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Studying the Quantum Size Effect in LiF-Based Thin Films with Ag and Cu Nanoclusters

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Abstract—The characteristic energy of distributions of Ag and Cu nanoclusters in LiF-based thin films is estimated from the slope of the $I–V$ characteristic, built in double logarithmic coordinates $\log I = f(\log U)$. It is shown that the energy states of small clusters lie above the bottom of the conduction band and form a potential barrier, while the energy states of large clusters lie below the bottom of the conduction band and form a potential well. The change in the positions of energy levels along with nanocluster size and the effect of quantum limitations imposed on the electrical and optical properties of the system are confirmed experimentally.

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INTRODUCTION

LiF-based thin films with Ag or Cu nanoclusters (NCs) are promising materials for the development of resistive switches and resistive random-access memory (ReRAM) elements [1]. The principle of ReRAM operation is based on the use of two stable states (high- and low-resistance) of a material. Nanoclusters release (in the low-resistance state) or capture (in the high-resistance state) electrons. It is therefore important to study the size distributions of NC energy states, i.e., the so-called quantum size effect. This term was introduced by Fröhlich [2] in 1937 on the basis of energy spectrum variation with particle size and geometry. The growth of the concentration of silver nanoclusters in LiF films deposited onto a glass surface via thermal evaporation in vacuum lowers the activation energy of electron transport. This behavior is also observed in LiF crystals implanted with silver ions, which we hypothetically interpreted in the context of the quantum size effect in [3]. Most studies are devoted to zero-dimension systems that include colloidal quantum dots, i.e., formations of bound atoms in a lithium fluoride film or crystal. A quantum dot must be small enough to make quantum effects appreciable. Characteristic dot size r can be estimated as

$$r = h\left(8\mu E_g\right)^{-1/2}, \quad (1)$$

where μ is the reduced exciton mass and E_g is the band gap [4]. As is well known, the size of a quantum dot is 2 nm or smaller in GaAs and 4.6 nm or smaller in Si. Since the radius of Ag^0 is 1.44 Å, the radius of Mg^0 is 1.6 Å, and the radius of Au^0 is 1.74 Å, silver NCs are obviously smaller than Mg and Au NCs. Since the size of Cu^0 copper atoms (1.45 Å) is similar to that of Ag atoms, LiF-based films with Cu NCs should also exhibit the quantum size effect.

EXPERIMENTAL

In this work, we investigated the electrical properties of LiF-based thin films with Ag and Cu NCs. The films were deposited on glass via thermovacuum chemical vapor deposition at 373 K. The residual pressure in the vacuum chamber was ~10^{-5} Torr. The film thickness was 500–700 nm. Metal NCs were controlled using optical absorption spectra in the plasmon resonance band (PRB) near ~400 nm for Ag NCs and ~330 nm for Cu NCs. We measured the temperature dependences of surface conductivity to determine the activation energy of electron transport and $I–V$ characteristics to establish the characteristic energy of the surface NC distribution from the slope of a curve built in double logarithmic coordinates $\log I = f(\log U)$. To study electron transport, silver electrodes were formed with a spacing of 1 mm. The temperature dependences of surface conductivity σ and $I–V$ characteristics were measured by standard means using the classical Curie scheme in vacuum (2.6×10^{-4} Torr). The cluster size and composition were estimated via electron microscopy on an FEI techno 2G TEM microscope and X-ray diffraction on a Shimadzu MAXima XRD-7000 diffractometer. The measured X-ray diffraction patterns were the dependences of the scattering intensity on the diffraction angle. Based on these data, we determined the lattice parameters. Optical absorption

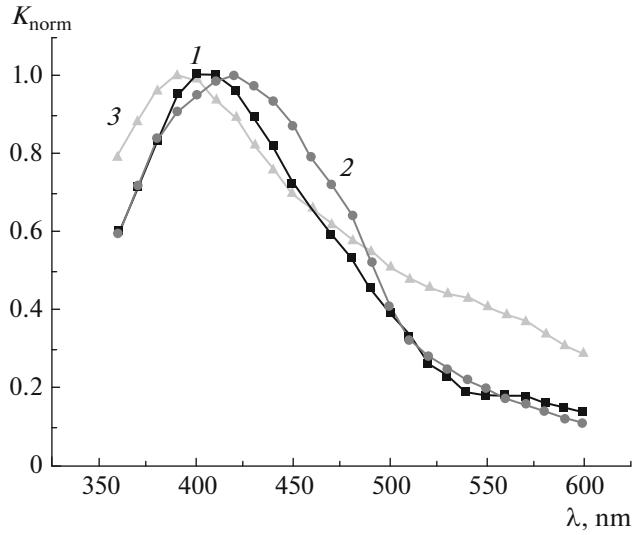

Fig. 1. Normalized absorption spectra of LiF-based films containing Ag NCs with radii of (*1*) 5, (*2*) 40, and (*3*) 45 nm.

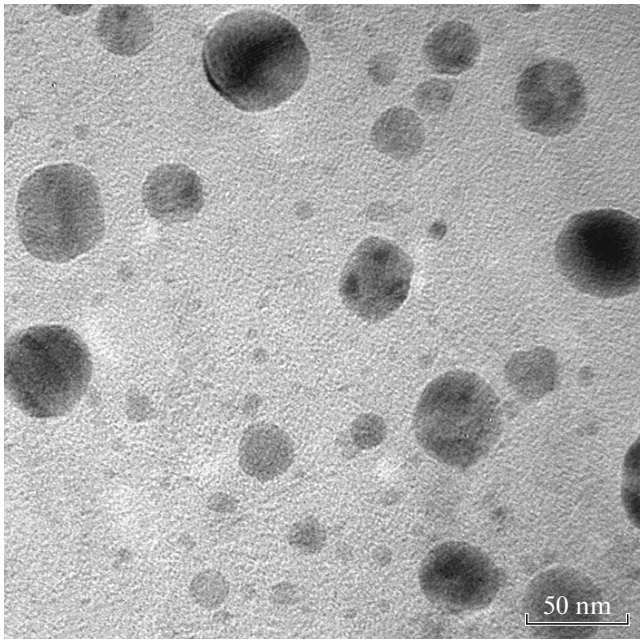

Fig. 2. TEM image (scale, 50 nm) of a LiF film with Ag NCs thermally deposited onto a glass surface in vacuum.

spectra of the investigated LiF-based films were measured on an MPS-50L spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 show the normalized optical absorption spectra of the investigated LiF-films with Ag NCs. Analysis of the spectra reveals a plasmon resonance frequency (PRF) of ~395 nm for the films with preferred NC radii of up to ~5 nm. The PRF shift to 420 nm and the occurrence of short-wavelength absorption near 380 nm are indicative of NC coarsening. Analogous changes in the absorption spectrum were observed in [5] upon annealing silver NCs on an LiF (100) surface and extending the radii to 40 nm. Extending the size of Ag NCs again to $R = 45$ nm led to long-wavelength absorption near ~550 nm and an increase in the contribution from the short-wavelength plasmon resonance peak near ~380 nm.

Figure 2 shows a transmission electron microscopy (TEM) image with clusters of different sizes. Analysis of the histogram (i.e., the particle size distribution) as a function of the number of particles revealed the maximum content of silver nanoclusters with radii of up to 5 nm. Figure 3 shows the I–V characteristic for this film in double logarithmic coordinates. We can determine parameter l from the slope of curve $\tan\alpha = l + 1$ and estimate the characteristic trap distribution energy by using the formula $E_o = lkT$ [6]. For the film with preferred NC radii of up to ~5 nm, we obtain $\tan\alpha = 0.84$. The level thus lies above the bottom of the conduction band at a distance of $E_o = 0.4 \times 10^{-2}$ eV from the bottom of the band; i.e., the surface states of small clusters form a potential barrier, which results in the bending of the LiF conduction band. The authors of [7] reported straining of the conduction and valence bands by metal (Ag and Au) nanostructures on the silicon surface. The high NC concentration apparently lowers the potential barrier due to the overlapping of the Coulomb potentials of neighboring NCs, which explains the low potential barrier height. The positions

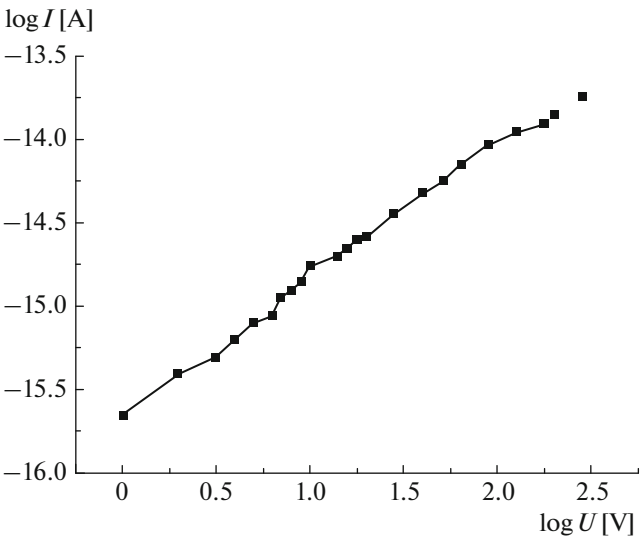

Fig. 3. I–V characteristics in double logarithmic coordinates for a LiF film with the preferred content of silver NCs with a radii of up to 5 nm.

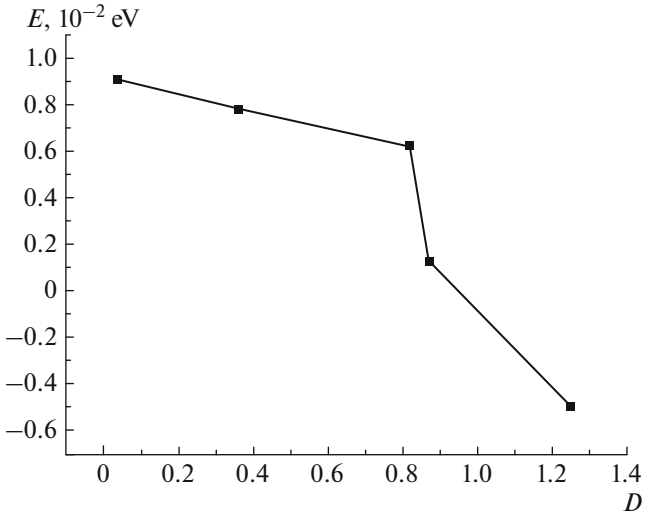

Fig. 4. Energy distribution of copper NCs as a function of optical density in 330-nm PRB in LiF thin films.

of energy levels for silver NCs with $R = 40$–45 nm were estimated from the I–V characteristics. For NCs with R values lower than 40 nm, we obtained $\tan\alpha = 0.88$. The surface states of silver NCs thus form an energy level above the bottom of the conduction band by $E_o = 0.3 \times 10^{-2}$ eV. For NCs with R values higher than 45 nm, however, we obtained $\tan\alpha = 1.03$. Parameter l changes its sign, so the position of the energy level moves to the energy band gap below the bottom of the conduction band by 0.77×10^{-3} eV. The subsequent growth in cluster size is probably accompanied by a shift of the electron energy levels deep in the energy band gap, so it is no coincidence that the temperature dependence of the conductivity contains sections with an activation energy of 0.28–0.36 eV [3]. The growth of NC size shifts the electron energy levels below the Fermi level and results in the formation of a potential well. Estimating the transmittance of the potential barrier walls according to the formula

$$D = D_0 \exp\left\{\left(-4\pi a/h\right)\left[2m\left(U - E\right)\right]^{1/2}\right\} \qquad (2)$$

yielded $D = 0.4D_0$ for a potential barrier with thickness $a = 5$ nm and $D = 9.8 \times 10^{-6} D_0 \sim 10^{-5} D_0$ for a potential well with a width of $a = 45$ nm. Our experimental data agree with the observed patterns: the smaller the silver nanoparticles, the weaker the electron affinity [8]. The probability of electron tunneling through a potential barrier at low temperatures and their participation in electron transport is therefore higher for small NCs. The growth of NCs upon annealing shifts the electronic levels below the Fermi level and reduces the transmittance of potential well walls. The mechanism of transport will thus change to over-barrier thermal activation. Let us consider the energy distribution of surface copper NCs in LiF-based films. As was shown in [9], the probability of larger copper clusters forming in $Cd_{0.8}Zn_{0.2}S$ films created via chemical deposition increases. In LiF-based films, the probability of larger copper clusters forming grows along with the optical density in the plasmon resonance width (330 nm). Figure 4 shows the dependence of the Cu NC energy distribution on the optical density in the PRB (330 nm). Note there are several portions with different slopes. As the optical density grows to $D = 0.87$, a potential barrier forms, the height of which shrinks from 0.9×10^{-2} ($D = 0.06$) to 0.1×10^{-2} eV as the NC concentration grows. This is probably due to the coarsening of copper NCs. When $D > 0.95$, the energy states of copper NCs form a potential well with a depth of up to 0.5×10^{-2} eV at $D = 1.25$. The existence of several portions with different slopes is indicative of the change in the electron transport mechanism. The potential barrier for small clusters is low, and electrons tunnel into the conduction band at low temperatures. With large copper NCs, electrons are released from the potential well by over-barrier thermal activation, as is confirmed by the change in the electron transport mechanism observed in the dependence shown in Fig. 4.

CONCLUSIONS

It was shown that the surface states of silver nanoclusters with radii of up to 40 nm form a system of energy levels that lie above the conduction band, and larger particles (45 nm and more) form energy levels that lie below the conduction band. For small silver or copper NCs, the probability of electrons tunneling through a potential barrier and participating in electron transport is higher at low temperatures. The increase in the size of NCs upon annealing shifts the electron levels below the Fermi level and lowers the transmittance of potential well walls. The mechanism of transport thus changes for over-barrier thermal activation. Our results confirm that the sizes of silver and copper NCs affect the energy level distribution; i.e., quantum limitations affect the electrical and optical properties of the system. This offers new opportunities for applying quantum dots with precisely determined properties in the development of different nano-optoelectronic devices and ReRAM.

ACKNOWLEDGMENTS

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