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Electrical Properties of LiF-Based Thin Films Containing Gold and Copper Nanoclusters

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Abstract—Temperature dependences of the surface conductivity of LiF-based thin films with Cu and Au nanoclusters are measured to determine the electrotransport activation energy and I–V characteristics of the films are obtained. The memristor effect is observed in the investigated thin films, and the ratio between film resistances at the moments the electric field is switched on and off is determined. The high potential of copper nanoclusters is demonstrated.

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INTRODUCTION

The plasmon resonance of metal (Au, Ag, Pt, Cu, and Mg) nanoparticles is used in creating chemical and biological sensors. Upon contact with biological objects, plasmon effects allow us to enhance the intensity of fluorescence signals by more than an order of magnitude, i.e., to significantly broaden the possibilities of bioobject detection and diagnostics. The main effect used is the local amplification of the electromagnetic wave field amplitude under the conditions of plasmon resonance [1]. Metal nanoparticles can be synthesized in a variety of ways: electrochemically; through chemical reactions in liquid and polymer media; with vacuum sputtering or laser ablation onto substrates; via ion implantation; and by other means. Both the electron and ion components in the conductivity of such structures can be used in developing different nano-optoelectronic devices, e.g., photovoltaic cells, IR detectors, and resistive switches (memristors). The memristor effect observed in TiO_x, NiO_x, CuO_x, and HfO_x oxides [2–5] consists of two states of resistance: low resistance at positive voltages and high resistance at negative ones. Bipolar conducting state switching is observed in metal-insulator-semiconductor (MIS) structures. Drawbacks of these structures are the high initial conductivity of the insulator, which prevents us from distinguishing between the open and closed states, and nonuniformity of the insulator material due to its polycrystalline structure [2]. Not all principles of the memristor operation have been established as of late. The authors of [3] noted the electrical properties and carrier transport mechanisms in memory cells based on arbitrarily oriented nanowire networks on ZnO surfaces and described switching in terms of the formation and breaking of conducting threads formed by oxygen vacancies on a structure's surface. Such memristors are classified as ionic commutation systems. There is another category of memristor that is based on electronic commutation systems when a device is switched on and off by filling and emptying electron traps [4]. Electron switches are more efficient, but ion motion during electron commutation cannot be completely eliminated. The authors of [4] showed that oxygen migration in $Pt/TiO_2/Pt$-based structures substantially degrades switching reliability. Such degradation is caused by the reduction of trap concentrations due to filling vacancies with oxygen ions. In the films we investigated, electrons were released from metal nanoclusters that do not interact with oxygen ions. Memristors based on these films are therefore expected to be highly reliable. Studying the electrical properties of thin films with metal nanoclusters based on LiF crystal is therefore of great practical importance.

EXPERIMENTAL

Considering the electron distribution in Au ($6S^1$) and Cu ($4S^1$) atoms, LiF-based films with gold and copper nanoclusters are promising memristor materials. In this work, we investigate the electrical properties of LiF-based thin films with Au (type I) and Cu (type II) nanoclusters. The films were formed on glass substrates via thermal vacuum chemical vapor deposition (CVD). The working pressure in a vacuum chamber was $\sim 10^{-5}$ Torr. Film thickness varied from 500 to 700 nm. Metal nanoclusters were detected from the optical absorption spectra in the plasmon resonance band near 530 nm for Au and 330 nm for Cu. Temperature dependences of the surface conductivity were measured to determine the electrotransport activation energy and I–V characteristics were determined to

establish the ratio between resistances R_{off} and R_{on} at the moments of switching the electric field on and off. Resistance R_{on} was determined from the current's value at a voltage of 2 V and resistance R_{off} at 0 V. Silver electrodes with a gap 1 mm wide were formed to study electrotransport processes. The temperature dependences of surface conductivity σ and I–V characteristics were determined using the standard technique with a classical Curie circuit in vacuum at a residual pressure of 2.6×10^{-4} Torr.

RESULTS AND DISCUSSION

The energy of electrotransport activation determined by the slope of the initial portion of curve $\log\sigma = f(1/T)$ in type I films indicates the electron surface conductivity. The activation energy of this process is ~0.40 eV, which is lower than the activation energy of the ion component (~1.03 eV). After annealing at 1020 K for 15 min in air, the surface conductivity in the temperature dependence $\log\sigma = f(1/T)$ fell by two orders of magnitude and the band of the plasmon resonance of Au nanoclusters shifts toward longer wavelengths in the optical absorption spectrum. According to the results in [6], the shift of the maximum from $\lambda = 510$ to 540 nm is due to gold nanocluster coarsening from $2R = 3$ to $2R = 8$ nm. Reducing the conductivity of a type I film degrades parameter R_{off}/R_{on}: at 2 V, it is 5×10^1. The values reported prior to our investigations were $R_{off}/R_{on} = 10$ for titanium oxide-based memristors [5], $R_{off}/R_{on} = 2 \times 10^2$ at 2 V for LiF with Mg nanoclusters [7], and $R_{off}/R_{on} = 3 \times 10^4$ for the LNO/BiFeZnO/Pt-based memristors [8]. We may therefore suggest that the reduced conductivity of type I films and the observed degradation of parameter R_{off}/R_{on} are due to the coarsening of gold nanoclusters during annealing. These experimental results are consistent with the data we obtained for LiF surface layers with implanted Mg [9].

In type I films, we established the great (~5×10^{-3} eV) depth of the traps formed by gold nanoclusters. Trap depth was calculated using the formula

$$E_0 = lkT, \quad (1)$$

where parameter l was determined from the slope of curve $\tan\alpha = l + 1$ in double logarithmic coordinates: $\log I = f(\log U)$. The final value indicates that the traps are located close to the conduction band, and electrotransport could be caused by the Schottky mechanism [10].

Figure 1 shows optical transmission spectra for our type II LiF-based films containing Cu nanoclusters in the UV (Fig. 1a) and visible (Fig. 1b) spectral ranges. It can be seen in Fig. 1b (curve *4*) that of our type II films, the one of greatest interest displays absorption in the range of 550–750 nm caused by copper ions [11]. To investigate the effect copper oxides have on the electrical properties of films prepared by thermal vacuum CVD, we fabricated films at low residual pressure (~10^{-4} Torr). In the I–V characteristic of this film, we observed asymmetry of the positive and negative voltage branches. The ratio R_{off}/R_{on} fell to 6.0. The presence of oxides thus negatively affects parameter R_{off}/R_{on}: copper protoxide Cu_2O raises the current in the switched-off state, while copper oxide CuO increases the film's resistance in the switched-on state.

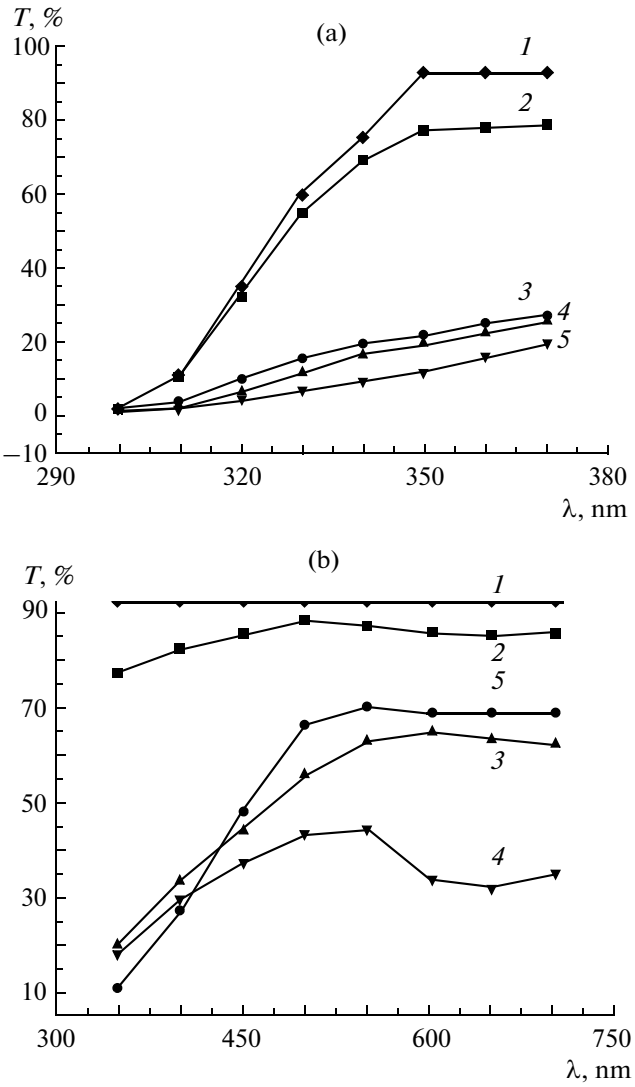

Fig. 1. Transmission spectra of LiF-based thin films with Cu nanoclusters, prepared via thermal vacuum CVD onto SiO_2 in the (a) UV and (b) visible spectral ranges at different copper concentrations. Optical destiny D at λ = 330 nm is (*1*) glass, (*2*) 0.04, (*3*) 0.47, (*4*) 0.72, and (*5*) 0.93.

The energy of electrotransport activation determined from the slope of the initial portion of curve $\log\sigma = f(1/T)$ for a LiF film with Cu nanoclusters (optical density, $D \approx 0.47$ at $\lambda = 330$ nm, curve *3* in Fig. 1) is $E = 0.45$ eV. An increase in the Cu nanocluster concentration ($D \approx 0.93$ at $\lambda = 330$ nm, curve *5* in

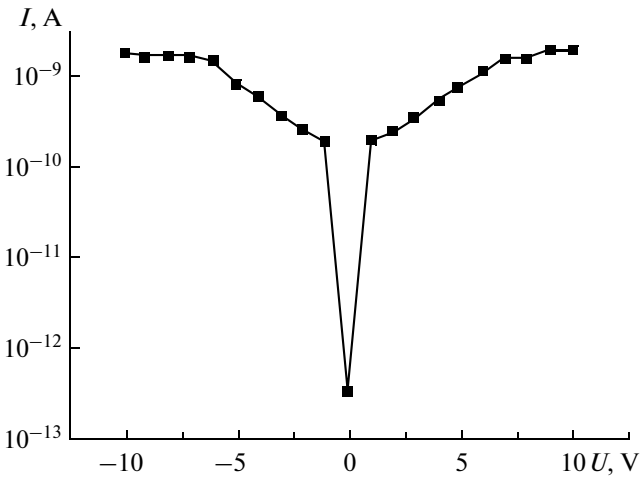

Fig. 2. *I–V* characteristic of the LiF film with Cu nanoclusters. The optical density at $\lambda = 330$ nm is $D = 0.47$.

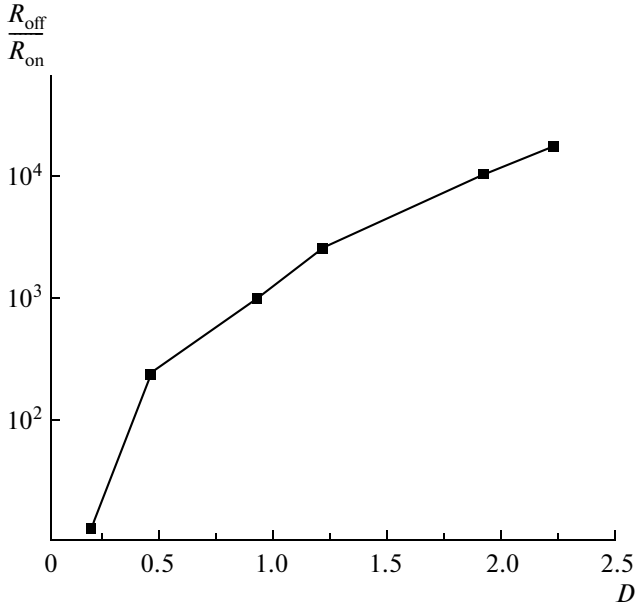

Fig. 3. Dependence of parameter R_{off}/R_{on} on optical density D of Cu nanoclusters at $\lambda \approx 330$ nm.

Fig. 1) is accompanied by a drop in the activation energy (down to 0.40 eV), due apparently to an increase in the number of carriers released from smaller Cu nanoclusters. The *I–V* characteristic of this film is shown in Fig. 2. The symmetry of the positive and negative voltage branches indicates the absence of a Schottky barrier, the release of electrons, and the filling of electron traps of one type with electrons.

The slope of the *I–V* characteristic in double logarithmic coordinates is $\tan\alpha = l + 1 \approx 1$ eV. Ohmic contact is observed when $\tan\alpha \approx 1$, indicating the presence of equilibrium carriers in concentration n_0 on a film's surface, resulting in surface current I:

$$I = \frac{en_0\mu U}{L}, \quad (2)$$

where μ is carrier mobility, U is voltage, and L is the distance between electrodes. Such carriers can originate from a group of very small donors, e.g., the surface states of Cu nanoclusters. Activation energy $E =$ 0.40–0.45 eV apparently corresponds to the value for the electron traps resulting from the presence of Cu nanoclusters in the volume at film thickness $d \approx$ 700 nm.

Figure 3 presents the dependence of parameter R_{off}/R_{on} on Cu nanocluster concentration. The latter was estimated from optical density D in the band of Cu nanocluster plasmon resonance at $\lambda = 330$ nm. For the film with high copper concentration annealed at 570 K ($D = 2.2$), we obtained $R_{off}/R_{on} \sim 9 \times 10^4$. This is currently the best result for the investigated films. Two last points in the Cu concentration dependence of parameter R_{off}/R_{on} (Fig. 3) correspond to annealed samples. As was shown above, however, nanoclusters coarsen upon annealing and the number of electrons participating in electrotransport falls. The ratio R_{off}/R_{on} can be enhanced considerably by preventing the formation of copper oxide during the thermal vacuum CVD of thin LiF-based films with Cu nanoclusters onto glass via, e.g., sputtering in a higher vacuum (at residual pressures of no more than 10^{-5} Torr) to reduce the concentration of residual oxygen.

CONCLUSIONS

In [7], we proposed a memristor material based on the surface layers of a lithium fluoride crystal with implanted magnesium and obtained the resistance ratio $R_{off}/R_{on} = 2 \times 10^2$ at 2 V. The use of Cu nanoclusters in thin lithium fluoride crystal-based films prepared via the thermal vacuum deposition of chemical vapor onto glass allows us to improve this parameter considerably: $R_{off}/R_{on} = 9 \times 10^4$ at 2 K. To meet the requirements for memristors, the R_{off}/R_{on} ratio should exceed 10^3 [8]. Considering the simplicity and low cost of the fabrication technology involved, lithium fluoride films with Cu nanoclusters are promising for application in memristors.

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