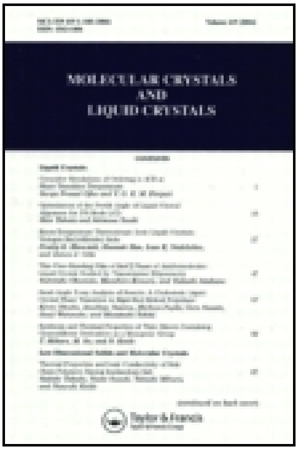

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F. V. Motsnyi [a]
[a] Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, 45, pr. Nauky, 252028, Kyiv, Ukraine

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Technology of Intercalation and New Effects in PbI_2 Single Crystals Intercalated by Hydrazine

F. V. MOTSNYI*

Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, 45, pr. Nauky, 252028 Kyiv, Ukraine

The hydrazine intercalated lead iodide single crystal technology was developed. A new type of excitons named as interlayer excitons is described. The amplification of polariton emission (Sugakov's phenomenon) and the structure phase transition under intercalation are found and studied.

Keywords: intercalation; lead iodide; hydrazine; polariton emission; phenomenon; interlayer excitons; polytypic transitions; optical spectra

INTRODUCTION

Layer semiconductors have high anisotropy of chemical bonding. They are considered as intermediate class between 2D- and 3D- solids, between molecular and ion-covalent crystals. Therefore the new phenomena can be observed in physical properties of layer crystals.

The present work devoted to investigation of new effects in intercalated layer crystals.

INTERCALATION METHODS

Lead iodide is a classical material for intercalation. As an intercalator to 2H-PbI_2 single crystals we choose hydrazine (N_2H_4) without water because it introduced well into interlayer space. But hydrazine is more explosive substance than nitroglycerine. Therefore we created a chamber [1] which ensures prevention of accidents and excludes the possibility of introducing of water in the lattice. The chamber is a glass tube (Figure 1) with three parts

* E mail: motsnyi@sun.semicond.kiev.ua

filled by dry air. The mixture of hydrazine and barium oxide (BaO) (for the absorption of remains of moisture) is situated in the low part of the tube.

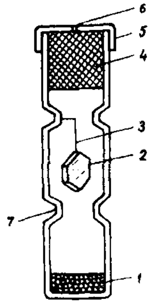

FIGURE 1. A schematic view of the glass chamber for intercalation.
1 – the N_2H_4 intercalator and the BaO absorbent, 2 – the sample, 3 – the glass thread, 4 – the KOH or BaO dryer, 5 – the cork, 6 – the hole, 7 – the narrowing.

The sample is suspended on a glass thread in the middle part of the tube. The upper part of the tube is isolated from outside by the dryer consistir.g of potassium hydrate (KOH) or BaO. The dryer is closed by a cork with a hole to reduce of pressure. The intercalation process consists in the following. The hydrazine vapours diffuse slowly through the narrowing. The sample absorbs hydrazine molecules and changes the colour that takes possibility to control lightly this process. The N_2H_4 intercalated lead iodide single crystals were prepared by this method.

Later we created the experimental setup which allows to get the N_2H_4 intercalated single crystals with given hydrazine concentration by means of the weighting of samples in process of intercalation.

SUGAKOV'S PHENOMENON

Polariton effects in layer crystals are studied insufficiently. The lines 4955 and 4964 Å in photoluminescence (PL) spectra of 2H-PbI_2 layer single crystals are caused by polariton of upper and low polariton branches [1-3] that indicates on the high quality of used samples.

The polariton emission is described by the following equation:

$$I_{PL}=\sum_{r=1}^{2}\int_{0}^{\infty} W_r(x,E)\exp(-\alpha_r(E)x)\,T_r(E)\,\rho(E)\,\Delta\Omega_r(E)\,\Delta E\,dx \quad (1)$$

were $W_r(x,E)$ is the probability of arising of r-branch polariton per unite time in point x of crystal with energy E and wave vector $\boldsymbol{k}$, $\alpha_r(E)$ is the absorption coefficient, $T_r(E)$ is the transition coefficient of polariton by the boundary of crystal, $\rho_r(E)$ is density of polariton states, $\Delta\Omega_r(E)$ is solid angle.

In polariton PL of initial and interercalated by hydrazine (N_2H_4) 2H-PbI_2 layer single crystals we had found and investigated new phenomenon [1-4] which consists in amplification of polariton emission from the upper polariton branch with increasing of excitation intensity of light, concentration of intercalated molecules (atoms), temperature and so on.

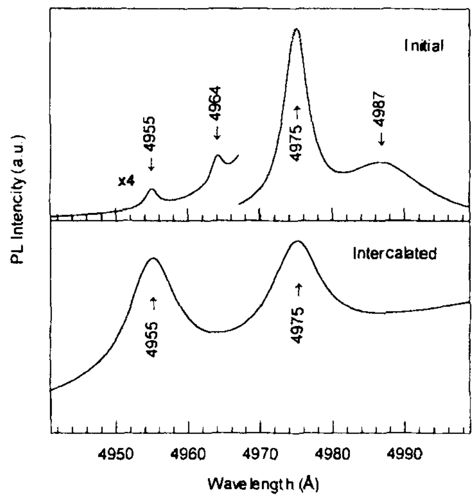

FIGURE 2. Excitonic PL spectra of PbI_2 single crystals: initial and intercalated by hydrazine (T=4.2 K, $\lambda_{excit.}$=4880 Å).

This phenomenon is illustrated on Figure 2. A strong increasing of intensity of line 4955 Å and disappearance of the line 4964 Å at low concentration of hydrazine molecules. It should be notice that the line 4955 Å disappears also at high concentration of intercalated molecules.

This phenomenon was early predicated theoretically by Sugakov [5,6]. The reason of Sugakov's phenomenon is the scattering of polaritons of lower polariton branch on different defects of crystal lattice. It is found that the experimental results agree satisfactory with the theory.

INTERLAYER EXCITONS

These are excitons which localized in interlayer space on intercalated molecules (atoms). The interlayer excitons were found by Lisitsa, Motsnyi and Sergeev[7] on reflectance and photoluminescence (PL) spectra of 2H-PbI_2 layer single crystals intercalated by hydrazine molecules at T=4.2 K. The weak doublet at 4928 and 4934 Å with more intensity long wave component which lies in the range of new reflectance oscillation with λ_{min}=4926 and λ_{max}=4933 Å belong to such excitons.

The exciton localization in interlayer space on intercalated molecules (atoms) had been considered theoretically by Zinets and Motsnyi [8] for a simple model of an exciton in layer semiconductors with the valence or ionic bonding in layers and Van der Waals bonding between the layers. The exciton in such layer crystals is supposed to behave both as the 2D Wannier-Mott exciton for the motion in layer and as the Frenkel exciton for the motion between the layers (the resonance transfer of excitation between layers). Intercalated molecules are located between the lattice layers. It is shown that there are solutions of the Schrödinger equation for the exciton wave function which exponentially decrease with the distance. The criterion of interlayer exciton formation is given by the formula:

$$\gamma=(h+\delta M)/M. \qquad (2)$$

Where h is the difference of exciton energies in layer excited and non-excited by intercalated molecules (atoms), δM is the energy change of resonance intercalation between layers which are neighboring to the layer of intercalator, M is the resonance interaction energy in an ideal crystal. The energy and radius of localized state of exciton are represented by the following equations:

$$\delta E=M\gamma^2/(1+\gamma) \quad \text{and} \quad r=a/\ln(1+\gamma) \qquad (3)$$

respectively. Here a is lattice constant in direction of optical axis.

So, these characteristics of the exciton localization are determined by the values of perturbation of matrix element of the resonance interaction between layers nearest to the intercalated layer (δM) and the difference between the exciton energies for perturbed and unperturbed layers (δE). In the simplest case the localization criterion is $(-\delta E/\delta M) >> 1$.

POLYTYPIC TRANSITIONS UNDER INTERCALATION

Characteristic distribution of PL intensity between the components 4928 and 4934 Å of the doublet indicates on the formation in crystal lattice two translationaly-nonequivalent positions of N_2H_4 molecules [1,7]. Besides that, the exciton oscillation with n=1 shifts in side of higher energies with increasing of hydrazine concentration. Therefore the introduction of hydrazine in 2H-PbI_2 lattice even in low concentration would be accompany by the formation of 4H-polytype embryon.

Raman spectra of these samples are shown on Figure 3. Only in case of intercalated crystals we can observe three new bands 13.2, 50.5 and 30.7 cm^{-1}.

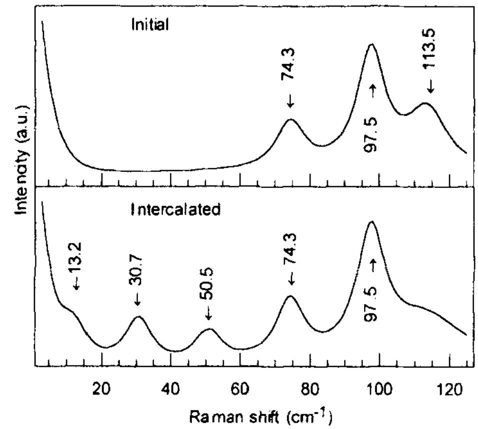

FIGURE 3. Raman spectra of 2H-PbI_2 before and after hidrazine intercalation. (T=300 K, $\lambda_{excit.}$=6328 Å).

The bands at 13.2 and 50.5 cm^{-1} belong to 4H-PbI_2 polytype. The band at 30.7 cm^{-1} is caused by hydrazine.

So, the presented data allow us to make the unambiguity conclusion about polytypic transition under intercalation.

The polytype transition 2H-PbI_2→4H-PbI_2 at intercalation differs from one caused by temperature annealed high stability in the time. This effect can be explained by the form of interlayer hydrazine more strong bondings with neighbor layers for example a type of "covalent bridges" [9].

CONCLUSIONS

On the base of studies of reflectance, PL and Raman spectra of 2H-PbI_2 initial and intercalated by hydrazine layer single crystals with different states of surface we have found the following new effects:

- Sugakov's phenomenon in polariton emission.
- Interlayer excitons.
- Polytypic transitions under intercalation.

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