Dielectric characteristics of GaSe nanocrystals intercalated with hydrogen

V.M. Kaminskii, Z.D. Kovalyuk, V.V. Netyaga, and V.B. Boledzyuk
I.M. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Chernivtsi Department
5, Iryna Vilde str., 58001 Chernivtsi, Ukraine; e-mail: chimsp@ukrpost.ua

Abstract. The results of investigations of dielectric characteristics of GaSe nanocrystals and their hydrogen intercalates are presented. By using the impedance spectroscopy method, it is established that the dielectric spectra of GaSe and H_xGaSe (x = 0.07 and 0.14) nanocrystals correspond to the exponent law of dielectric response. It is found that there is an increase of the dielectric constant ε_∞ for the intercalated samples in comparison with that of the initial sample. We have obtained the frequency dependences of the real and imaginary parts of the conductivity, whose dispersion is due to the presence of two-dimensional defects. Equivalent electrical circuits which determine electrical characteristics of the crystals under study are proposed.

1. Introduction

The anisotropy of physical properties of layered III-VI semiconductors is caused by peculiarities of their crystal structure and can be essentially increased when they are in a form of nanocrystals, as well as due to topochemical reactions of intercalation (the insertion of foreign atoms into the interlayer spaces). The insertion of hydrogen into the lattice of layered materials makes it possible to apply intercalation systems for the preparation of hydrogen-containing materials with high hydrogen content, hydrogen sensors, and solid electrolytes with high proton conductivity [1, 2].

Earlier, the electrical and optical properties of hydrogen-containing GaSe and InSe crystals were investigated in [3-5]. In this work, we present the result of investigations of dielectric characteristics of GaSe nanocrystals intercalated with hydrogen.

2. Experimental

Single crystals of GaSe were grown by the Bridgman method from a stoichiometric melt. By using the Weissenberg method, it is found that the grown GaSe crystals belong to the ε-modification (space group D_{3h}^1).
Nanopowders of GaSe were obtained by means of the ultrasonic treatment of micron-sized powders (a grain dimension of about 75 μm) in a liquid medium (acetone or ethyl alcohol) under cavitation conditions. From the X-ray data, it is established that the average dimensions of the obtained nanoparticles are 70 to 75 nm along the crystallographic direction [001] [6]. The obtained nanoparticles were pressed at a pressure of 10^7 Pa into disks of 9 mm in diameter and 2.3 mm in thickness destined for further investigations.

Intercalation of GaSe nanopowders with hydrogen has been carried out by the method of "drawing" electrical field from a 0.1 N aqueous solution of HCl at potentials that are below the potential of hydrogen reduction from this solution (φ = 0.36 V with respect to AgCl electrode). The density of inserted protons was determined from the amount of charge carried out through an intercalation cell by measuring the current density and the intercalation time [7].

Room-temperature impedance spectra were measured by means of an impedance spectrometer "Solartron 1255" in the frequency range 0.1 to 10^6 Hz at an applied signal of 100 mV.

3. Results and discussion

Figure 1 shows the measured frequency dependences of complex capacitance $C^* = C' - jC''$ for nanocrystalline samples of GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe. It was established in [8] that the dielectric spectrum of low-resistance GaSe single crystals correspond to the universal exponential law
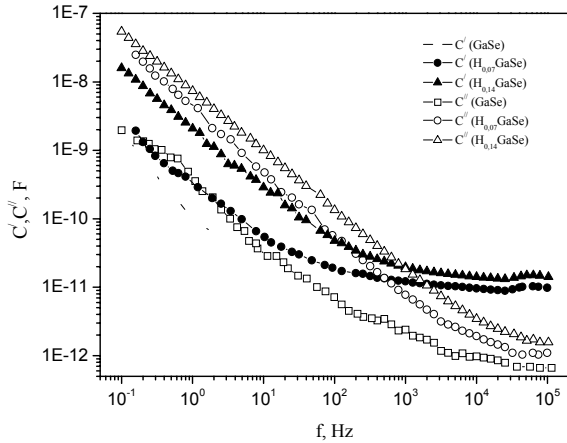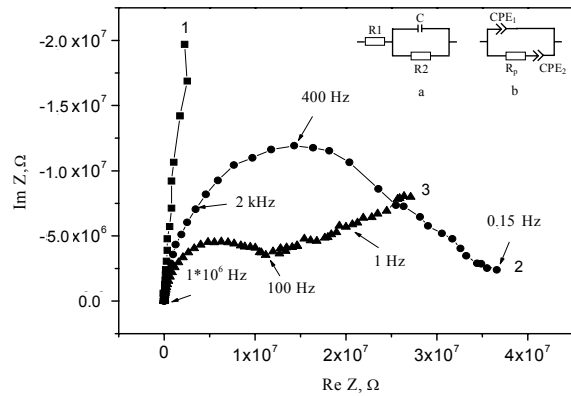
Fig. 1. Dielectric spectra expressed in the form of complex capacitance for nanocrystals of GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe.

Fig. 2. Nyquist plots for samples of GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe (curves 1 to 3, respectively) and equivalent circuits for the initial GaSe (insert *a*) and its intercalates (insert *b*).

$$C^* = B(j\omega)^{n-1} = B\left\{\sin\frac{n\pi}{2} - j\cos\frac{n\pi}{2}\right\}\omega^{n-1} ,$$

where $0 < n < 1$ and B is a constant.

As one can see from the presented data for GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe nanocrystals under investigations (Fig. 1), the frequency dependences of C' and C'' can be also described by the exponential law at $0 < n < 1$. For the $C'(\nu)$ dependences in the high-frequency spectral range, there are linear parts with the slope angle tangent equal to zero, the linear cuts off of which at the ordinate axis correspond to the high-frequency capacitance C'_∞. Using the obtained C'_∞ values, we have established the comparative increase of the high-frequency permittivity ε_∞ for the intercalated samples in comparison with that of the initial GaSe sample which is equal to 1.02 and 1.51 for the $H_{0.07}$GaSe and $H_{0.14}$GaSe samples, respectively. This takes place because of changes in the polarization processes in the intercalated materials. At low frequencies, the $C''(\nu)$ dependences have the linear parts with the slope angle tangent equal to -1 what is due to the dc conductivity of the samples.

Figure 2 shows the Nyquist plots for the investigated nanomaterials. The presence of deformed semicircles in the high-frequency range (curves 2 and 3) is their peculiarity for the intercalated $H_{0.07}$GaSe and $H_{0.14}$GaSe samples. From the obtained data, we have established the electrical equivalent circuits of the investigated samples (Fig. 2, inserts *b* and *c*) and the

parameters of their elements (Table). Here, CPE_1 and CPE_2 are constant phase elements being used in equivalent circuits. This allows us to describe the deformed semicircles at the Nyquist plots (Fig. 2, curves 2 and 3) for the samples under investigation. The parameters Y_1 and Y_2, as well as n_1 and n_2, determine numerical values and the behavior type (resistive or capacitive) of the CPE_1 and CPE_2 elements, respectively. The parameter C_δ is the geometrical capacitance of the investigated sample. As follows from the listed data, the effective capacitance Y_1 of the CPE_1 element for the $H_{0.14}$GaSe sample is increased by several orders of magnitude in comparison with that of $H_{0.07}$GaSe, and simultaneously the resistance R_p becomes essentially decreased (by 10^8 times). On the contrary, the parameter Y_2 decreases with increase in the density of inserted hydrogen. This indicates that the circuit (CPE_1 (R_p–CPE_2)) determines the "bulk" electrical properties of porous nanopowdered H_xGaSe samples.

The availability of a weak van der Waals bonding between the layers of GaSe and a strong ionic-covalent bonding within them foreordains the possibility of the insertion of protons into tetrahedral and octahedral sites of the interlayer spaces. According to the law of hexagonal close packing [9], one octahedral and two tetrahedral empty sites correspond to each atom of Se. Additionally, as distinct from GaSe single crystals, the intercalated samples can localize hydrogen in pores.

Table. Parameters of equivalent circuits for nanocrystalline GaSe samples and their hydrogen intercalates.

Samples	CPE$_1$		R_p, Ohm·cm^2	CPE$_2$		R_1, Ohm·cm^2	C_δ, F/cm^2	R_2, Ohm·cm^2
	Y_1, cm·s$^{0.5}$/cm^2	n_1		Y_2, Cm·s$^{0.5}$/cm^2	n_2			
GaSe	–	–	–	–	–	$2.4 \cdot 10^5$	$9.3 \cdot 10^{-12}$	$1.6 \cdot 10^8$
$H_{0.07}$GaSe	$3.52 \cdot 10^{-11}$	0.92	$6.1 \cdot 10^6$	$4.49 \cdot 10^{-8}$	0.21	–	–	–
$H_{0.14}$GaSe	$2.4 \cdot 10^{-8}$	0.05	0.16	$2.95 \cdot 10^{-11}$	0.9	–	–	–
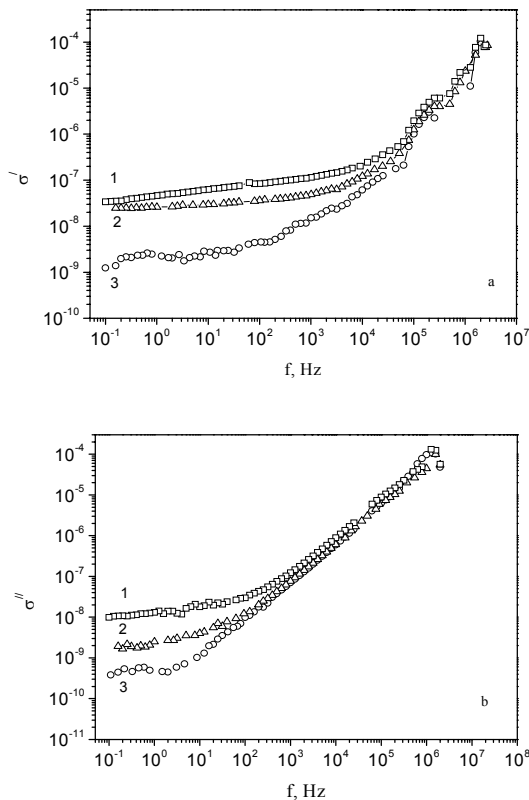
Fig. 3. Frequency dependences of the real σ' (*a*) and imaginary σ'' (*b*) parts of the conductivity of GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe nanocrystals (curves 1 to 3, respectively).

The low-frequency linear part for $H_{0.14}$GaSe (Fig. 2, curve 3), which most likely defines the electrical properties of hydrogen inserted into pores, is a result of the formation of a space charge nearby the contact electrodes due to the migration of protons of the adsorbed electrolyte to the electrodes. As the relaxation of the processes of ion migration takes place over a long period of time, it prevails in the low-frequency impedance. For the intercalated $H_{0.07}$GaSe and $H_{0.14}$GaSe samples, the obtained values of the relaxation time τ are $4 \cdot 10^{-4}$ and $2.6 \cdot 10^{-4}$ s, respectively.

Figure 3a, b shows the frequency dependences, $\sigma'(\nu)$ and $\sigma''(\nu)$, of the real and imaginary parts of the conductivity of the initial and intercalated nanocrystalline samples of GaSe (curves 1-3) (ν is the linear frequency). The increase of σ' and σ'' with frequency can be supposed to be due to two-dimensional defects (stacking faults) creating the potential barriers, which can lead to the dependence of the conductivity on frequency [10, 11]. The nonlinear behavior of $\sigma'(\nu)$ and $\sigma''(\nu)$ is probably caused by the influence of intergrain boundaries on the processes of charge transfer in the pressed nanocrystalline GaSe samples. The decrease of the real and imaginary parts of the conductivity of the intercalated samples is due to a decrease of the carrier mobility because of a deformation of the nanostructures. During the intercalation, the inserted ions deform the GaSe lattice, which follows from the X-ray investigations on broadening the rocking curves for reflection (004) obtained in the scheme of two-crystal spectrometer.

4. Conclusion

It is established that the dielectric spectra of the nanocrystalline samples of GaSe, $H_{0.07}$GaSe, and $H_{0.14}$GaSe correspond to the exponential law of dielectric response. From the carried out measurements of the impedance, we have constructed equivalent circuits which determine electrical characteristics of the investigated crystals, and the increase of the permittivity ε_∞ for the intercalated samples in comparison with that of the initial GaSe ones is found. We have obtained also the frequency dependences of the real and imaginary parts of the conductivity, whose dispersion is due to the presence of two-dimensional defects.

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