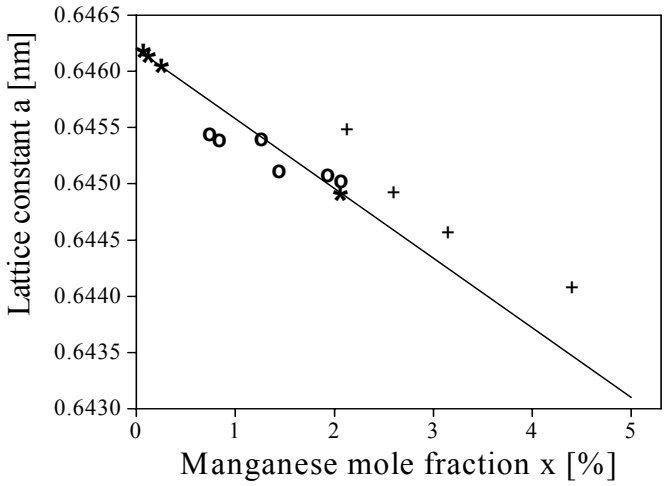


Figure 2: Lattice constant vs. manganese mole fraction for $Pb_{1-x}Mn_xTe$ obtained by Bridgman (*), by MBE on BaF_2 (o) and by MBE on KCl (+). Vegard' rule is presented by full line: a(x) = (0.6462 ± 0.0632x) nm [3]

Figure 2 shows lattice constant a as a function of manganese mole fraction x for $Pb_{1-x}Mn_xTe$ single crystals obtained on different ways (by Bridgman method (*) and Molecular Beam Epitaxy (MBE) on cleaved (111) surface of BaF_2 (o) and KCl (+)). Sample of 10% Mn grown by Bridgman is not present in Figure 2 as it is polycrystal. The relative errors are about 0.1% for all samples grown by Bridgman, and less than 0.3% for the others. It can be seen from Figure 2 that only samples obtained by Bridgman method obey the Vegard's rule, while to other samples grown by MBE satisfied it only approximately. In our opinion there are two reasons for that: first, we believe that (100) is the most suitable plane for crystal growth as it is dominant plane during the Bridgman growth. Second possibility is that Mn atoms in $Pb_{1-x}Mn_xTe$ are off-centres, when x>0.02. The existing of off-centres is registered in $Pb_{1-x}Ge_xTe$ and $PbTe_{1-x}S_x$ [12, 13]. This effect means that small impurity atoms (in our case Mn) that substitute for larger ones (Pb), are displaced from the regular sites in lattice, for about 0.5-1Å [12]. Experimental results [14, 15] strongly support our assumption.

About sample with 10 at.% Mn: it was found in literature [13] that content of Mn can extend up to 12%, and that was reason while we choose mentioned one. The lowering speed was the same

(1 mm/h) for all contents of Mn in Bridgman grown crystals, and it was suitable especially for sample with 2% Mn (it could be seen that on Figure 1). It could be proposed that crystal growth rate (lowering speed in the case of Bridgman method) has to change if it is want to obtain single crystals with various contain of Mn, which is in accordance with equation for distribution of constituents.

4. Conclusion

The $Pb_{1-x}Mn_xTe$ lattice constants grown by Bridgman method agree to Vegard's law, while $Pb_{1-x}Mn_xTe$ layer deposited both on BaF_2 and KCl substrate satisfied that approximately. The solution of 5 vol.% Br_2 in an HBr at the room temperature after exposure for 2 minutes is determined as a suitable polishing solution. The solution of 20g KOH in 1 ml H_2O_2, 2ml glycerol ($C_3H_8O_3$), and 20 ml H_2O at the room temperature after exposure for 6 minutes was found to be a suitable etching solution.

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