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Crystal Growth and Properties of PbI_2 Doped with Fe and Ni

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Abstract—A procedure is described for doping PbI_2 single crystals with Fe and Ni during vapor-phase growth in a closed system in the presence of excess iodine. The rate of mass transport in the system and the doping level of the crystals are shown to be governed by the dopant content in the source material and the source temperature. The effect of Fe and Ni doping on the low-temperature (5 K) exciton photoluminescence spectrum of PbI_2 is discussed.

INTRODUCTION

PbI_2 layered crystals are of scientific interest for gaining greater insight into electronic processes in highly anisotropic systems and have considerable potential for use in nonlinear optical devices and x-ray and gamma detectors [1–3]. Doping of PbI_2 single crystals with 3*d* transition metals is of interest for the development of new materials—quasi-two-dimensional diluted magnetic semiconductors [4].

The vapor-phase growth of PbI_2 crystals in a closed system in the presence of excess iodine was described in [5–7]. The vapor-phase growth of PbI_2 crystals doped with Fe and Ni has not yet been investigated in sufficient detail.

The purpose of this work was to study the effect of transition-metal dopants on the rate of mass transport in crystal growth of PbI_2, the quality of the resultant crystals, and their photoluminescence (PL) spectra.

EXPERIMENTAL

Given that the introduction of elemental dopants (M = Fe or Ni) adds much complexity to processes in the PbI_2–I_2 system, the dopants were introduced in the form of MI_2 or PbI_2–MI_2 alloys.

FeI_2 and NiI_2 were synthesized from stoichiometric high-purity ($\leq 10^{-5}$ at % impurities) elemental mixtures, which were sealed in silica ampules under vacuum. The ampules were mounted in a two-zone furnace and held for 3–5 h at a source temperature of 1000–1200 K and deposition temperature of 700–750 K. For further purification, the synthesized iodides were transferred to precleaned silica ampules, which were sealed off under vacuum and placed in a lower gradient (8–10 K/cm) furnace, in which the source temperature was 880–900 K, and the deposition temperature was 700–750 K. After synthesis and purification, FeI_2 and NiI_2 were stored in evacuated ampules.

For mass transport studies, 2 g of a PbI_2–MI_2 alloy (0.001–2 at % M) or mixture of PbI_2 and MI_2 (5–30 at % M) and a capillary containing iodine were sealed in an ampule under vacuum. Next, the capillary was opened, and the ampule was mounted in a gradient furnace so that the charge was situated in the low-temperature zone and melted. After homogenization for 2 h, the thermal conditions were set to initiate crystal growth, which was conducted for 2–4 h. After cooling and opening the ampule, the grown single crystals were withdrawn, and the residual charge (alloy) was weighed.

The dopant concentration in the source material and crystals was determined by x-ray microanalysis. The structural perfection of the crystals was examined on optical and scanning electron microscopes.

Low-temperature PL spectra were measured near the main excitonic transition in PbI_2 crystals. Excitation was provided by the 442.1-nm cw He–Cd laser line. The spectral slit width was 0.02 nm. Thermal control during measurements near 5 K was accomplished with a well-proven UTREKS system.

RESULTS AND DISCUSSION

The doping level of vapor-grown crystals depends primarily on the dopant content of the source material and the temperatures of the source and deposition zones. In addition, at considerable dopant (MI_2) concentrations in the system, the doping level of the crystals is also influenced by the relationship between the rates of PbI_2 and MI_2 transport. The effect of process parameters on the rate of PbI_2 transport in the absence of impurities was studied experimentally and theoretically in [6]. In this work, mass transport was studied

Table 1. Doping of PbI_2 with Fe (FeI_2)

Run no.	at % Fe (alloy)	Flux $\times 10^5$, mol/(m^2 s)	Results
1	0.5	4.41	PbI_2 single crystals 10×1 mm^2 in area containing ~0.03 at % Fe
2	1	3.47	Crystals 3×1 mm^2 in area containing 0.1 at % Fe
3	3	2.94	Single crystals 2×1 mm^2 in area containing ~0.2 at % Fe
4	5	2.29	No PbI_2 crystals; deposition of polycrystalline material in the 630- and 690-K zones
5	10	1.5	Deposition of polycrystalline material in the 690-K zone

Note: At a source temperature of 1120 K, we obtained small PbI_2 single crystals containing ~0.3 at % Fe from an alloy containing 6 at % Fe.

Table 2. Doping of PbI_2 with Ni (NiI_2)

Run no.	at % Ni (alloy)	Flux $\times 10^5$, mol/(m^2 s)	Results
1	0.5	4.32	PbI_2 single crystals 5×1 mm^2 in area containing ~0.02 to 0.03 at % Ni
2	1	3.56	Crystals 3×1 mm^2 in area containing 0.2 at % Ni
3	3	3.04	Crystals 2×1 mm^2 in area containing 0.3–0.4 at % Ni
4	6	2.54	No single crystals; deposition of polycrystalline material in the 630- and 760-K zones
5	10	1.72	No single crystals; deposition of polycrystalline material in the 760-K zone

Note: At a source temperature of 1120 K, we obtained small single crystals containing ~0.7 at % Ni from an alloy containing 7.2 at % Ni.

under the optimal conditions for the crystal growth of undoped PbI_2: source temperature of 770 K, deposition temperature of 650 K, iodine overpressure of 8.5 kPa (PbI_2 flux of 4.5×10^{-5} mol/(m^2 s)), and growth time of 2–4 h. The rate of FeI_2 and NiI_2 transport was found to be an order of magnitude lower than that of PbI_2 transport.

The Fe and Ni contents of the source material were varied from 0.001 to 30 at %. The rate of PbI_2 transport and the doping level of the grown crystals were determined as functions of the dopant concentration in the source under the optimal conditions for the crystal growth of undoped PbI_2 and also as functions of the source temperature at a fixed dopant content of the source material.

At dopant contents of the source from 0.001 to 0.1 at %, the rate of mass transport was on the same order as in the undoped system. The dopant concentration in the crystals was found to be proportional to that in the source material.

Our results on mass transport and crystal quality at dopant contents from 0.1 to 30 at % are summarized in Tables 1 and 2. At dopant contents of the starting alloy from 0.1 to 0.5 at %, the reduction in the rate of PbI_2 transport was within 5%, but the dopant content of the crystals was an order of magnitude lower than that of the source.

The introduction of 0.5 to 5 at % dopant (Fe, Ni) reduced the PbI_2 deposition flux by a factor of 1.5–2, obviously because of the increase in MI_2 concentration in the vapor phase. The dopant content of the crystals was an order of magnitude lower than that of the alloy. With increasing MI_2 concentration in the source material, the crystal size decreased, and the deposition zone broadened (toward higher temperatures) owing to the deposition of polycrystalline material. As the dopant content of the source material was raised from 5 to 10 at %, the rate of mass transport dropped by a factor of 2, and another, well-defined deposition zone (670–770 K) appeared. In the 630- to 660-K zone, polycrystalline material containing ~0.1 at % dopant was deposited. Increasing the source temperature to 1020–1090 K increased the rate of mass transport and led to the growth of small crystals containing 0.5–2 at % dopant in the 640- to 660-K zone.

At dopant contents from 10 to 30 at % and a source temperature of 1270 K, no crystal growth occurred: mass transport increased markedly, and polycrystalline material containing 3–5 at % dopant was deposited.

X-ray microanalysis data indicated that the dopant profile in the crystals grown from alloys containing 1–5 at % dopant was nonuniform.

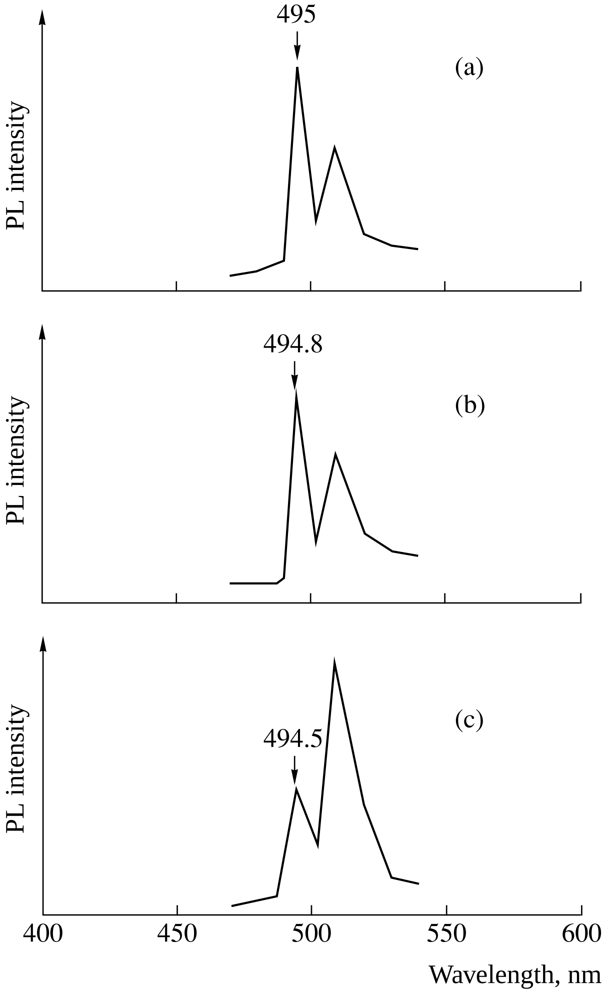

Fig. 1. 5-K PL spectra of PbI_2 crystals doped with (a) 0.001, (b) 0.005, and (c) 0.01 at % Ni.

In the case of separate PbI_2 and MI_2 sources, MI_2 was found to react with PbI_2 in the source zone. The reaction had a significant effect on the rate of mass transport and impeded control over the doping process. For this reason, the doping process and the effect of doping on PbI_2 transport could only be studied with PbI_2–MI_2 alloys as evaporation sources.

Understanding the processes involved in the doping of PbI_2 crystals with transition-metal ions requires knowledge of the vapor composition in the PbI_2–MI_2 system.

The study of the exciton spectra of doped semiconductors is of special interest because the shape of exciton luminescence peaks is very sensitive to various lattice defects, which allows one to gain detailed information about microscopic processes in crystals. The low-temperature (5 K) exciton PL spectra of the vapor-grown PbI_2 single crystals doped with Fe or Ni to 0.001–0.01 at % during growth indicate that doping has the following effects on the structural and optical properties of the crystals:

1. Doping leads to predominant growth of 4*H*-PbI_2 crystals (different PbI_2 polytypes can be identified readily be decomposing exciton resonances [8]).

2. Doping during vapor growth gives rise to one-dimensional structural disordering: formation of stacking faults in the 4*H* polytype.

3. Increasing the doping level leads to a nonlinear broadening and weakening of the exciton peak.

Typical low-temperature (5 K) PL spectra of Ni-doped PbI_2 crystals are shown in Fig. 1. Increasing the Ni content from 0.001 to 0.01 at % shifts the exciton peak to shorter wavelengths by 0.5 nm and reduces its intensity. Moreover, the full width at half maximum (FWHM) of the exciton peak increases by almost a factor of 2, from 26 to 46 meV.

Table 3 lists the spectral parameters of the exciton luminescence in doped PbI_2 crystals. It can be seen that the parameters are monotonic, nonlinear functions of dopant content. The concentration coefficient of peak position is dE/dN = 2.5 meV for both Fe and Ni, whereas the concentration coefficient of broadening, d(WHM)/d*N*, for Ni doping is almost twice that for Fe doping.

Table 3. Parameters of the exciton luminescence in doped PbI_2 crystals

Dopant	at %	λ, nm	FWHM, meV	Relative intensity	dE/dN, meV	d(FWHM)/dN, meV
Ni	0.001	495	26	1	2.5	20
	0.005	494.8	40.5	0.71		
	0.01	494.5	46	0.44		
Fe	0.001	495.2	37	1	2.5	10.5
	0.005	494.7	42	0.71		
	0.01	494.1	47.5	0.55		

Note: λ is the peak position, dE/dN is the concentration coefficient of peak position, and d(FWHM)/dN is the concentration coefficient of broadening.

To understand the origin of the nonlinear variation of FWHM and $E(N)$ with dopant content and predict the coefficients dE/dN and $d(\mathrm{FWHM})/dN$, quantitative analysis of the doping effect on the parameters of exciton luminescence is needed. The potential field of impurity centers is the most difficult to analyze theoretically. In the case of the interaction between excitons and impurities with a short-range potential, the FWHM of the exciton peak is expected to be a weak function of N at low doping levels and to vary as $N^{1/2}$ at limiting N values [9]. For impurities with a long-range potential, the FWHM is expected to vary as N^2 at low N and as $N^{1/2}$ at high N values, almost sufficient for the formation of substitutional solid solutions.

Earlier results for doped PbI_2 [10, 11] suggest that, to understand the variation of FWHM and E with N, one must take into account both the doping effect on the internal structure of the exciton (and the longitudinal–transverse splitting Δ_{L-T}) and the exciton–impurity interaction during exciton migration over the crystal with consideration for the spatial distribution of the interaction potential.

CONCLUSIONS

The present results demonstrate that PbI_2–MI_2 (M = Fe, Ni) alloys are suitable evaporation sources for doping PbI_2 single crystals with Fe and Ni during vapor-phase growth. The introduction of 0.001–0.5 at % Fe or Ni into the PbI_2–I_2 system has little effect on the rate of mass transport (a reduction in PbI_2 deposition flux by 5%). Increasing the dopant content of the source material from 1 to 30 at % decreases the rate of mass transport by a factor of 2–3 and reduces the number of grown crystals and their size, to the extent that only polycrystalline material is deposited. At doping levels above 0.1 at %, the dopant content of the crystals is an order of magnitude lower than that of the source material. To obtain PbI_2 single crystals doped with Ni or Fe to a level of several percent, the source temperature must be raised by 100–200 K.

Doping PbI_2 crystals with 0.001–0.01 at % Fe or Ni leads to a reduction in the intensity and nonlinear broadening of the exciton peak in the low-temperature PL spectra of the crystals.

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