Plasmon effect in DMAAS ferroelectric crystal with silver nanoparticles on their surface

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1. Introduction

Usually, the main attention is devoted to study of the nanoparticles of a noble metals influence on the properties of a matrix. On the other hand, the influence of a matrix on the plasmon effects demands a special attention. From this point of view the most interesting is study of the composite “ferroelectric crystal+nanoparticles of noble metals”. It is clear that the ferroelectric phase transitions would considerably affect the parameters of surface plasmon resonance in the above mentioned composite. So far as we know, the effects of such a type have not been investigated yet. Therefore, in this paper we studied the morphology of silver nanoparticles deposited on a surface of single crystalline DMAAlS and impact of the ferroelectric phase transition of “order-disorder” type on the surface plasmon resonance in the obtained metal-dielectric nanocomposite.

2. Experimental

- The silver nanoparticles were deposited on a surface of previously polished DMAAlS single crystals and simultaneously – on a standard glass substrate using the method of thermal deposition of silver vapor. The single crystalline substrate was prepared as a thin platelet with the two largest parallel planes oriented normally to the ferroelectric axis *a.* The thickness of the investigated composite sample was 0,9 mm. The process of deposition was performed just before the measurements. The morphology of a sample surface was analysed using Atomic Force Microscope (AFM) Solver P47-PRO.
- The nonpolarised absorption spectra were measured using computerised site based on AvaSpec–2048L spectrometer with a CCD camera as a photodetector. The halogen and deuterium lamps were used as the light sources.

3. The surface topography

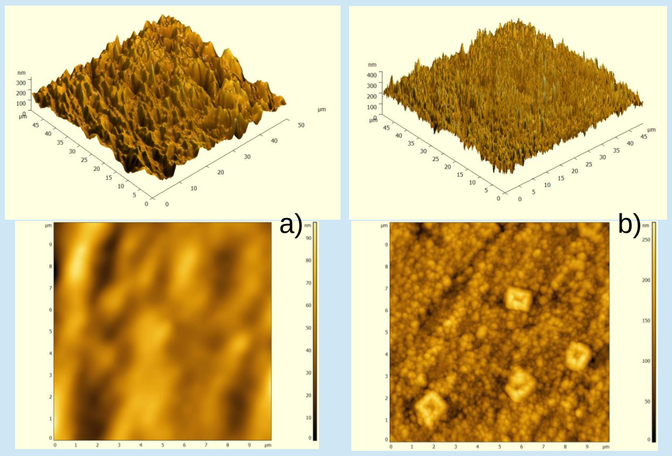

Fig.1. The surface topography of initial DMAAlS crystal (a) and the same crystal covered with Ag nanoparticles (b) obtained by AFM at different magnification

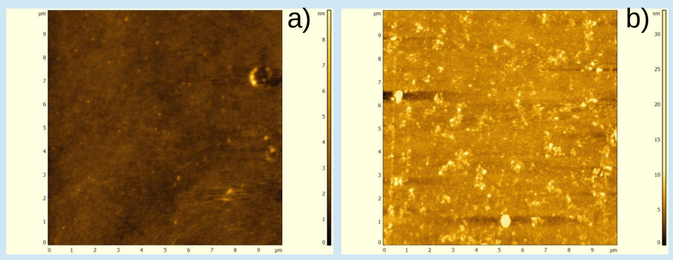

Fig. 2. The topography of surface of the pure glass plate (a) and the same plate with Ag nanoparticles (b)

The data presented in Fig. 1 testify that the RMS for different images of DMAAlS crystal surface covered with NPs is varied in the framework of 20-30 nm.

The topography of DMAAlS crystal surface with the NPs looks clearly different from those for the initial single crystal. The latter possesses a smoothed surface with a clear relief caused by polishing defects. In the composite sample this smoothed surface is superimposed with NPs of small sizes. Beside these small particles one can observe the much larger elements in a shape of “nanowells” that are evenly distributed on the sample surface (Fig.1b).

Analysis of the AFM images with application of masks testified that the average radius of the silver NPs sputtered on the crystal surface varied within the framework of 60-90 nm, whereas this parameter for the nanowells was found to be 450-630 nm.

The parameters describing the topology of surface of the investigated samples

Sample	Scanning window size	RMS, nm	δ, nm	σ, nm
Glass	(10 mkm)	0.42	0.31	226.2
	(10 mkm)	0.51	0.35	100.9
Glass+ Ag NPs	(10 mkm)	1.02	0.95	48.8
	(10 mkm)	1.44	1.32	54.0
	(50 mkm)	5.27	5.06	228.5
DMAAlS crystal	(20 mkm)	21.2	21.6	231.2
	(50 mkm)	33.3	32.7	469.7
DMAAlS crystal+ Ag NPs	(2 mkm)	18.5	18.6	37.5
	(10 mkm)	38.4	37.0	72.8
	(20 mkm)	34.8	32.1	136.6
	(50 mkm)	37.6	33.3	236.5
	(100 mkm)	48.2	40.7	685.8

The mechanism of growth of the specific nanowells on the surface of DMAAlS was proposed. This process is connected with absorption of the atmospheric water that is followed by dissolving of a sample on its surface. Afterwards, when the temperature rises the solution becomes supersaturated and the nanocrystals start to grow. The latter serve as the nuclei at formation of the “nanowells”. At the process of sputtering silver vapor is much faster deposited on these nuclei due to a better adhesion. It was shown that deposited silver, in fact, visualize the nano- (micro-) crystals arising on the surface of DMAAlS single crystal.

4. The absorption spectra

The absorption spectra were measured at cooling both for the initial single crystal substrate and for the composite “DMAAlS single crystal+silver NPs”. The corresponding spectra obtained at room temperature are compared in Fig. 3. The performed analysis shows that deposition of silver NPs on the crystals surface is followed by arising of the additional absorption in their transmittivity region (Fig. 3). As it follows from the difference absorption spectra the contributions into this absorption are caused, at least, by three mechanisms. The absorption at the wavelengths shorter than 380 nm would be related to the low energy “tail” of the absorption edge.

The broad band observed above 400 nm at room temperature would be related to the surface plasmon resonance (SPR) in the silver NPs. At room temperature this band is superimposed with the absorption edge. The SPR band is clearly seen in the difference absorption spectrum of “DMAAlS single crystal+silver NPs”. A more distinct SPR band with the maximum at 400 nm was observed at enough low temperatures (*T*=133 K in Fig. 4).

At lower temperatures the SPR bands would be seen in their initial shape (Fig. 5), that makes possible the detailed investigations of the ferroelectric phase transition impact on the SPR parameters.

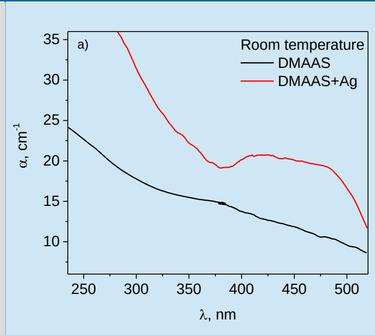

Fig. 3. Absorption spectra of DMAAlS single crystal substrate and the composite “DMAAlS single crystal+silver NPs”

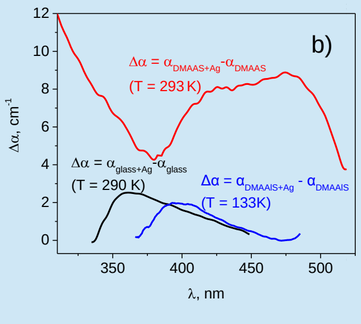

Fig. 4. Difference absorption spectra for glass (black line) and DMAAlS single crystal at T=293 K (red line) and T=133 K (blue line)

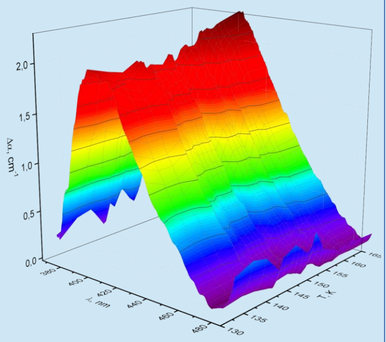

Fig. 5. Temperature dependence of the difference absorption spectra of “DMAAlS single crystal+silver NPs”

5. SPR in the vicinity of ferroelectric phase transition

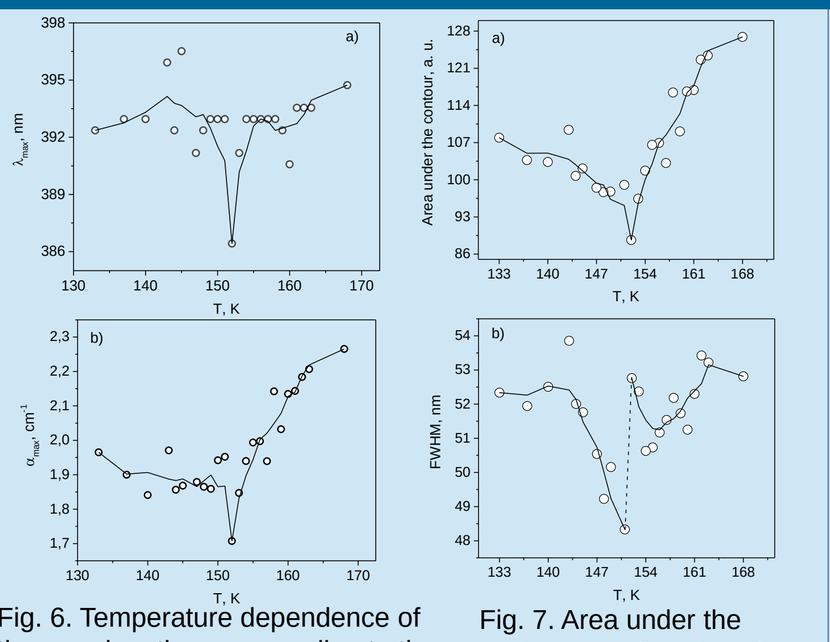

Fig. 6. Temperature dependence of the wavelength corresponding to the position of the SPR band maximum (a) and the absorption coefficient at the plasmon band maximum (b)

Fig. 7. Area under the contour as a function of temperature (a) and temperature dependence of the SPR band half width (b)

All parameters (Fig. 6, 7) show an anomalous behavior in vicinity of the phase transition temperature. Such behavior of the SPR band parameters at T_c is connected with formation of the clusters with a certain orientation of their dipole moments in respect to the crystal surface. The sizes of these correlated dipole clusters critically depend on temperature in vicinity of the Curie point. If the cluster sizes are commensurate with the sizes of silver NPs there is observed the interaction of a resonance type between the clusters and nanoparticles. Presence of the clusters with a different sign of charge on the crystal surface causes arising of the local electric fields with alternating change of charge sign. These local fields lead to polarization of the silver NPs in the plane parallel to the substrate surface – due to the shift of free electrons in respect to the positively charged ion core (Fig. 7 a). Under such conditions the polarizability of the NPs under the influence of the high frequency electric field of light wave should decrease (the direction of light polarization lies in a plane of the substrate surface). As a result, the intensity (oscillator strength) of the SPR band also should decrease.

The situation is considerably changed just below T_c. The arising ferroelectric domains generate the different surface charges causing a shift of the charge carriers in the nanoparticles in different directions. This process also affects the frequency of plasmon resonance in them. The different sign of the SPR maxima shift is observed for the negative and positive charges of the surface (Fig. 7 b, c).

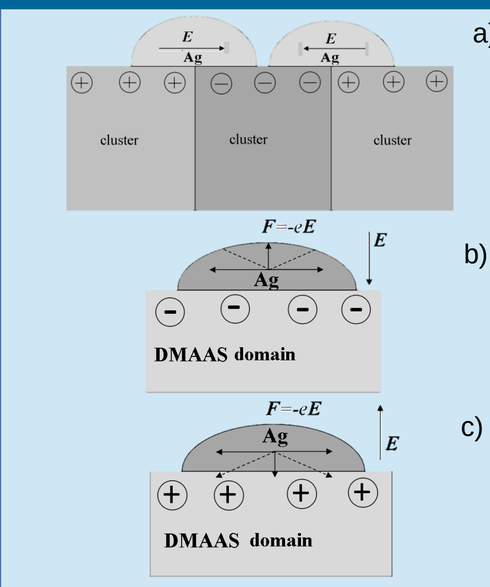

Fig. 7. The schemes explaining influence of the sign of cluster polarization (a) and of the spontaneous polarization in the neighboring domains (b, c) on the surface plasmon resonance

6. Conclusions

On the basis of comparative study of the morphology of silver nanoparticles deposited on a surface of single crystalline DMAAlS and glass and absorption spectra of these composites we investigated the impact of the ferroelectric phase transition of “order-disorder” type on the surface plasmon resonance.

It has been found that all parameters of the SPR band manifest anomalous behavior in vicinity of the Curie point. In the most cases one can observe the inverted λ-like anomalies – for the temperature dependences of the position of SPR band maximum, corresponding absorption coefficient, area under the contour. The resonance-like anomaly was observed for the temperature dependence of the half-width of the SPR band. These anomalies were explained in terms of the resonance type coupling between the dipole clusters arising in a narrow region in vicinity of the Curie point and the free electron within the silver nanoparticles which is followed by decreasing of these particles polarizability under the influence of the high frequency electric field of the propagating light photons.

The mechanism of growth of the specific nanowells on the surface of DMAAlS was proposed. This process is connected with absorption of the atmospheric water that is followed by dissolving of a sample on its surface. Afterwards, when the temperature rises the solution becomes supersaturated and the nanocrystals start to grow. The latter serve as the nuclei at formation of the “nanowells”. At the process of sputtering silver vapor is much faster deposited on these nuclei due to a better adhesion. It was shown that deposited silver, in fact, visualize the nano- (micro-) crystals arising on the surface of DMAAlS single crystal.

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