ON THE POSSIBILITY TO USE SOME LAYERED CRYSTALS FOR HYDROGEN ACCUMULATION

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Layered crystals possess high anisotropy of chemical bonds: ion-covalent bonds inside their layers and van-der-Waals ones between them. As a result, the interlayer space (size of which, e.g. in InSe and GaSe crystals, comprises approximately 40 to 45% of the total crystal bulk) rather easy takes impurity atoms as well as small organic molecules.

In this work, the samples of semiconductor single crystals γ-InSe and ε-GaSe grown using the Bridgman method were placed in accord with [1] into solution of hydrochloric acid and intercalated electrochemically with hydrogen by using the method of sweeping electric field. The hydrogen concentration in intercalates was determined measuring the charge amount passing through the sample.

Adduced in this work are the results of NMR, X-ray diffraction, electron-microscopic, energy-dispersion and electrophysical investigations of semiconductor layered GaSe and InSe crystals.

In particular, NMR study allowed to amend the model for hydrogen penetration into these layered crystals offered in [1] and to show that:

a) intercalated hydrogen enters both to intralayer and interlayer spaces mainly in the molecular state H_2;

b) in the case of low concentrations $\boldsymbol{x} < 2.0$ (where $\boldsymbol{x}$ is the number of hydrogen atoms per one formula unit of the crystal), H_2 molecules are mainly located in interlayer spaces, and only very little amount of them is inside the layers as well as in the regions of lattice spatial defects. While for $\boldsymbol{x} > 2.0$, the H_2 amount in the layer space is essentially increased.

At the same time, our electrophysical study shows that the concentration of free electrons in InSe crystals at $T = 80$ K after their intercalation with hydrogen increases from $n = 1{\bullet}10^{15}$ cm^{-3} up to $1{\bullet}10^{16}$ cm^{-3}. Using the analogy with metal hydrides, one can draw a conclusion that in the process of intercalation hydrogen corresponds not only to H_2 molecules but atoms as well, which are chemosorbed within the range of point (e.g., In, Ga vacancies) and spatial defects (dislocations) in crystalline lattice where broken bonds take place. In the process of hydrogen chemosorption, created in these regions are additional structural defects that result in creation of shallow donor levels D^0_H located by 5 to 7 meV lower than the conduction band bottom.

Therefore, at the temperatures $T \geq 80$ K donor ionization $D^0_H \rightarrow D^+_H$ +e takes place, which is accompanied by electron transition into conduction band of the crystal. At the same time, as shown by calculations, the concentration of protons H^+ chemosorbed inside layers is 4 to 5 orders lower than that of molecular hydrogen, i. e. it is comparable with the concentration of intrinsic point defects in this crystalline structure. By another words, we deal with hydrogen passivation of broken bonds.

Our estimations as to perspectives of using the layered crystals InSe, GaSe, GaS as solid state accumulators for hydrogen show that in powders made of these crystals the mass fraction of accumulated hydrogen at $\boldsymbol{x} = 6$ can reach 1.5; 2.03 and 2.25 % of the total mass, respectively. And presented results can be used when creating various prototypes of operation elements in solid state hydrogen accumulators based on low-dimensional structures.

References

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