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Destruction of the conducting state by ac electric field in naphthalocyanine complexes

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Abstract. It is shown that in naphthalocyanine films, conductivity occurs due to electron transport along metal nanowires. In an alternating electric field, reversible partial rupture of nanowires may take place. Active resistance for film with partial nanowire ruptures is frequency dependent and can be more or less than that of film without ruptures. A model for this effect is proposed. The prediction of the response of a system to an external influence simplifies the use of materials for practical applications.

Keywords: nanowires, resistive switching, alternating electric field

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Материалы конференции
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Разрушение проводящего состояния переменным электрическим полем в комплексах нафталоцианинов

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Аннотация. Показано, что в пленках нафталоцианинов проводимость осуществляется за счет транспорта электронов по металлическим нанонитям. В переменном электрическом поле может происходить обратимый частичный разрыв нанонитей. Активное сопротивление пленки с частичным разрывом нанонитей зависит от частоты и может быть больше или меньше, чем у пленки без разрывов. Предложена модель этого эффекта. Прогнозирование реакции системы на внешнее воздействие упрощает использование материалов для практических приложений.

Ключевые слова: нанонити, резистивные переключения, переменное электрическое поле

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Introduction

Low-dimensional semiconductors are actively used for many practical applications [1]. One of promising effects is resistive switching. This effect lies in the possibility of a controlled reversible transition between two states with different electrical resistances (Ron and Roff). One of the variants of the structure with this property is a composite based on organic matrix permeated with metal nanowires [2]. The formation of nanowires can occur in strong electric fields due to the injection of metal ions from the contact and their self-organization. As the field strength increases, nanowire fragments are formed first, with their subsequent integration into full-fledged network, connecting the two electrodes [3]. At the same time, when critical currents are reached, a thermal-induced break in the system occurs. Thus, Ron corresponds to the situation when nanowires connect contacts, and Roff corresponds to multiply non-connected fragments.

The behavior of such system in AC field simultaneously characterizes the speed of switching between states with different nanowire configurations and stability under to external interference.

Materials and Methods

Solutions and films based on naphthalocyaninates with a central magnesium ion (NaPh-Mg) were studied. 3,4,12,13,21,22,30,31-Octa-(2-naphthoxy)-2,3-naphthalocyaninato magnesium complex was obtained starting from 6,7-di(2-naphthoxy)naphthalene-2,3-dicarbonitrile according to the previously described procedure [4]. The NaPh-Mg molecules have planar shape with average size of 21×21×2 Å. Films were obtained by deposition from solution onto glass substrates with ITO conducting layer. 1.5 and 1.0 μm films were obtained by drop-cast, 0.2 μm films by spin coating method. Film thickness was determined by white light interferometry with thickness variation less than 5% for all films. The top contact to the films with an area of 0.4 mm2 was formed using the Kontaktol silver paste.

Optical spectroscopy, DC and AC conductivity measurements were used as experimental methods. All measurements were performed at room temperature. Before conductivity measurements, all sample were shielded from external radiation and kept in dark conditions until complete relaxation. An 1 Ohm load resistor was series-connected to the sample.

Absorption spectra for solutions and films in the range of 300–900 nm were obtained using an Avantes AvaSpec-2048 spectrometer. For films spectral data was obtained before creation of upper contact. The current-voltage characteristics for the films were obtained using a Kietley 2612 instrument. Frequency dependencies of the conductivity in the range of $1–10^6$ Hz were obtained using a QuadTech 1920 Precision LCR Meter. The experimental data was cross-checked based on the coincidence of curves on repeated cycling both at increasing and decreasing voltage (DC mode) and frequency (AC mode).

Results and Discussion

The absorption spectra for solution and films in visible spectral range has a set of local maxima and is formed by various electronic transition between molecular levels in NaPh–Mg (Fig. 1). The absorption for all films varies in intensity, but does not demonstrate any significant differences in the shape and position of local maxima. The solution-film transition is accompanied by a decrease in intensity in the range of 550–800 nm, but the position of local absorption maxima is reproduced well. The latter allows to assert that that no significant distortion of the spatial configuration of NaPh-Mg molecules occurs in the films [5]. Films can be considered as identical media of varying thickness.

The formation of metal nanowires and resistive switching in all the samples was confirmed via I–V characteristics (Fig. 2).

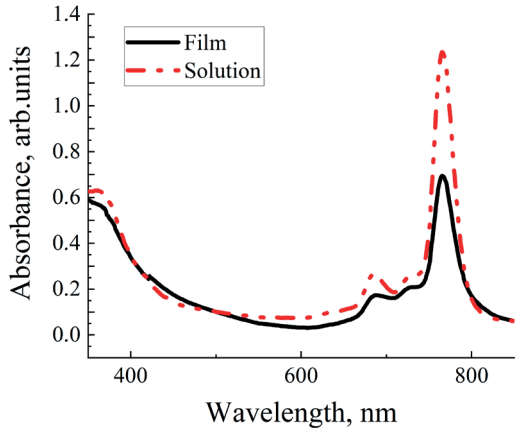

Fig. 1. Optical absorption for NaPh-Mg solution (dashed line) and 1.0 μm film (solid line)

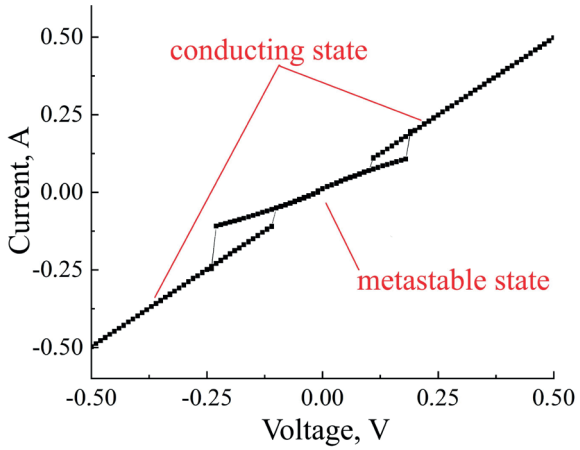

Fig. 2. Typical I–V characteristic for NaPh-Mg films. The specific graph corresponds to 0.2 μm film thickness

In addition to conducting and non-conducting, a set of metastable states also exist for all films. In metastable states, the structure is in dynamic equilibrium. Nanowires are continuously separated into individual fragments, which are joined again not necessarily in the initial configuration. The transport of charge carriers in the metastable state is determined by not only the structure of nanowire network, but also by energy barriers separating fragments. In comparison with the conducting, metastable states are characterized by increased electrical resistance and appearance (or increase) of capacitance [3].

In DC mode with voltage $U > 0.3$ V, all films were in stable conducting state. AC mode experiments were carried with $U = 1.0 + 0.5 \sin(wt)$, which corresponded to voltage range of 0.5–1.5 V. Varying film thickness resulted in varying values of electric field strength E.

In AC mode, the stability of the conducting state was preserved only in the low frequency range (3000, 500, 300 Hz for films with a thickness of 1.5, 1.0 and 0.2 μm, respectively). In this frequency range conducting state was characterized by active resistance Z' (equal to film resistance in DC mode), and reactive resistance Z'' (Z'' was lower than Z' by several orders of magnitude). At higher frequencies, two different behaviors (MI and MII) were observed. Both could take place simultaneously, with MI happening at lower frequencies. The dominance of specific behavior could be enforced by altering the I/U ratio in the film, which was achieved by adding a second load resistor in parallel to the sample (insets in Fig. 3, *a*, *b*).

MI (Fig. 3, *a*) was characterized by a spontaneous reversible transition of the system to a state with increased active resistance Z'. Simultaneously the reactive resistance Z'' decreased to negative values, which indicated appearance of capacitive contribution. Such behavior marks this state as metastable with nanowire fragmentation [3]. For metastable state Z' decreases nearly linearly, while capacity changes very little. A decrease in the film thickness leads to a shift of frequency range towards lower values.

MII (Fig. 3, *b*) was characterized by a decrease of the active resistance Z' to values below those of conducting state. Negative values for Z'' indicated capacity presence and thus, the metastable nature of this state. A decrease in the film thickness leads to an increase in the frequency range at which this effect was observed both towards lower and higher values.

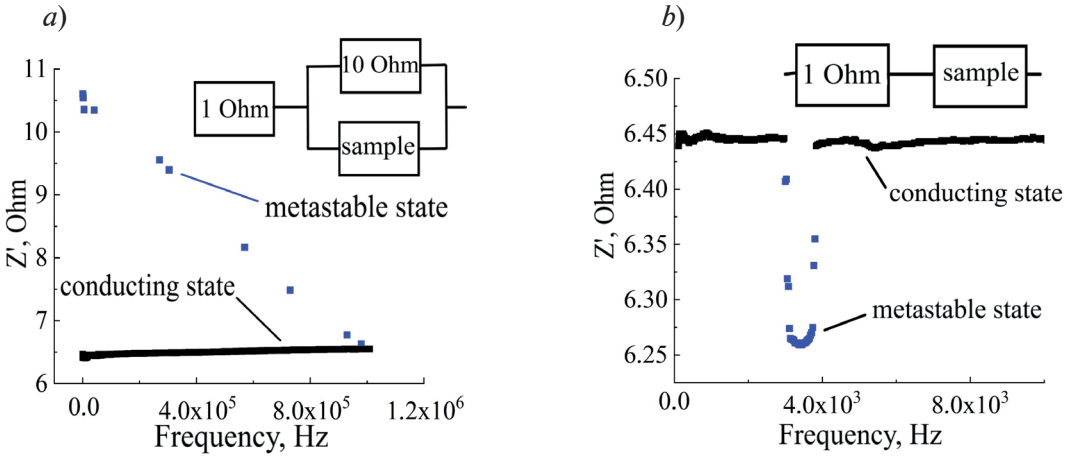

Fig. 3. Frequency dependence for active resistance Z' based on I/U ratio in 1.5 μm film.
The inset schematically demonstrates the load resistors configuration

It is possible not only to observe MI and MII simultaneously, but also to see several configurations for metastable state in each of them (Fig. 4) with indistinguishable reactive resistance Z'' and capacitance values (inset in Fig. 4). This means that both metastable configurations are characterized by the same degree of nanowire fragmentation (number of ruptures the electron must pass to get from one contact to another).

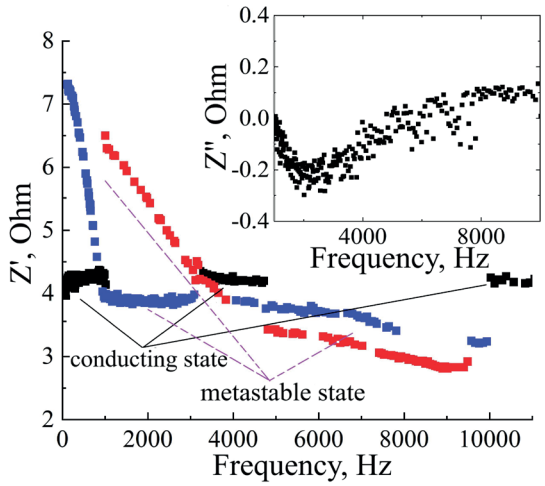

Fig. 4. Frequency dependence for active resistance Z' in 1.0 μm film
The inset demonstrates indistinguishable reactive resistance Z'' for metastable states

In order to explain all of the observed effects, a model of "mobile" nanowire fragments was proposed. The stability of nanowire configuration is determined by the value of applied electric field (stabilizing factor) and heat generation due to current flow (destabilizing factor). In alternating electric field thermal power is proportional to the square of the frequency for low frequencies *w*. When the rupture of a nanowire occurs, the fragments and separate metal ions, that composed said nanowire, have excessive thermal energy. With enough energy, they can instantly reform, either by themselves, or by attaching to non-ruptured nanowire. Compared to initial configuration (Fig. 5, *a*), re-formation can lead to both increase (Fig. 5, *b*) and decrease of active resistance (Fig. 5, *c*). The qualitative resistance value is shown below the corresponding diagrams.

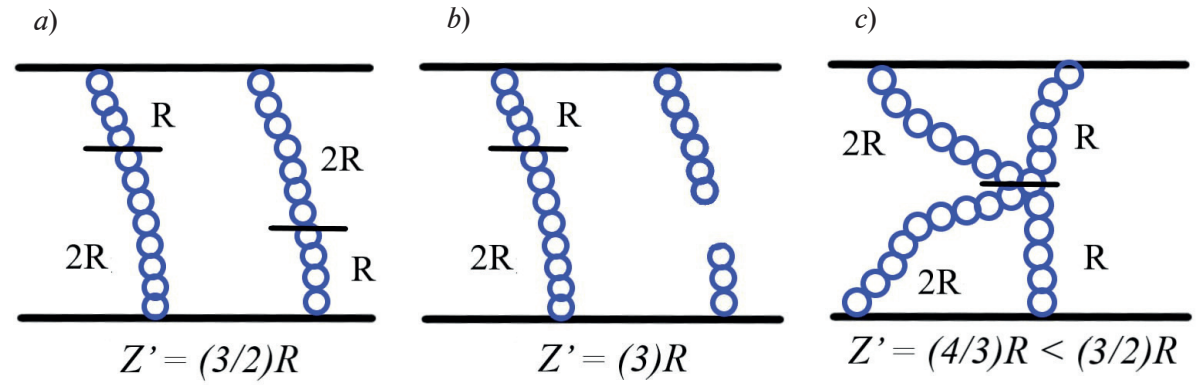

Fig. 5 Schematic illustration for nanowire re-form with change of active resistance Z'

Transition from conducting to metastable state with increased active resistance Z' (Fig. 4) can be associated with fragmentation of nanowires. Such process is always accompanied increase of capacitance and negative impact on Z'', which is inversely proportional to frequency (inset in Fig. 4). The best approximation for $I-V$ curves for metastable state (Fig. 2) is achieved with two parallel conduction mechanisms, namely, drift (unbroken nanowires) and activation (ruptured nanowires). As the frequency increases the re-formation of ruptured nanowires become more intense, resulting in Z' decrease.

After some critical frequencies (~ 2000 Hz on inset in Fig. 4) the degree of fragmentation begins to decrease. This is accompanied by consequent slow decrease of active resistance Z' for metastable state. Such behavior may be explained by ruptured nanowire fragments attaching to non-ruptured nanowires. The difference in active resistance Z' for different configurations of metastable state (Fig. 4) may be due to how the nanowire fragments are attached to the overall system.

The stability of new configuration is determined by the amount of generated heat from current flow and excessive energy that is still present in system after previous rupture. At high frequencies, the decrease of Z' invokes instant overheating, so metastable state cannot exist. This corresponds to system returning to MI on high frequencies (> 10000 Hz in Fig. 4).

Conclusion

It was shown that in naphthalocyanine films, conductivity occurs due to electron transport along metal nanowires. Based on the nanowires configuration, 3 main states of the system can be distinguished: conductive (nanowires are intact), metastable (some of the nanowires are broken) and non-conducting (all nanowires are broken). Switching between states is fully reversible. In DC mode the system state is determined by the values of applied electric field and the magnitude of the flowing current.

AC electric field can induce destruction of conducting state due to additional frequency dependent heat generation. Behavior of ruptured nanowires is frequency dependent. They can exist independently, providing activation contribution to the total conductivity. But within specific frequency range, ruptured fragments attach to non-broken nanowires, lowering overall resistance for the system. The lower frequency of this range is determined by the condition of sufficient energy to ensure mobility of the fragment when initial nanowire rupture occurs. Higher frequency is determined by the ability of a system with reduced resistance to pass currents with high heat generation without nanowires breaking to fragments.

REFERENCES

1. **Fang J., Zhou Z., Xiao M., Lou Z., Wei Z., Shen G.,** Recent Advances in Low-Dimensional Nanomaterials for Photodetectors, InfoMat. 2 (2019) 1–27.

2. **Yang L., Qingyun Q.,** Recent advances in organic-based materials for resistive memory applications, InfoMat. 2 (2020) 995–1033.

3. **Kotova M.S., Drozdov K.A., Dubinina T.V., Kuzmina E.A., Tomilova L.G., Vasiliev R.B., Dudnik A.O., Ryabova L.I., Khokhlov D.R.,** In situ impedance spectroscopy of filament formation by resistive switches in polymer based structures, Sci. Rep. 8, 9080 (2018).

4. **Dubinina T.V., Maklakov S.S., Petrusevich E.F., Borisova N.E.,** Photoactive layers for photovoltaics based on near-infrared absorbing aryl-substituted naphthalocyanine complexes: preparation and investigation of properties, New Journal of Chemistry. 45 (2021) 14815–14821.

5. **Djurovich P.I.,** Measurement of the lowest unoccupied molecular orbital energies of molecular organic semiconductors, Organic Electronics. 10 (2009) 515–520.

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