APPLICATION OF LAYERED InSe AND GaSe CRYSTALS AND POWDERS FOR SOLID STATE HYDROGEN STORAGE

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Introduction

Distinctive feature of layered crystals is sharp anisotropy of chemical bonds - strong ion-covalent inside crystal layers and weak van-der-Waals between them. For InSe and GaSe crystals volume of van-der-Waals gap makes under the attitude to all volume of a crystal about 40 - 45 %. Therefore given space gap easily includes atoms and even small organic molecules, which is capable essentially change optical and electrical properties of these crystals.

Results and discussion

In present work bulk γ-InSe (spatial group C^5_{3v}) and ε-GaSe (D^4_{6h}) single crystals were grown using the Bridgman method. Hydrogen intercalation of single crystal samples (thickness d=10-20μm) was carried out using the electrochemical method from 0.1 normal solution of hydrochloric acid with sweeping electric field in the galvanostatic regime. The hydrogen concentration in H_xInSe and H_xGaSe was determined via the quantity of electrical charge transported through the sample placed into the special cell. Here x is the amount of introduced atoms per one formula unit of the crystal bulk.

Conducted investigations of hydrogen intercalation in layered InSe and GaSe crystals shown that hydrogen in atomic state enter in van-der-Waals gap and forms H_2 molecules which with the growth of hydrogen concentrations up to x=2 have a tendency to occupy translation ordered states in the gap and causes there a pressure resulting in experimentally observed and predicted by our calculations growing interlayer lattice parameter C_0.

At x=2 and T<80K this state of H_2 in the gap can be treated as quazy-liquid monolayer. At x>2 atomic hydrogen begins to incorporate into interstices of the crystal lattice due to quantum-size effects arise in the gap and strong repulsion of between H_2 molecules.

It was found that the observed at T=80K non-monotonic shift of the n=1 exciton absorption band peak with x stems from the increasing dielectric permeability ε_0 of the crystal due to presence of H_2 molecules in the gap. A growth of exciton anisotropy parameter $\varepsilon^*(x)$ at x<0.5 results in decrease of the exciton binding energy R_0. When $\varepsilon^*(x)$ exceed critical value $\varepsilon^* \leq 2$ (at x > 0.5), 2D localization of exciton motion in the crystal layer plane followed by growth of R_0 takes place, which causes, reduction and then at x>1 stabilization of sizes both for the exciton and quantum well.

Deintercalation of hydrogen from H_xInSe and H_xGaSe crystals was carried out for 3 - 9 hours at T=110^0C using permanent pumping out. Degree of their deintercalation increases linearly from 60% at $x \to 0$ up to 80-85 % at $x \to 4$. The further investigation of intercalation-deintercalation processes of a given crystal powders with size of grains about 1-5 μm have shown that the concentration of hydrogen can reached x=6 and degree of deintercalation achieved values up to 90 %. Repeated cycles of hydrogen intercalation-deintercalation do not result in essential worsening of physical parameters of InSe and GaSe crystals.

Conclussions

Conducted investigation shown that layered InSe and GaSe crystals and their powders may be considered as working elements for solid state hydrogen storage.