Photocontrolled Superconductivity

DOI: 10.1002/anie.200904548

Reversible Optical Manipulation of Superconductivity**

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Since the disappearance of electrical resistivity in mercury at low temperatures was observed by Onnes in 1911,[1] much attention has been paid to the study of superconducting materials. The main objectives of such studies are to discover new classes of materials, to improve their properties, or to clarify their superconducting mechanisms.[2–6] Manipulation of the electronic states of condensed matter by external stimuli is a key topic in the field of modern electronics, and optical stimuli are of considerable importance because they present many possibilities for realizing optical memory or switching devices. To date, photoinduced changes in superconducting properties have been reported in several systems such as yttrium barium copper oxide (YBCO) films,[7] YBCO/LCMO (lanthanum calcium manganese oxide) heterofilms,[8] and the alkali-metal fullerides.[9] However, such photoinduced effects were based on structural changes or on photoinduced excitation of the electrons, thus no reversible photoinduced effects on superconductivity have been reported. In the field of superconducting materials, the electric-field tuning of surface carrier density using a metal–insulator–semiconductor field effect transistor (FET) structure is the most common method of manipulating electronic states.[10–12] As existing microelectronics approaches its technological and physical limits, the future of nanoelectronics must lie in molecular-based or hybrid devices. Recent studies reveal that a cooperative effect involving charge transfer occurs at the interfaces between organic–inorganic hybrids such as self-assembled monolayer (SAM) films on conductive substrates.[13] These charge-transfer processes induce field-effect-like behavior, and result in the alternation of conducting properties in metals,[14] semiconductors,[15] and even in superconductors.[16] These phenomena open new opportunities to control the superconducting properties in solids by passivation with functional organic molecules. Since the two isomeric forms of some photochromes differ not only in their absorption spectra but also in their various physical and chemical properties,[17] these compounds can be used to control solid-state properties by photoirradiation.[18,19]

We have designed an azobenzene-containing self-assembled monolayer (SAM) on an Nb thin film (10 nm thick including a ca. 2.7 nm native oxide layer[20]) with which we can realize the reversible phototuning of superconducting properties. A schematic representation of such a system is illustrated in Figure 1 a. It is known that well-organized SAMs on oxidized Nb surfaces can be obtained by using a silane functional group.[16,21] In the present study, we used a silane-terminated azobenzene molecule (AZ). A grazing-incidence X-ray diffraction (GIXRD) pattern (Figure 1 b) showed negligible changes during the surface passivation of AZ or after subsequent photoirradiation, thus indicating that almost no structural effects occurred on changing the superconducting properties.

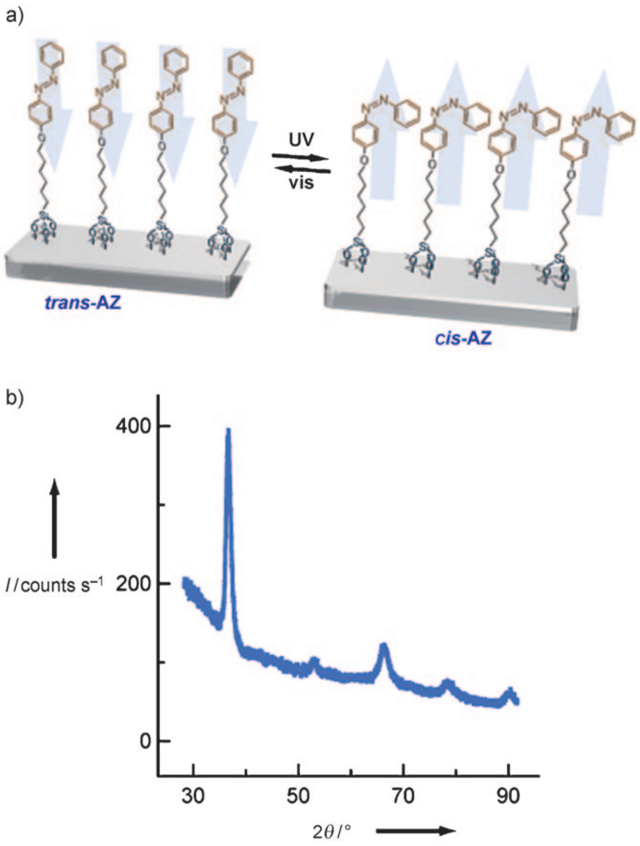

Figure 1. a) Representation of the hybrid films and their preparation procedures. The AZ monolayer was formed on the surface of the Nb film by immersing the bare Nb film into AZ solution for 48 h. The arrows show the direction of the surface dipole layer, which arises from cooperative effects of the intrinsic molecular dipole moment. b) GIXD patterns of a bare Nb film on a glass substrate. The five peaks that are observed for (110), (200), (211), (220), (310) are consistent with a face-centered cubic crystal structure of Nb with lattice constant $a = 3.29$ Å, which is ca. 5 % smaller than the corresponding value for bulk Nb (3.45 Å).

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[**] This work was supported by a Grant-in-Aid for Scientific Research in Priority Areas "New Frontiers in Photochromism (no. 471)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. Also, we thank Prof. T. Iyoda and Dr. K. Ito (Tokyo Inst. of Tec.) for helping to measure the water contact angle of the films and for useful discussion.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904548.

The superconducting properties of the bare Nb film and the hybrid film were determined from electrical measurements made using a four-point scheme. The bare Nb film was superconducting with a zero-resistance temperature (T_c^{ZERO}; T_c = critical superconducting temperature) of 4.2 K, which is in good agreement with the reported value for a 10 nm thick Nb film,[22] while the hybrid film had a T_c^{ZERO} of 5.2 K (Figure 2a). On the other hand, the initial critical superconducting current (I_c) value was dramatically decreased after the formation of the AZ monolayer (Figure 2b). Furthermore, the values of I_c, T_c, and resistance (Rn) for the hybrid film could be reversibly controlled by employing alternating photoillumination with UV and visible light (Figure 3).

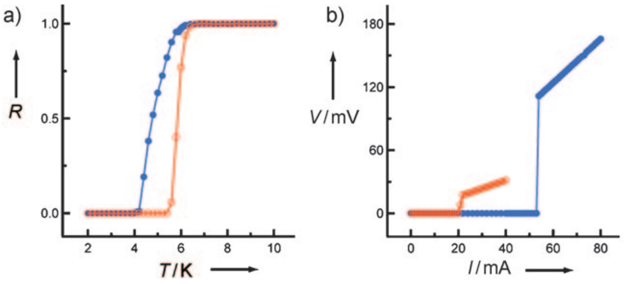

Figure 2. a) Temperature dependence of the Nb film resistance before (filled blue circles) and after (open red circles) the surface passivation of the AZ monolayer. Resistance values are normalized. b) *V–I* measurements of the Nb film before and after the surface passivation of the AZ monolayer at 2 K. The I_c value of 53 mA for the bare Nb film (filled circles) decreased to 20 mA after surface passivation (open circles).

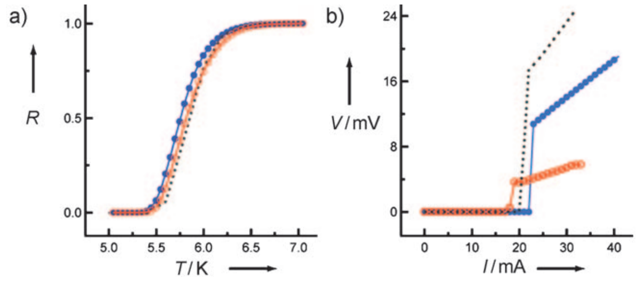

Figure 3. a) Temperature dependence of the resistance of the hybrid film for the initial state (dashed line), the UV photostationary state (filled blue circles) and the visible photostationary state (open red circles). Resistance values are normalized. b) *V–I* measurements of the hybrid film for the initial state (dashed line), the UV photostationary state (filled blue circles), and the visible photostationary state (open red circles) at 2 K.

Table 1 summarizes the values of T_c, I_c, and resistance for the each state. Comparative experiments revealed that Nb films passivated with silane molecules that do not contain an azo group (e.g., hexadecyltrichlorosilane) did not show any photoinduced changes in their superconducting properties, despite showing similar passivation-induced effects. Therefore the observed photoinduced effects must originate from photoisomerization of the AZ. Furthermore, the same measurements were also performed on thick Nb films (ca. 100 nm). In this case, the hybrid system did not show any passivation-induced or photoinduced effects, thus confirming that the observed passivation-induced and photoinduced effects are surface-dominated phenomena.

Table 1: Superconducting transition temperature, critical current and resistance value for the Nb films in each state.

	Bare Nb	Hybrid film (initial state)	UV p.s.s.[a]	Vis p.s.s.[a]
T_c^{ZERO} [K]	4.2	5.2	down	up
I_c [mA]	53	20	23	17
Rn [Ω] on T_c[b]	2.2	0.71	0.50	0.21
Rn [Ω] on I_c[c]	2.1	0.79	0.47	0.18

[a] p.s.s = photostationary state. [b] The resistance values on T_c were defined as the resistance value at 7 K. [c] The resistance values on I_c were extracted from the slope of the *V–I* plots.

One possible explanation for the surface passivation-induced or photoinduced effects is the theory of critical current in type II superconductors.[16,23–25] In a type II superconducting thin film, the surface pinning potential is very strong because of the nonuniformity of the electron density along the surface.[26] When a SAM is formed on a type II superconducting thin film, charge is transferred at the surface between the superconductor and the organic layer in order to reduce repulsion within the organic layer, thus resulting in a uniform distribution of the charge density along the surface.[13,16] As a result, variations in the electron density at the film surface that are induced by the absorbed organized molecular layer are responsible for the dramatic decrease in the I_c value. These explanations are also consistent with enhancement of the T_c^{ZERO} value. Type II superconductors exhibit superconducting mixed states around their superconducting transition temperature. Such effects make a superconducting mixed state extend over a wide temperature range and result in a lower T_c^{ZERO} value. Hence, the presence of a more uniform distribution of charge density along the surface caused by the charge transfer process increases the T_c^{ZERO} value.

Since charge-transfer processes from the substrate to the organic monolayer act as a "trigger" for the alternation of superconducting properties, these effects must be controlled by using the metal work function, which is linearly related to the dipole moment density perpendicular to the surface.[27,28] Since the *trans*- and *cis*-AZ monolayer have different dipoles, they can be used to change the work function of the substrate by photoirradiation.[18,19,29] In the current system, the values of $\mu\cos\theta$ for AZ were calculated as −0.15 D and 1.53 D for *trans*- and *cis*-AZ, respectively. Hence, the magnitude of the electron transfer in the initial *trans*-AZ becomes smaller in the *cis*-AZ under UV illumination, and it recovers to around its initial value under visible light illumination. Schematic illustrations of the changes in the work function that arise from the photoisomerization of AZ are shown in Figure 4.

The observed reversible photoswitching of superconductivity can be summarized as follows. The work function of bare Nb substrates was reduced by the negative surface dipole of *trans*-AZ upon surface passivation, and charge transfer

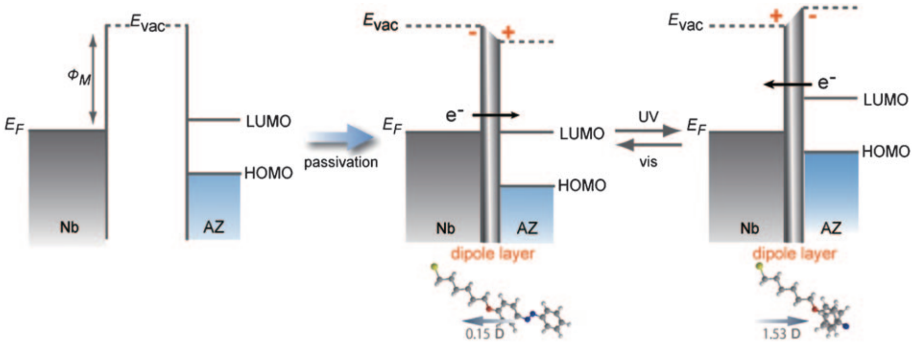

Figure 4. Changes in the work function arising from the photoisomerization of AZ. Schematic energy level diagrams for an untreated interface (without surface passivation; left); passivation of *trans*-AZ imposes an interface dipole that decreases the local vacuum energy level (E_{vac}; center); photoisomerization to *cis*-AZ imposes an interface dipole that increases the local vacuum energy level (E_{vac}; right).

from the Nb substrate to the organic monolayer was induced. Such charge-transfer processes decrease the inhomogeneities of the electron distribution along the surface. After UV illumination, the charge transfer could be reversed with *trans*-to-*cis* photoisomerization because of the positive surface dipole of *cis*-AZ. As a result, the values of I_c and T_c could be controlled by employing alternating photoillumination with UV and visible light, which caused changes in the electron density along the surface because of the photoisomerization of AZ.

Received: August 14, 2009
Revised: October 29, 2009

Keywords: nanostructures · photochromism · self-assembly · superconductors · thin films

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