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Dielectric spectroscopy of AgI films doped Cu

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It has been found that the doping of AgI films with Cu atoms significantly reduces the concentration of equilibrium electrons. It turns out to be so small that the array of free electrons in the conduction band of the nanocrystallites of the film is not able to completely shield the external probing electric field applied to the sample in the method of dielectric spectroscopy. It is shown that this circumstance opens up the possibility of a clear observation in the study of dielectric spectra of AgI:Cu drift of free electrons, free holes, and massive silver ions. The parameters of the thermal hysteresis loop of the frequency position of the maximum function of the frequency dependence of dielectric losses [$\varepsilon''(F)$], recorded in the semiconductor-superionics OP region, are determined. The Maxwellian relaxation times for electrons, holes, and a system of „molten" silver ions are also determined.

Keywords: dielectric spectra, superionics, silver iodide, AgI films, semiconductor-superionic phase transition.

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1. Introduction

Silver iodide (AgI) exists in three different crystal modifications: γ, β and α-phases, between which thermal phase transitions may be made. The most interesting is β-α-transition, which is characterized by the fact that at $T_c = 147\,^\circ\mathrm{C}$ β-phase changes into stable α-phase, i. e. thermal superionic phase transition (PT) takes place. AgI:Cu films with thickness of 80 nm studied in this paper were synthesized on a mica substrate, which prevented passage of through current via a specimen in process of studies. Synthesis of AgI:Cu films doped with copper with copper content of around 4 and 8 vol. % was carried out by two-stage method, at the first stage of which laser ablation at mica substrate temperature of 50°C was used to apply a metal layer on it in a combination of Ag-Cu, and at the second stage of synthesis at 170°C the combined metal later was iodized.

Dielectric spectra (DS) were measured on a spectrometer from Novocontrol Technologies, in the frequency range of 10^{-2} Hz-10^7 Hz. Temperature T of the specimen varied monotonously in the range of $70-180$°C, with increment 5°C.

This article continues studying the features of the electric response in thin AgI films [1]. Its objective is the study of the effect from fill doping with an acceptor admixture (copper) at such characteristics of electric response of AgI:Cu films as frequency dependences of real $\varepsilon'(F)$ and imaginary $\varepsilon''(F)$ parts of complex dielectric permittivity $\varepsilon^* = \varepsilon' + i\varepsilon''$, and also at the ability of superionic PT in the doped AgI:Cu film. The selection of the doping degree designation in the form of „weak" or „strong" was made by the authors on the basis of the principle of the differences in the degree of effect of doping admixture at dielectric spectra of specimens.

2. Results

2.1. DS of AgI:Cu films lightly doped with copper (4 at.%)

Figure 1 presents the dependences of the real $\varepsilon'(F)$ and imaginary $\varepsilon''(F)$ parts of dielectric permittivity of AgI:Cu film specimen lightly doped with copper on frequency F applied to the electric field specimen. Frequency dependence $\varepsilon'(F)$ contains a pronounced high-frequency step and low-frequency step that appears with temperature growth. Two maxima $\varepsilon''(F)$ correspond to these steps. Figure 1 demonstrates experimental Cole-Cole diagrams — dependences $\varepsilon''(\varepsilon')$: high-frequency semi-circles and starts of low-frequency semi-circles. As this figure shows, the shape of the diagrams practically do not depend on temperature. Besides, thermal hysteresis loops were studied in the frequency position of the maximum ($F_{\max}(T)$) of the frequency dependence function $\varepsilon''(F)$ for AgI:Cu film lightly doped with copper. Dramatic rise of the heating branch is observed at 160°C, lowering of the cooling branch — at 145°C. A specific feature of lightly doped AgI:Cu films is the fact that the parameters of the loops of thermal hysteresis in the frequency position of DS features are close to similar characteristics of non-doped films [2–4]. However, for the doped AgI:Cu film the resonant frequency

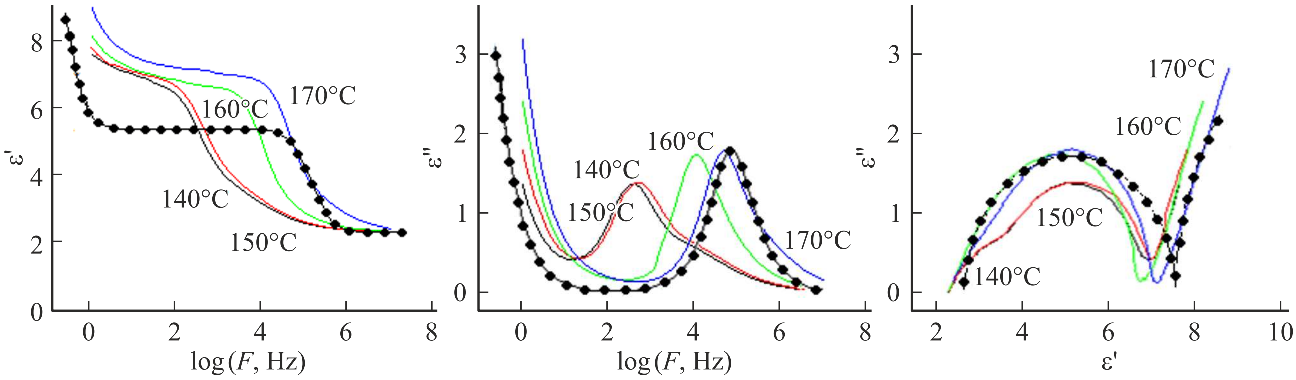

Figure 1. DS and Cole-Cole diagram of thin AgI:Cu film, lightly (4 at.%) doped with copper. The dots indicate frequency dependences calculated using formula (1) for the real ε' and imaginary ε'' parts of dielectric permittivity, CC diagram — dependence $\varepsilon''(\varepsilon')$. The calculates were made for $T = 170°C$.

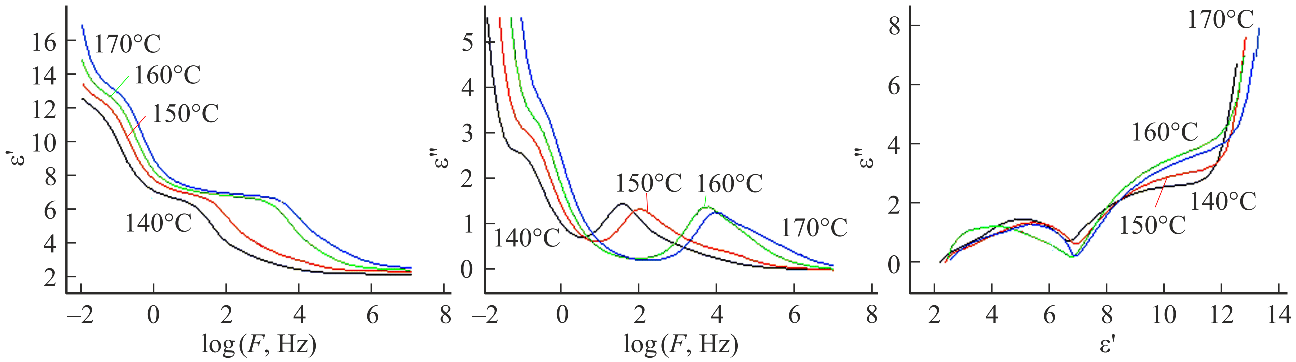

Figure 2. Frequency dependences of real ε' and imaginary ε'' parts of dielectric permittivity, and also Cole-Cole diagram of Agl:Cu film heavily doped (8 at.%) with copper in temperature range 140–170°C.

of the high-frequency step turns out to be next lower order, and its sweep is 1.5 less than for the non-doped one, which indicates the substantial effect of the copper admixture at DS characteristics.

2.2. DS of AgI:Cu films more heavily doped with copper (8 at.%)

Figure 2 presents DS of AgI:Cu film specimen with higher doping concentration (8 at.%) compared to the case described above. It turned out that in this case DS contain not two, but three steps on the curve of the function $\varepsilon'(F)$ and three maxima on the curve of the function $\varepsilon''(F)$.

Cole-Cole diagrams $\varepsilon''(\varepsilon')$ of heavily doped AgI:Cu film (8 at.%) present distorted semi-circles, they are practically invariable in the entire temperature range, except for the area of high temperatures: at $T > 160°C$ at low frequencies the considerable share of the third semi-circle is seen clearly.

The noted displacement of high-frequency features of DS in AgI:Cu doped films in the region of $T = 150–160°C$, and also appearance of the additional step of the function $\varepsilon'(F)$ and maximum of the function $\varepsilon''(F)$ at lower frequencies (10^{-2}–10^{-1} Hz) and appearance of the additional semi-circle on the Cole-Cole diagrams at temperatures above 160°C, indicate a PT of superconductor — superionic in respect to Agl:Cu at displaced $T \approx 155°C$ [5,6].

3. Calculation of dielectric spectra

DS calculations were made by us from the positions of the Debye theory. For two types of relaxers with times τ_1 and τ_2 for each type the expression for complex dielectric permittivity is as follows:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (i\omega\tau_1)} + \frac{\Delta\varepsilon_2}{1 + (i\omega\tau_2)}, \qquad (1)$$

where ω-angular frequency ($\omega = 2\pi F$), ε_∞ — high-frequency limit of real part of dielectric permittivity ε^*, $\Delta\varepsilon$ — difference between low-frequency and high-frequency limits of real part ε^*.

Curves built using formula (1) are presented in Figure 1. Frequency dependence $\varepsilon'(F)$ has two steps, dependence $\varepsilon''(F)$ — two maxima at the same frequencies, Cole-Cole diagram $\varepsilon''(\varepsilon')$ — two regular semi-circles of different diameters.

The comparison of the curves calculated according to formula (1) with the measurement results of Figure 1 shows that the Debye theory explains qualitatively the DS type of silver iodide films lightly doped with copper (4 at.%). To calculate DS of films heavily doped with copper (8 at.%), another summand with specific time τ_3 into formula (1), since additional features appear in the DS of heavily doped films.

4. Discussion

1. For lightly doped AgI:Cu films (4 at.%) the values of DS parameters depend on a certain type of relaxers. Characteristics of the high-frequency features of DS are due to the physical properties of the array of free electrons, and the low-frequency ones — of positively charged free silver ions. Displacement of DS features with growth T towards higher frequencies is explained by increased conductivity of the semiconductor as a result of increased rate of thermal generation of free electrons, i.e. decrease in time of Maxwell relaxation.

Copper is an admixture of acceptor type, and concentration of free electrons in doped AgI:Cu films turns out to be lower than in the non-doped ones. This results in the fact that the resonant frequency of the electronic component decreases when doped with copper, and the sweep of the high-frequency steps of real part of complex dielectric permittivity ($\Delta\varepsilon' = 5$) turn out to be lower than the difference $\varepsilon_0 - \varepsilon_\infty = 7$, necessary for complete screening of the external probing electric field inside film nanocrystallite and its displacement to the dielectric substrate — Figure 1. Partial screening provides for the ability to clearly observe both the drift of free electrons and the drift of massive silver ions released from partial melting of silver sublattice at temperatures above superionic PT. This manifests in the continuing thermal growth of value $\Delta\varepsilon'$ in the region of temperatures above T_c superionic transition.

2. For heavily doped AgI:Cu films (8 at.%) Maxwell relaxation time for electrons at $T = 140^\circ$C is next higher order compered to lightly doped films and two orders more compared to the non-doped ones. Besides, appearance of additional features of DS at medium frequencies is related, in our opinion, to the slow drift of heavy holes that appeared in a certain limited quantity when heavily doped with copper.

As for hysteresis events, one can state that temperature decrease by 15°C from $T_c = 155^\circ$C in this paper is not accompanied with the change in the frequency position of DS features. Hence it appears that the width of hysteresis loops in DS features is knowingly more than the specified 15°C. Detailed study of hysteresis events will be the subject of further investigations.

In general one can state that Agl film doping with copper causes displacement of high-frequency features of DS towards the low frequencies. This is explained by the reduction in the electric conductivity of a semiconductor (increased time of Maxwell relaxation) as a result of reduction of free electron concentration due to their partial capture at acceptor levels of copper. Besides, under heavy doping with copper at temperatures below PT the dielectric spectroscopy records ambipolar conductivity, i.e. hole conductivity also appears in addition to the electronic one. Besides, DS makes it possible to obtain information also about the parameters of supercooled ion liquid, which is not available for other methods of research.

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Conflict of interest

The authors declare that they have no conflict of interest.

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