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Relaxation Polarization in Hydrogenated GaSe Layered Crystals

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The dielectric properties of hydrogenated Gallium Selenide crystals are investigated. It is shown that the frequency dependences of ε′ and ε″ permittivity components in H_xGaSe have relaxation character and are described by the Cole-Cole distribution.

Keywords: gallium selenide, permittivity, polarization.

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Introduction

The insertion of hydrogen atoms, which have high diffusion mobility, into the matrix of layered III-VI semiconductors allows to vary smoothly the properties of initial crystals and can lead to new physical effects as hydrogen atoms form an intrinsic impurity subsystem. Furthermore, such hydrogen-containing materials are attractive for hydrogen energy [1].

The results of the study of hydrogen insertion into GaSe layered semiconductor crystals from gas phase are reported in [2, 3]. It was shown that the concentration of the hydrogen inserted into H_xGaSe at high pressure (4.2 - 4.7 MPa) is 0.47-2.22 formula units. Electrical and optical (in the exciton absorption region) properties were also investigated. Electrical impedance-spectroscopic measurements of hydrogenated GaSe crystals were carried out in [4]. The relaxation character of polarization processes in these materials was established.

In this work we report the results of investigations of the relaxation polarization in H_xGaSe single crystals.

I. Experimental

The initial GaSe crystals (ε-modification, space group D^1_{3h}) were grown by the Bridgman method. The hydrogen insertion from gas phase was carried out by the volumetric gas method using a Siverts equipment during two hours. The first group of the samples was hydrogenated at a temperature of 290 K and at a pressure of 4.56 MPa, and the second one – at 470 K and 3.04 MPa. Rectangular samples for the measurements had dimensions of 5×5×1 mm^3 with ohmic contacts, which were prepared using In-Ga eutectic.

The dielectric properties of the H_xGaSe crystals were investigated by the dielectric spectroscopy method by using a “Solartron 1255 FRA” frequency response analyzer (frequency range is 1–10 MHz, amplitude of a sinusoidal signal is 100 mV). The real part of dielectric constant (ε') was defined as the sample capacity to geometric capacitance ratio, and the imaginary part is $\varepsilon'' = \varepsilon' \cdot \mathrm{tg}\,\delta$, where δ is the dielectric loss angle.

II. Results and discussion

Similarly to metals [5], hydrogen insertion from gas phase into GaSe single crystals can occur into the tetrahedral and octahedral cavities between neighboring layers. Physical processes in hydrogenated crystals are associated with the diffusion of hydrogen atoms due to thermal lattice vibrations. At low temperatures the quantum mechanism of diffusion, sub-barrier tunneling of hydrogen atoms from one interstitial site to another, is possible whereas the over-barrier diffusion mechanism takes place at higher temperatures [6]. Lattice structure defects (point defects, dislocations, stacking faults, etc.) can be considered as some traps for hydrogen atoms. In metals hydrogen preferably is in atomic state and rarely in the state of proton H^+ or ion H^- in dependence on binding energy. But in the case of semiconductors hydrogen can easily interact with dangling bonds or to be in molecular state due to a low binding energy [7].

The frequency dependences of ε' and ε" in the hydrogenated H_xGaSe samples (Figs 1 and 2) have the shape typical for relaxation processes. They can be approximated by a function, which takes into account the relaxation polarization described by Cole-Cole distribution [8] and the dielectric losses due to

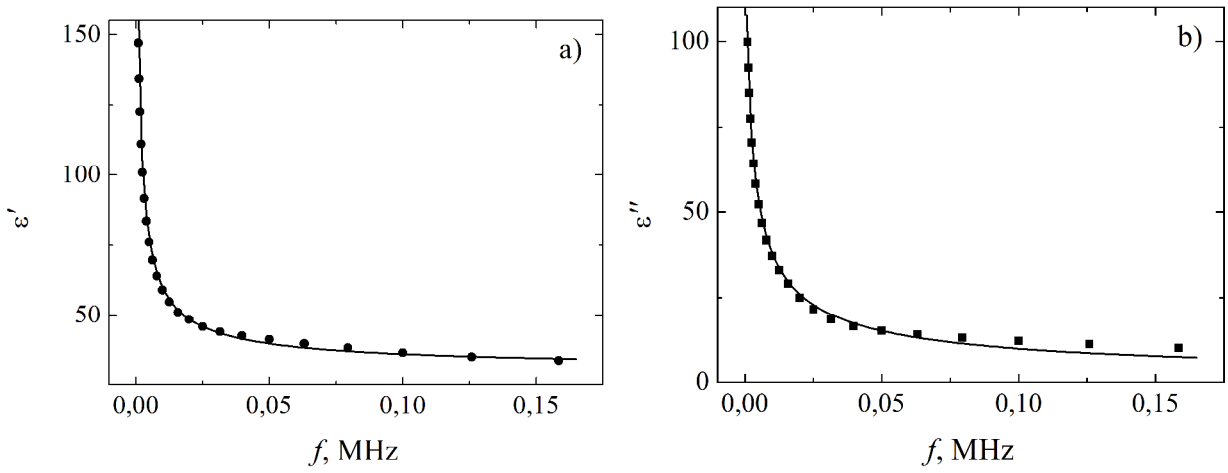

Fig. 1. Frequency dependences of the effective values of the permittivity ε'(*f*) and ε"(*f*) components for H_xGaSe single crystals (sample 1).

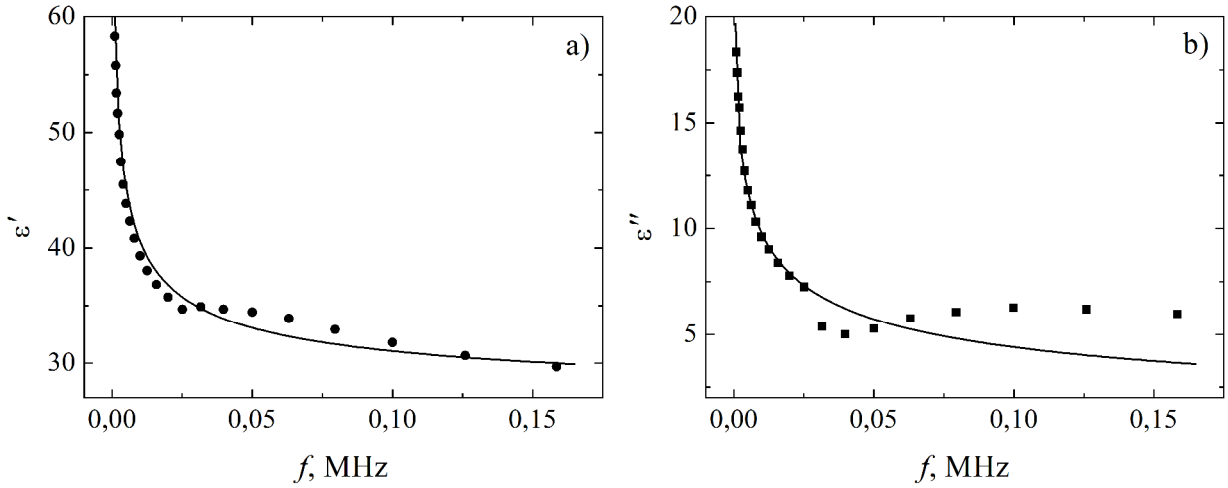

Fig. 2. Frequency dependences of the effective values of the permittivity ε'(*f*) and ε"(*f*) components for H_xGaSe single crystals (sample 2).

conductivity of the sample:

$$e = e_\infty + \frac{e_0 - e_\infty}{1+(iwt)^{1-a}} - i\frac{s}{e_0 w}, \qquad (1)$$

From Eq. (1) we obtain

$$e' = e_\infty + (e_0 - e_\infty)\frac{1+(wt)^{1-a}\sin\frac{pa}{2}}{1+2(wt)^{1-a}\sin\frac{pa}{2}+(wt)^{2(1-a)}} \qquad (2)$$

$$e'' = (e_0 - e_\infty)\frac{(wt)^{1-a}\cos\frac{pa}{2}}{1+2(wt)^{1-a}\sin\frac{pa}{2}+(wt)^{2(1-a)}} + \frac{s}{e_0 w} \qquad (3)$$

where τ is the average relaxation time, α is the parameter, which determines the width of relaxation time spectrum ($0 < \alpha < 1$), σ is the conductivity, ε_0 is the dielectric constant, and ω is the cyclic frequency. The closer α to 1 is, the more broad distribution function of relaxation times becomes, and at $\alpha = 1$ expression (1) turns into the Debye distribution of frequencies. The Cole-Cole distribution has used to describe materials, which are characterized by more broad dispersion range than in the case of the Debye distribution.

Our approximation of the experimental data based on Eqs. (2) and (3) was carried out by means of the least squares method. The initial settings for the approximation were chosen starting from the experimental data and the results of [4]. The obtained dependences of ε'(*f*) and ε"(*f*) are shown in Figs 1 and 2 (solid lines). The average errors were 4.9 % for ε' and 7.9 % for ε" (sample 1) and 3.9 % for ε' and 12.4 % for ε" (sample 2).

It is seen from Figs 1 and 2 that the approximation results quite well correlate with the experimental data. Some discrepancy can be explained by the contribution of several various relaxation processes to the permittivity.

Taking into account the relaxation time value ($\tau \approx 0.15$ - 0.17 ms) obtained from the approximation it can be assumed that in the H_xGaSe crystals the dipole-relaxation polarization occurs due to a large number of point defects. According to [9], at high concentrations of defects, which create energy levels in band gaps, different dynamic effects caused by a hopping exchange

by charges between the defects can be observed in semiconductors. As a result, the quasidipoles oriented in the same direction appear (for example, an impurity ion - the nearest anion or a lattice imperfection) [10]. They lead to additional polarization and electrons participate in the hopping conduction during the hopping. These dipoles can cause an increase in the permittivity of the crystals.

Conclusion

In paper carried out approximation of the frequency dependences of ε' and ε" indicates on the occurrence of a wider distribution of the relaxation times in the H_xGaSe crystals than that in the Debye case. The average value of the relaxation time in the samples has been determined. It was established that in the analysis of the ε'(f) and ε"(f) dependences the available conduction should be taken into account.

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Релаксаційна поляризація у воденьмісних шаруватих кристалах GaSe

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Досліджено діелектричні властивості воденьмісних кристалів селеніду галію. Показано, що отримані частотні залежності компонент ε′ і ε″ діелектричної проникності в H_xGaSe мають релаксаційний характер і описуються формулою Коул-Коула.

Ключові слова: селенід галію, діелектрична проникність, поляризація.