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OPTICAL PHASE TRANSITIONS IN ORGANO-METALLIC CHARGE-TRANSFER COMPLEXES

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Abstract Semiconducting organometallic films such as copper tetracyanoquinodimethan (CuTCNQ) have been observed to switch between two stable states when exposed to optical radiation. Observations of switching between two states in these films have been made by Raman spectroscopic methods and direct observation of electrical resistance changes. Line or pattern generation is observed for exposure above certain threshold levels. These effects are observed in a wide range of Cu and Ag organometallic compounds. Optical switching in films such as copper and silver tetra cyanoquinodimethan (CuTCNQ and AgTCNQ) can be erased using CO_2 laser radiation. Results on the wavelength and irradiance dependence of the optical switching threshold are also presented and interpreted in light of proposed switching mechanisms in these organic materials.

INTRODUCTION

We have recently reported optical and optoelectronic switching between two states in polycrystalline organo-metallic semiconductor films[1-4] using the 488.0 and 457.9 nm lines of an argon ion laser.[5] Although the optical measurements have largely concerned films of copper or silver complexed with the electronic acceptor tetracyano-quinodimethan (TCNQ), preliminary results on other

acceptors indicate similar effects. It has been postulated that the effect of the applied electric field on the initial charge-transfer salt (e.g., CuTCNQ) is to induce a phase transition resulting in the formation of a non-stoichiometric complex salt containing neutral TCNQ:

$$[Cu^{+}(TCNQ^{\bullet -})]_n \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Cu_x^0 + [Cu^{+}(TCNQ^{\bullet -})]_{n-x} + (TCNQ^0)_x. \quad (1)$$

The reaction shown in Eq. (1) is reversible, and the initial phase can be easily reformed by heating the film. The reaction proceeds readily, because the simple $Cu^{+}(TCNQ^{\bullet -})$ has been shown to be thermodynamically more stable than the complex salt containing neutral TCNQ ($TCNQ^0$), shown on the right-hand side of Eq. (1).[6]

The previous results on optical switching in the class of semiconducting organo-metallic films such as copper and silver tetracyanoquinodimethan (CuTCNQ and AgTCNQ) have been extended to show that switching can be erased using CO_2 laser radiation. The effect can be observed by Raman spectroscopy and visually. Results on the wavelength and irradiance dependence of the optical switching threshold show that the optical switching occurs over a wide spectral range, and can be interpreted in light of proposed switching mechanisms in these organic materials.

Erasable Optical Switching

Two switching effects in the organo-metallic films can be induced by optical radiation, depending on the irradiance (W/cm^2) of the incident laser beam. At low irradiance levels, optoelectronic switching from a high to a low electrical impedance state can be induced, while at higher

irradiance levels, high-contrast patterns can be generated by forming macroscopic amounts of $TCNQ^0$. Both these effects remain stable until the film is heated, which causes neutral TCNQ molecules and the corresponding metal atoms to undergo a solid-state reaction [Eq. (1)] and form the original metal-TCNQ charge-transfer complex.

We have now demonstrated that defocused laser radiation can be used as a source of thermal energy to reverse or erase switched regions of the film. Shown in Figure 1 are the results on reversing the optical switching using a CO_2 laser as a source of thermal energy. The high and low impedance states exhibit marked differences in the Raman spectrum, especially in the 1300-1500 cm^{-1} region due to the ν_4 band (C=C stretching).[5,7] In this spectral region, the initial charge-transfer complex in the high impedance (insulating) state has only one strong Raman band at 1375 cm^{-1}, corresponding to the $TCNQ^-$ anion species (Fig. 1a). In all cases, the laser power of the probe beam was sufficiently low that the equilibrium state of the film was not perturbed. After irradiation with an argon laser, the film is switched to the low-impedance (conducting) state, and an additional band is observed at 1450 cm^{-1}, corresponding to neutral TCNQ (Fig. 1b). The film in the conducting state can be driven back to the original insulating state, using defocused CO_2 laser radiation, as shown in Figure 1c. For thin CuTCNQ films on a copper substrate, the CO_2 laser irradiance required to reverse the film state was approximately 200 W/cm^2. It should be emphasized that this exposure was necessary because of the efficient heat

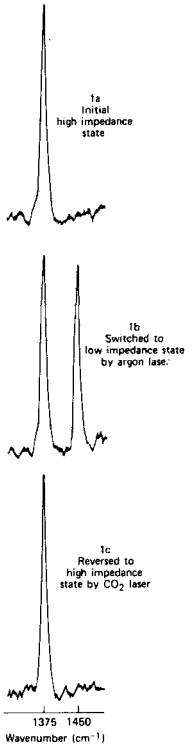

FIGURE 1. Raman spectra in the 1300-1500 cm^{-1} region demonstrating the use of CO_2 laser radiation to reverse the optoelectronic switching.

dissipation from the film to the metal substrate. Much lower exposures, however, can be used when the films are on thermally insulating substrates. Other defocused laser sources can also be used as a source of thermal energy to reverse the reaction[(Eqn. (1)].

CO_2 laser radiation can also be used to erase high-contrast patterns which contain macroscopic amounts of $TCNQ^0$. This effect for AgTCNQ on a glass substrate is shown in Figure 2, where an array of nine spots was produced by a focused CO_2 laser beam, and the central spot was almost totally erased by a defocused CO_2 laser beam. Each spot was initially produced by a 50 msec exposure

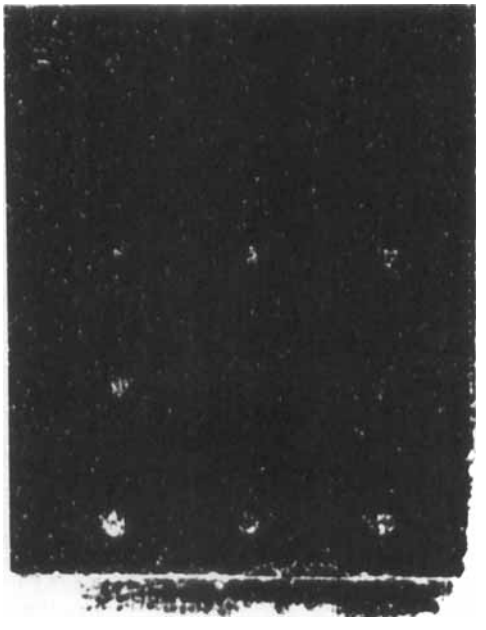

FIGURE 2. High contrast spots produced on AgTCNQ by a focused CO_2 laser. The central spot was erased using defocused CO_2 radiation.

from a 1W CO_2 laser; the laser irradiance at the sample was approximately 600 W/cm^2. The central spot was erased by defocusing the lens to achieve a beam diameter of 2 mm at the sample and then irradiating at a power 2W (I ~ 60 W/cm^2).

Wavelength Dependence of Optical Switching

The wavelength dependence of the optical switching threshold for CuTCNQ and AgTCNQ was studied to obtain information about the switching mechanism. Wavelengths from three different CW lasers were used: 457.9, 488.0, and 514.5 nm from an argon ion laser; 632.8 nm from a helium-neon laser and 10,600 nm from a carbon dioxide laser. At each wave-length, the metal-organic films were irradiated at various laser powers and at several locations on the film. The switching threshold (i.e., the laser irradiance at which neutral TCNQ was produced) was measured by Raman spectroscopy. By varying the laser spot size, it was determined that the threshold was dependent on the irradiance and not on the laser power. The results are presented in Table I. Variations in the observed thresholds are due largely to spatial inhomogeneities in the film, with the exception of the value at 10,600 nm for CuTCNQ. It is evident that the optical switching threshold for AgTCNQ is approximately one-half the value for CuTCNQ. The threshold for AgTCNQ is essentially independent of wavelength, while the threshold for CuTCNQ is relatively constant in the visible spectral region, but is approximately four times higher in the infrared.

In order to determine the effect of optical absorption on the threshold values, absorption spectra

(shown in Fig. 3) were measured on KBr pellets containing 0.22% AgTCNQ and 0.08% CuTCNQ. The prominent feature in the spectrum is a pronounced low energy (0.3 eV) transition that has been observed in other TCNQ salts, and is associated with an inter-radical charge-transfer excitation $TCNQ^- + TCNQ^0 \rightarrow TCNQ^0 + TCNQ^-$.[8,9] This

TABLE I Optical switching threshold for AgTCNQ and CuTCNQ at various wavelengths.

LASER SOURCE	WAVELENGTH NM	PHOTON ENERGY eV	INCIDENT LASER IRRADIANCE AT THRESHOLD (W/cm^2)	
			AgTCNQ	CuTCNQ
ARGON ION	457.9	2.71	800	1500
	488.0	2.54	600	1500
	514.5	2.41	1000	1500
HELIUM-NEON	632.8	1.96		2000
CARBON DIOXIDE	10600.0	0.12	600	8000

transition is of comparable energy to the activation energy of electrical conductivity in the metal TCNQ salts.[10] Thus, if the switching mechanism involved a photon-induced transition, we would expect the incident irradiance at threshold to be significantly higher at 10,600 nm (0.12 eV) because the absorption is quite low. As can be seen from the data in Table I, however, this is clearly not observed for AgTCNQ. Even for CuTCNQ, the increase in the threshold at 10,600 nm is not as large as would be expected if the switching mechanism involved a photon-induced transition. Furthermore, multiphoton processes can be ruled out,because they are extremely inefficient when induced by low-power cw lasers.

Thus, it seems unlikely that the optical switching mechanism is due to a photon-induced transition. Thermal

effects should be negligible because heat drives the reverse process to form the original (unswitched) complex

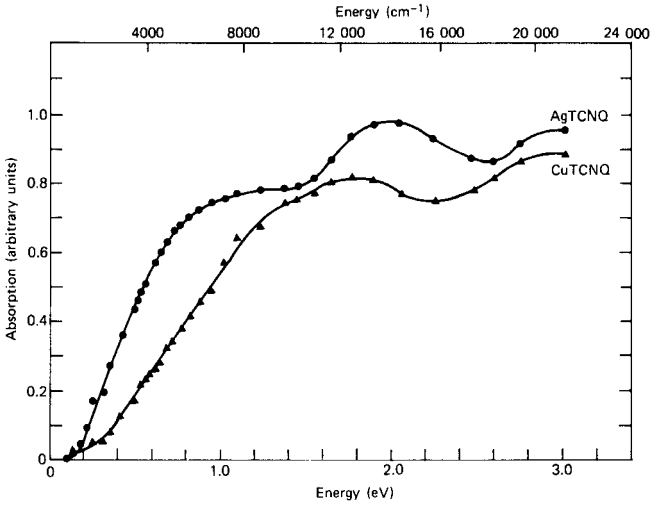

FIGURE 3. Optical absorption spectra of AgTCNQ and CuTCNQ in a KBr pellet. The results have been corrected for transmission and reflection.

[see Eq. (1)]. This suggestion that the optical switching mechanism is associated with the electric field of the optical radiation. This field-induced mechanism should be relatively independent of optical wavelength, which is in agreement with the results.

Optical Transmission Associated with Switching

An area of significant interest is the change in macroscopic optical properties of the CuTCNQ films in a radiation field. The potential for large changes in transmission and reflection in CuTCNQ and other members of

this family under intense radiation fields is of significant practical interest. A very preliminary investigation of this process is beginning. It is, of course, obvious that the macroscopic properties of CuTCNQ and AgTCNQ films, when irradiated, are dramatically changed in that the films undergo a change from their respective blue and violet colors to a rather pale yellow, characteristic of neutral TCNQ. The transmision spectra of regions which exhibit this color change should show also significant changes in their transmission properties. We have begun to investigate the transmission spectra of irradiated thin films formed on glass substrates. As shown in Figure 4, a typical CuTCNQ film formed by solid state diffusion is rather poorly transmitting from the mid-visible into the near infrared in the vicinity of 1100 nm, and there is a substantial increase in transmission extending into the infrared. Upon irradiating the CuTCNQ film with a Nd:YAG laser at 532 nm scanned over a sufficient region to perform simple transmission measurements, one observes a large change in the transmission, as also shown on Figure 4. A significant increase in transmission throughout the spectrum from the mid-visible to the IR is observed. Extremely dramatic increases are observed in the red end of the spectrum and the near IR, particularly those regions which are of interest with respect to many of the principal laser sources. These preliminary transmission measurements demonstrate a very large change in the optical transmission, which is clearly of practical interest.

The transmission properties of an AgTCNQ film are shown in Figure 5. In contrast to the changes observed in

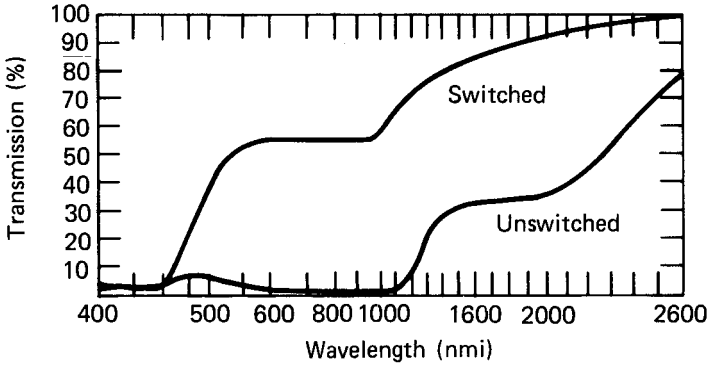

FIGURE 4. Typical CuTCNQ transmission switch - 30 mJ pulses from frequency doubled Nd: YAG laser (532 nm).

CuTCNQ, the switched and unswitched films are quite similar in the infrared portion of the spectrum. However, large changes in transmission are noted in the visible part of the spectrum between 400 and 600 nm. The switched AgTCNQ becomes strongly transmitting in a band centered at 500 nm,while the unirradiated film is poorly transmitting in the same region.

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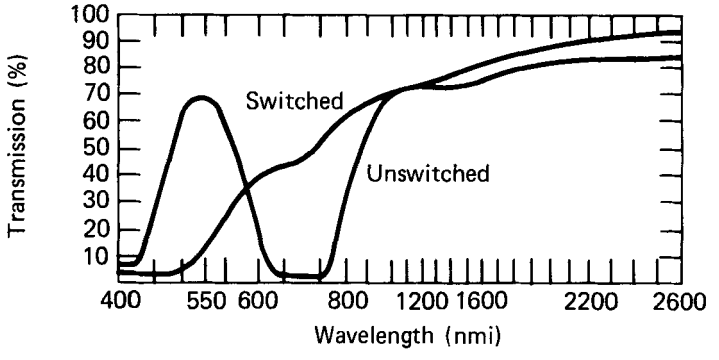

Figure 5. Typical AgTCNQ transmission switch - 45 mJ pulses from frequency doubled Nd: YAG laser (532 nm).