

## BRIEF COMMUNICATIONS

### THE AGING MECHANISM OF A LiF FILM WITH COPPER NANOCLUSTERS AND ITS INFLUENCE ON THE MEMRISTOR PERFORMANCE

L. I. Shchepina,<sup>1</sup> V. L. Papernyi,<sup>1</sup> A. A. Chernykh,<sup>1</sup> and N. A. Ivanov<sup>2</sup>

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Currently the most promising lines of research are the development of nanosized bit-cell memory and designing microelectronic devices a few nanometers in the size. The resistive switches relying on thin-film elements have been recently reported [1]; it should be noted that a positive voltage bias on the specimen gives rise to a low-resistance state (on), while a negative voltage bias – to high-resistance state (off). In particular, this character of the current-voltage characteristics was observed in the LiF films with copper nanoclusters (Cu NCs) [2]. The memristor operation parameter, determined from the ratio of the currents in the on- and off states, was found to be equal to  $5 \cdot 10^6$  at the voltage 0.6 V. During the half-a-year storage of the films, this parameter decreased to  $4 \cdot 10^3$ . The purpose of this study is to identify the aging mechanism. We investigated the current-voltage characteristics (CVCs) of cross conduction and the optical absorption spectra of LiF films with Cu NCs, which were deposited by magnetron sputtering on the substrates from current-conducting glass by the process described elsewhere [3]. The CVCs were measured using a standard procedure according to a classical scheme, where a U5-11 electrometer was used to measure the voltage drop on a reference resistance switched in series with the specimen. For this purpose the point electrodes with the contact area  $1 \cdot 10^{-3} \text{ mm}^2$  were used. The voltage drop on the specimen was measured within 0–10 V and the concentration of Cu NCs was monitored from the absorption spectrum in the band of a volumetric plasmon resonance of Cu NCs in the region  $\sim 500 \text{ nm}$  [4].

In order to find the energy distribution of the electron traps, the experimental CVCs were constructed in the log-log coordinates (Fig. 1). As it is evident from Fig. 1, we obtained straight lines. This implies that the current flowing through the conductor is limited by the bulk space charge (BSC) [5]. In this case the current has a power-law dependence on the voltage ( $U$ ) and the dielectric thickness ( $L$ )

$$I = e\mu N_c \left( \frac{\varepsilon\varepsilon_0}{N_t} \right)^\ell \frac{U^{\ell+1}}{L^{2\ell+1}},$$

where  $N_t$  is the concentration of traps and  $N_c$  is the effective number of states in the conduction band.

As it follows from the formula, in the log-coordinates the CVC would be presented as a straight line with a tilt of  $\text{tg } \alpha = \ell + 1$ . Knowing  $\ell$ , one can find the energy distribution of the traps using the formula  $E_0 = \ell kT$ . The measurements for the freshly prepared film demonstrated that  $\ell = 0.04$ . Considering that  $kT = 2.6 \cdot 10^{-2} \text{ eV}$ , the position

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<sup>1</sup>Irkutsk State University, Irkutsk, Russia, e-mail: schepina@api.isu.ru; papernyi@math.isu.runnet.ru; ivnik@istu.edu; <sup>2</sup>Irkutsk National Research Technical University, Irkutsk, Russia. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 2, pp. 166–167, February, 2018. Original article submitted July 19, 2017; revision submitted October 13, 2017.

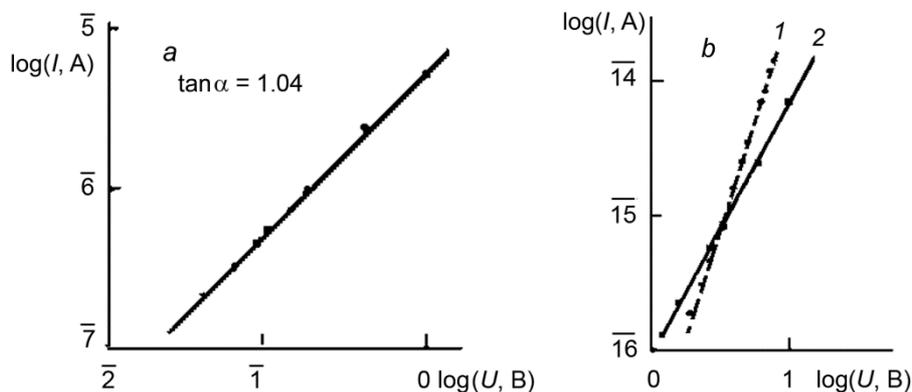


Fig. 1. CVCs of a freshly prepared film (a) in log-log coordinates (a) and the films aged for one year (curve 1) and 6 months (curve 2) (b).

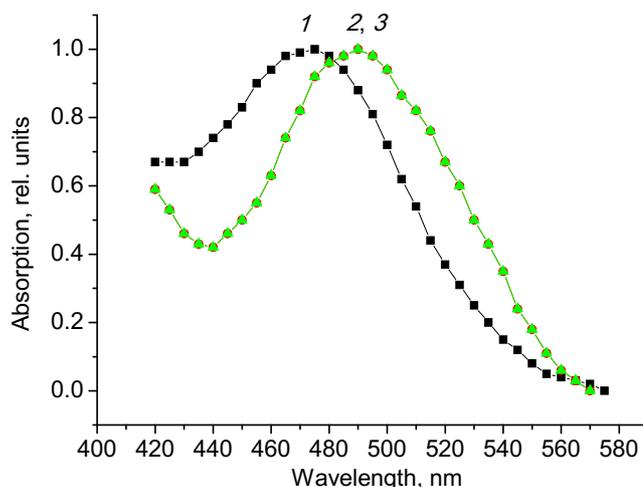


Fig. 2. Normalized absorption spectra of the freshly prepared (curve 1) film based on LiF with Cu NCs and the film aged for one year: the measurement temperatures 300 K (curve 2) and 78 K (curve 3).

of small traps  $E_0 = 1 \cdot 10^{-3}$  eV nearly coincides with the conduction band bottom. After 6 months of storage, the level of the small traps is found at the depth 0.03 eV ( $l = 1.07$ ), in a year – at the depth 0.04 eV ( $l = 1.42$ ). Earlier [6] we reported that the displacement of the energy level of Cu NCs towards the Fermi energy edge is an indication of coarsening of Cu NCs. It is well known that coarsening of Au or Ag nanoclusters in photosensitive glasses is accompanied by a displacement of the plasmon resonance band towards the long-wavelength region of the spectrum [4]. In Fig 1 we for the first time present the normalized absorption spectra of the LiF films with Cu NCs.

The absorption band maximum is observed to displace towards the long-wavelength region of the spectrum (Fig. 2, curve 2) as a result of temporal aging. Taking into account that the film surface was not protected from penetration of oxygen, it is necessary to check the possibility of oxidation of the Cu NCs to form  $\text{Cu}_2\text{O}$ . The latter compound is characterized by strong dipole absorption in the region of 452 and 478 nm and forbidden transitions in the region 540 and 565 nm [7]. On the other hand, the measurement of the absorption spectrum at the temperature 78 K demonstrated a coincidence with the spectrum measured at 300 K, which is typical for the plasmon absorption. Relying

on this, we draw a conclusion that Cu NCs during storage undergo coarsening giving rise to a larger ratio of memristor resistances in the on- and off states.

Thus, a possible mechanism of film aging is associated with the coarsening of Cu NCs.

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