MOLECULAR SWITCH BASED ON POLYSILANE COMPOSITES

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Introduction

Amorphous silicon is a good semiconductive material for many applications. It is a member of the large class of silicon compounds which comprise silicon clusters, silane oligomers, poly(siloxanes), and poly(silanes). The last mentioned polymers are of considerable interest because of their unusual electrical and photoelectrical properties, namely the high charge carrier drift mobility, unusually high for polymeric charge transporting materials. It has been shown that in these polymers the effect of σ-electron delocalization is strong and charge carrier transport can proceed along the Si backbone. Because of high charge mobility these polymers are suitable for the preparation of electrically active composites.

In this paper we report the properties of electronic molecular switch based on the composite consisting of poly[methyl(phenyl)silylene] (PMPSi) matrix with admixed spiropyrane molecules.

Experimental

Materials

Matrix: PMPSi was prepared by sodium mediated Wurtz coupling polymerization. The low-molecular fraction was extracted with boiling diethylether. The residual polymer, obtained in c. 17 % yield, possessed a unimodal but broad molar mass distribution, $M_w = 4 \times 10^4$ g mol^{-1}.

Additive: Spiropyrane (SP), 1',3',3'-trimethyl-6-nitrospiro[2H-1-chromene-2,2'-indoline], was obtained from Aldrich Co. and used without further purification.
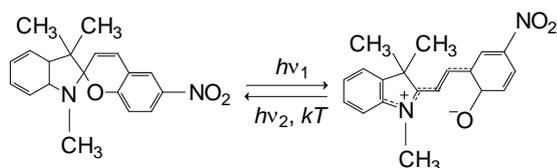
Scheme 1 Chemical structure of spiropyrane (SP, left) with photochemical transformation into merocyanine (MR, right).

Samples

Sandwich sample configuration ITO/PMPSi-SP/Al was used for the studies. On a glass substrate covered by indium tin oxide (ITO), film of PMPSi with admixed spiropyran (SP) was prepared by spin coating toluene solution. On the top Al electrode was vacuum evaporated. The concentration of the admixed SP amounted to 5 wt %.

Results and discussion

Charge transport in PMPSi

From the data published earlier it is evident, that the transport of charge carriers in PMPSi is governed by a superposition of both disorder and polaron effects. From the disorder model, i.e., charge carrier hopping among molecules; energetically: transport among distributed electronic tail states above the edge of the valence band, follows that the temperature (T) dependence of the mobility can be expressed as

$$\mu(T, F \to 0) \sim \exp\left[-\left(2\sigma^* / 3kT\right)^2\right] \qquad (1)$$

where σ^* is the width of the energy distribution of the hopping sites, F is the electric field and k is the Boltzmann constant.

The strong electron-phonon coupling causes carrier self-trapping and creates a quasiparticle, a polaron, which can move to an adjacent molecule only by carrying along the associated molecular deformation. Formation of polarons is accompanied by stretching of Si–Si bonds, by the deformation of Si–Si–Si angles and charge redistribution on 1D skeleton of the macromolecule. Taking into account the contributions both from the dynamic disorder, i.e. the polaronic barrier, and from the static disorder, i.e. the variation of the potential energy of the carrier as a result of the environment, the effective zero-field activation energy of the mobility can be expressed by the relation:

$$E_a^*(F \to 0) = E_a^{pol} + E_a^{dis} = \frac{E_p}{2} + \frac{8}{9}\frac{\sigma^2}{kT} \qquad (2)$$

where E_a^{pol} and E_a^{dis} represent the polaronic and disorder contributions. In the model polymer, PMPSi, the "on-chain" charge mobility was determined by time-resolved microwave photoconductivity as 2×10^{-6} m^2 V^{-1} s^{-1}. The mobility decreases in 3D system to the value of 2×10^{-8} m^2 V^{-1} s^{-1}, $= 0.08$ eV.

According to quantum chemical modeling the deformation contribution to the polaron binding energy, which, for PMPSi, is $E_p = 0.16$ eV, consists mainly of electron-phonon coupling and chain deformation terms; the deformation contribution is about five times higher than electron-phonon term.

Temperature and electric field dependences of charge carrier mobility can be utilized for the distinguishing between polaron and polaron-free transport. It was developed an analytical theory based on the effective medium approach to describe nondispersive hopping charge transport in a disordered organic material where polaron effects are important. The treatment of polaron transport with superimposed disorder is based on the Marcus jump rate equation, while the conventional Miller-Abrahams formalism is used to describe charge mobility in polaron-free systems. The results of the model are in good agreement with experimental data.

As follows from Fig. 1, the charge carrier mobility can be modified by additives. The value of the mobility depends on the electron affinity and the concentration of the additive.
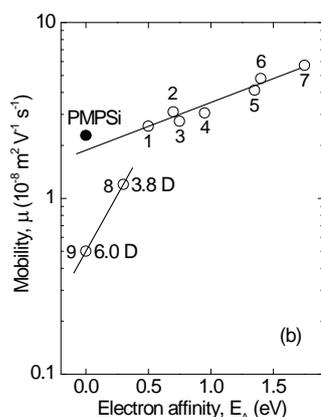

Fig. 1 Charge carrier mobility (μ) of doped PMPSi films vs. electron affinity of the dopants. Full circle – μ of undoped PMPSi. Electric field strength 4×10^7 V m^{-1}. Dopands: point 1 – anthracene, point 2 – tetracene, point 3 – p-dinitrobenzene point 4 – p-benzoquinone, point 5 – chloranil, point 6 – bromanil, point 7 – tetracyano-p-quinodimethane.

Two materials with electron affinity 0.3 and 0.0 eV (m-dinitrobenzene (point 8) and o-dinitrobenzene (point 9)

exhibit an unusual behaviour. They are materials with quite high dipole moment, 3.8 and 6.0 D, respectively. Thus, using the dipolar aditives we are able to modify charge carrier mobility of PMPSi.

Switching

If some material which changes dipole moment under some stimulus (light) is used as the additive, e.g., photochromic SP, we can change the mobility of charges flowing through PMPSi film [1]. SP is a molecule able to undergo a reversible photochemically driven reaction, resulting in the production of zwitterionic, high polar metastable merocyanine (MR, see Scheme 1, right), 1,3,3-trimethyl-2[2-(5-nitro-2-oxidophenyl) vinyl]-3*H*-indol-1-ium). Thus, we can construct a device with "on" and "off" state; optical input – electrical output. Theoretically for the change of the dipole moment of the additive from 2 to 10 D one can arrive $\mu^{(off)}/\mu^{(on)} \approx 10^6$ at ambient temperature. At present, the experimental value $\mu^{(off)}/\mu^{(on)} \approx 10$ was obtained.

Conclusion

The results reported in this paper demonstrate the possibility of the construction of photoactive switch based on the photo-induced dipolar field. Suitable photochromic reaction can modulate the transport of charge carriers between source and drain electrodes in a semiconducting film in the composite consisting of charge transporting polymer and photochromic molecules. The speed of the switching is limited by the speed of the photochromic transformation; in suitable systems with large polymer free volume it can reach even several miliseconds. Theoretically the speed can further be improved using the polarity of excited states where nonosecond scale can be reached. The experimental results presented here, leading to the decrease of charge carrier mobility and therefore of the electrical current by factor ca. 10, strongly depend on the sample geometry, thicknesses of the film and the concentration and orientation of photochromic additive in the transporting layer.

Reference

1. Nešp rek, S., Toman, P. and Sworakowski, J. *Thin Solid Films* **438-439** (2003) 268-278.