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Peculiarities of Crystallization of Amorphous Silver at 77 K in Conditions of Laser Herschel Effect

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The synthesis of new nanomaterials with designed functionalities have rapidly growing importance and many applications including energy conversion and storage, electronics, photonics, plasmonics, catalysis and biomedical engineering. This synthesis demands studying the nucleation and growth mechanisms of nanoparticles including new achievements in molecular chemistry, nanochemistry, physics of amorphous solids and solid state physics. In this work, we experimentally investigated the crystallization of amorphous silver clots at a temperature of 77 K on the surface of emulsion AgBr microcrystals extracted from the photo-layer SP-1 with a sensitivity of 6 units under the action of infrared laser radiation using a transmission electron microscope BS-613 Tesla with a resolution not worse than 4.5 Å. To obtain electron microscopic photographs, the method of collodion replicas was used. Replicas from emulsion AgBr microcrystals were not shaded by coal but were cooled with liquid nitrogen before and during photographing in an electron microscope. It is shown that an increase in the laser power and the amount of absorbed laser energy at 77 K leads to the formation of latent image centers. When the emulsion AgBr microcrystals were exposed for 300 s at 77 K by laser radiation with a wavelength of $\lambda = 633$ nm and a power of $P_1 = 2.5$ mW, the coagulation centers were formed and the normal Herschel laser effect was observed. But under the same conditions and power of $P_2 = 10$ mW and at 77 K, the latent image centers were formed and the positive Herschel laser effect was observed.

Keywords: Crystallization, Normal Herschel laser effect, Positive Herschel laser effect, Latent image centers, Coagulation centers, Laser light, Transmission electron microscopy, Low temperature.

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1. INTRODUCTION

The crystal structure determines a number of properties of substances in a condensed state; therefore, the crystallization process is one of the most important physicochemical processes [1]. Most modern advances in materials science are based on the achievements of crystallography and crystal chemistry [1]. Thus, phase change technologies are now widely used for storing information in rewritable DVDs, when a reversible phase transition from amorphous to crystalline state occurs in the GeSbTe amorphous semiconductor alloy under the action of laser pulses with a wavelength of 650 nm (1.91 eV) switches amorphous semiconductor from highly resistive to conducting state [2, 3].

Over the past decades, interest in crystallization mechanisms has increased dramatically due to the rapid development of two key areas of material science development: synthesis and research of nanomaterials and biomaterials [1]. It is important to establish crystallization mechanisms for the development of new types of functional materials, such as composite nanomaterials, hybrid organic-inorganic materials, multilevel hierarchical materials, and others [1].

Ag nanoparticles (NPs) are used in molecular diagnostics, electronics, catalysis, encryption strategies, gene therapy [4], optics [5], etc. Also, a system of AgBr microcrystals (MCs) and Ag NPs on their surface serve as a photocatalyst (Ag@AgBr), which greatly increases the absorption of visible light ($300 \text{ nm} < \lambda < 800 \text{ nm}$) due to localized surface plasmon resonance (PR) [6-10] and is effectively used to clean the environment from organic pollutants. Therefore, the study of the crystallization mechanism of amorphous silver clots at 77 K under the action of infrared (IR) laser radiation (LR) is an important task.

The AgBr MCs are wide-gap ionic semiconductors [11]. Semiconductors have a very high sensitivity to external influences: to changes in temperature and pressure, to lighting, to bombardment by charged particles, and to the content of impurities [12]. The latent image (LI) centres with development property as crystalline silver particles [13] are the main carriers of information in photography.

At 77 K, the effect of thermal light sources on the photolayer does not lead to the formation of coagulation centers (CCs) and LI centers. The photographic sensitivity of the photolayer at 77 K is greatly reduced [14] due to a decrease in the diffusion of the resulting photoelectrons. The surface energy density of LR influences the possibility of overcoming the thermodynamic barrier of crystallization of silver clots [15].

There is a difference between normal and positive Herschel laser effect (HLE). If the photolayer is first illuminated with white light, and then, before the development process, one has to re-illuminate a part of the photolayer with IR laser radiation and then develop the photolayer, then a decrease in the developed optical density is observed at the sensitogram in places of double exposure. Such a HLE is called normal (NHLE). If, however, in places where the photolayer is re-illuminated, not a decrease, but an increase in the developed optical density compared with the developed optical density from white light is formed, then this HLE is called positive (PHLE). The existence of NHLE for a laser wavelength $\lambda = 633$ nm at $T = 77$ K is wellknown since 1967, although at a room temperature LR with $\lambda = 633$ nm gives a PHLE.

It was of interest to investigate whether there are CCs and LI centers at 77 K in conditions of PHLE and NHLE and what are their peculiarities done in this work.

2. RESEARCH METHODOLOGY

The photolayer SP-1 with a sensitivity of 6 units was investigated. If the exposure to actinic light and LR is performed at $T = 77$ K, then NLEH is observed. The development of the photolayer SP-1 with a sensitivity of 6 units was carried out in the K.V. Chibisov's developer at a temperature $T = 293 \pm 0.1$ K. The washing and fixing of the photolayer was carried out in the standard way. The beams of IR light were emitted by lasers with the following parameters: wavelength $\lambda = 633$ nm, power $P_1 = 2.5$ mW, power $P_2 = 10$ mW. Clean of gelatins, unexposed AgBr MCs placed onto a preparation glass were received from photographic plate emulsion SP-1 with sensitivity of 6 units at a weak red light. This preparation glass with clean AgBr MCs was immersed into liquid nitrogen on the depth of $2 \cdot 10^{-2}$ m. Exposure of AgBr MCs with white light lasted 5 s, and repeated exposure with a laser beam lasted 300 s. The CO-13 light filter was placed on the path of the LR beam. This filter did not let the blue light through, which was partially generated by a He-Ne laser. The preparation glass with AgBr MCs at 77 K was not heated between exposures with white and IR light. The collodion replicas from illuminated AgBr MCs were prepared in the darkened room under a weak red light. The collodion replicas were prepared without shadowing with a coal, and cooling was performed with liquid nitrogen before and during the photographing in the electron microscope BS-613 «Tesla» with a resolution not worse than 4.5 Å.

3. EXPERIMENTAL RESULTS

The CCs and LI centers at 77 K are shown in Fig. 1 and Fig. 2.

Fig. 1 presents an electron microscopic photograph (EMF) of a collodion replica from AgBr MCs illuminated with white light for 5 s and with repeated exposure to He-Ne laser light with $\lambda = 633$ nm, power $P_1 = 2.5$ mW, duration 300 s through light filter CO-13 and liquid nitrogen. Both exposures were carried out at a temperature $T = 77$ K. The CCs at 77 K are not compact and contain the chains of individual silver particles.

Fig. 2 shows the EMF of a collodion replica from the AgBr MCs of the photolayer SP-1 with sensitivity of 6 units with LI centers that are created at a temperature of 77 K from laser light with $\lambda = 633$ nm and power $P_2 = 10$ mW through a CO-13 optical filter. The exposure to white light through liquid nitrogen lasted 5 s, the exposure to laser light through liquid nitrogen lasted 300 s. The creation of LI centers depends on the surface density of the laser radiation energy.

Fig. 2 shows that the LI centers were formed at the temperature of 77 K from the gas laser with a power of $P_2 = 10$ mW (large silver particles have crystal faces).

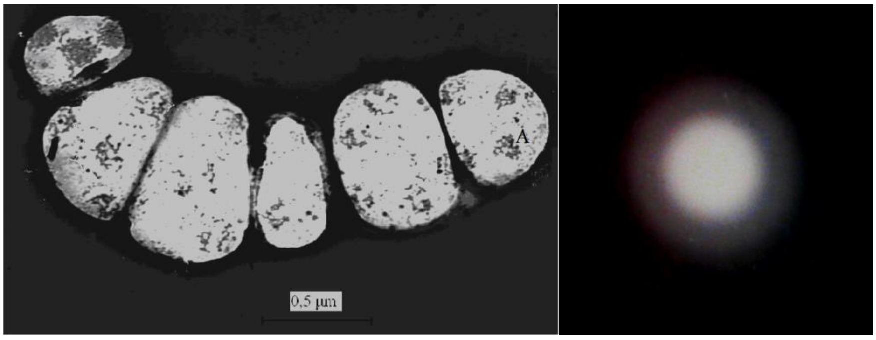
4. DISCUSSION

When exposing AgBr MCs with light, there occurs a photochemical functional "separation" of MCs into developable, "remembered" effects of light in a latent form – in the form of a LI, and undevelopable (without a LI) that create a veil during the development [13].

LR has a high intensity, sufficient to convert a significant fraction of silver atoms or molecules of a photolayer into an excited state. The electronic excitation energy is converted into the interfacial energy of the emerged nucleus of the metallic silver phase at the time of formation of the LI centers [13]. An oscillating electric field in a laser beam accelerates the crystallization of metallic NPs [16].

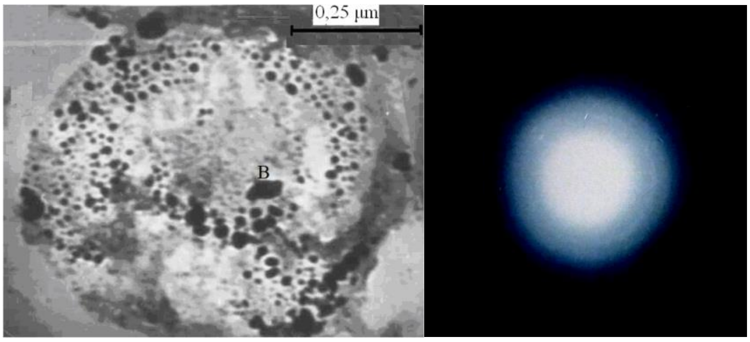
On the other hand, when a photolayer is exposed to light at a temperature of 77 K, the rate of emergence of the nuclei of a new silver phase decreases rapidly and the energy of their appearance increases, which makes it difficult for the LI centers to grow.

The thermal energy sharply decreases at a temperature of 77 K, and the energy of the interaction of charges increases under the action of the electric field of the laser beam. If in the electronically excited state the interaction energy between atoms and Ag^+ silver ions increases, then one can expect the appearance of



a b

Fig. 1 – a) Exposition was held at $T = 77$ K, lighted with white light AgBr MCs for 5 s and with repeated light exposure of helium-neon laser with $\lambda = 633$ nm, laser light power $P_1 = 2.5$ mW and 300 s duration through light filter and liquid nitrogen. The electron microdiffraction in 1b corresponds to the silver particle in the place A in 1a. The electron microdiffraction in 1b has no diffraction rings; therefore silver particle is amorphous in the place A in 1a



a b

Fig. 2 – Latent image centers created at 77 K, laser light with $\lambda = 633$ nm, laser light power $P_2 = 10$ mW through light filter. White light exposure through liquid nitrogen lasted 5 s, laser light exposure through liquid nitrogen lasted 300 s. The electron microdiffraction in 2b corresponds to the silver particle in the place B in 2a. The electron microdiffraction in 2b has two diffraction rings, therefore silver particle is crystalline in the place B in 2a

silver nuclei and LI centers [13]. We observed experimentally such formation of LI centers and CCs at 77 K on the surface of AgBr MCs of the photolayer SP-1 with sensitivity of 6 units.

It is visible in Fig. 1, that small silver particles are formed, and also CCs are formed at a temperature of $T = 77$ K. The CCs form symmetric figures on the surface of AgBr MCs. In the area of CCs, spherical silver particles are not compactly located relative to each other, but form chains like the Weigert effect, whereas silver particles are compactly arranged in CCs formed at room temperature. In Fig. 2, LI centers were formed from the laser with a power of $P_2 = 10$ mW, and only CCs were formed during the same time at a laser power of $P_1 = 2.5$ mW. The formation of LI centers at 77 K is also influenced by the LR power.

It is also known that near PR, effects that depend on the radiation frequency can greatly change the polarization of the nucleus and exponentially change the nucleation rate [17]. PR in spheroidal metal NPs depends on temperature [18]. Electron emission from metal NPs, which is observed at moderate irradiation intensities, is most likely due to nonequilibrium heating of electrons in such NPs [19]. The increase in the energy of a metal nanoparticle associated with plasmons can be significant enough to change the phase equilibrium and be the trigger mechanism for the nucleation of metal NPs, which is not present without a field [16].

Thus, under the action of low-power laser radiation $P_1 = 2.5$ mW at a wavelength of $\lambda = 633$ nm for 300 s for small particles of amorphous silver located on the surface of AgBr MCs, there is no significant increase in the polarization of ions and electrons of amorphous Ag particles under constant conditions of cooling these particles with liquid nitrogen. Therefore, it is not enough energy to transfer the silver atoms to the positions of stable equilibrium and the formation of a crystalline structure. Increase in laser power equal to $P_2 = 10$ mW under the same conditions leads to the local heating and an increase in the polarization of the ions and electrons of the amorphous Ag particles, sufficient to overcome the thermodynamic nucleation barrier and the formation of crystalline silver particles.

5. CONCLUSIONS

In the normal Herschel laser effect ($\lambda = 633$ nm), at $T = 77$ K, coagulation centers are formed, on the area of which silver particles form chains in the same way as in the Weigert's effect.

1. Latent image centers can be formed under the action of He-Ne laser beam with a power of $P_2 = 10$ mW at 77 K and an exposure time of 300 s due to the increased polarization of ions and electrons of amorphous silver particles.
2. The amount of absorbed light energy of laser light affects the formation of latent image centers.
3. The coagulation centers were formed and the normal Herschel laser effect was observed at 77 K under the action of laser radiation with $\lambda = 633$ nm and power $P_1 = 2.5$ mW on the photolayer of SP-1 with a sensitivity of 6 units, and latent image centers were formed. There is not enough energy to transfer the silver atoms to the positions of stable equilibrium and for the formation of a crystalline structure. The positive laser Herschel effect was observed at the same wavelength and power of $P_2 = 10$ mW of laser radiation. There is sufficient energy to transfer the silver atoms to the positions of stable equilibrium and for the formation of a crystalline structure.

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Особливості кристалізації аморфного срібла при 77 К в умовах лазерного ефекту Гершеля

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Синтез нових наноматеріалів з заданими функціональними властивостями швидко зростає і має багато застосувань, включаючи перетворення та зберігання енергії, електроніку, фотоніку, плазмоніку, каталіз та біомедичну інженерію. Цей синтез вимагає вивчення механізмів зародження і росту наночастинок, включаючи нові досягнення в молекулярній хімії, нанохімії, фізиці аморфних твердих тіл і фізиці твердого тіла. В даній роботі експериментально досліджена кристалізація аморфних срібних згустків при температурі 77 К на поверхні емульсійних мікрокристалів AgBr, видобутих з фотошару СП-1 з чутливістю 6 одиниць, під дією інфрачервоного лазерного випромінювання з використанням про-свічуючого електронного мікроскопа BS-613 фірми «Тесла» з роздільною здатністю не гірше 4.5 Å. Для отримання електронно-мікроскопічних фотографій використовувався метод колодієвих реплік. Репліки з емульсійних мікрокристалів AgBr вугіллям не відтінялися, а охолоджувалися рідким азотом до і під час фотографування в електронному мікроскопі. Показано, що збільшення потужності лазерного випро-мінювання а також кількості поглинутої лазерної енергії при 77 К призводить до утворення центрів прихованого зображення. При експонуванні емульсійних мікрокристалів AgBr протягом 300 с при 77 К лазерним випромінюванням з довжиною хвилі $\lambda = 633$ нм і потужністю $P_1 = 2{,}5$ мВт утворилися коагуляційні центри і спостерігався нормальний лазерний ефект Гершеля. Але при тих же умовах і потужності $P_2 = 10$ мВт при 77 К утворилися центри прихованого зображення і спостерігався позитивний лазерний ефект Гершеля.

Ключові слова: Кристалізація, Нормальний лазерний ефект Гершеля, Позитивний лазерний ефект Гершеля, Центри прихованого зображення, Коагуляційні центри, Лазерне світло, Просвічуюча електрона мікроскопія, Низька температура.