

## Preparation and electrical/optical bistable property of potassium tetracyanoquinodimethane thin films

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### Abstract

Potassium tetracyanoquinodimethane (K(TCNQ)) thin films were prepared using physical vapor deposition combined with solid state chemical replacement reaction. Reversible electrical bistable behavior at or even above room temperature was observed; and, the optical bistable property of K(TCNQ) film was observed.

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### 1. Introduction

Unique electrical and optical properties of certain charge–transfer complexes formed with metals and (7,7,8,8) tetracyanoquinodimethane (TCNQ) were reported [1]. Literature has suggested that metal–(TCNQ) thin films, such as Ag(TCNQ) and Cu(TCNQ), have potential applications in photoelectric switches [2], electrical bistable memories and erasable photochromic optical storages [3].

In recent years, studies on preparations of bulk crystals of organic charge–transfer complexes using alkali-metal and TCNQ, such as K(TCNQ) and Ru(TCNQ), were published. The negative resistance effect of these bulk crystals at low temperature was reported and its theoretical explanation was attempted [4–9]. For making devices using alkali–metal and (TCNQ) complexes, however, would require the material to be prepared as thin films rather than bulk crystals. In addition, increasing the operating temperature from the low temperature to room temperature or higher would make the device application more viable economically. Unlike Ag(TCNQ) and Cu(TCNQ), alkali–metal–(TCNQ) thin films cannot be fabricated using direct metal evaporation

method, because alkali-metals like K and Na are very active. In this article, we report the successful preparation of K(TCNQ) thin films combining solid state chemical replacement reaction with physical vapor deposition (PVD). The K(TCNQ) thin films were prepared by evaporating potassium iodide (KI) or potassium-hydroxide (KOH) and TCNQ on to a substrate in vacuum followed by a process of solid state chemical replacement reaction. The investigation of optical/electrical bistable properties of the K(TCNQ) thin films at room temperature is also reported.

### 2. Experimental details

A PVD process was employed for preparing K(TCNQ) thin film. TCNQ and KI (or KOH) were simultaneously evaporated on to a substrate of choice, e.g. NaCl single crystal or glass, from separate sources in vacuum. The base vacuum pressure was at  $1.50 \times 10^{-1}$  Torr. The substrate temperature was controlled at 25 °C. The evaporating temperature of TCNQ was set at 200 °C. The evaporating temperatures of KI (or KOH) were varied depending on required evaporating rate, typically above 800 °C. After the PVD, the film was annealed at 120 °C in vacuum for 1 h to let solid state chemical replacement reaction take place.

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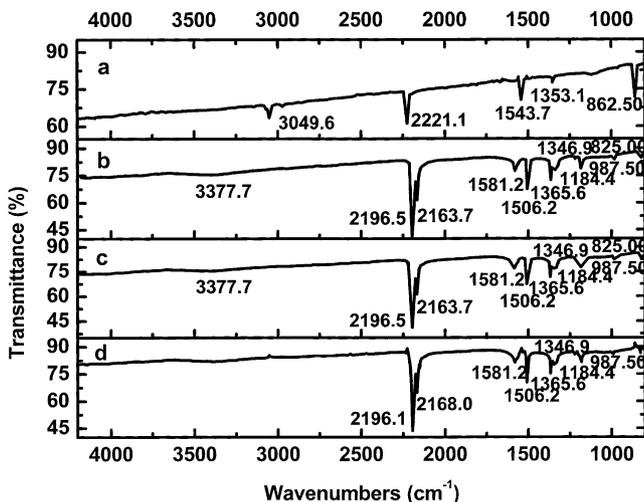


Fig. 1. IR absorption spectra of (a) TCNQ and (b) K(TCNQ) thin films prepared with KOH, (c) after heat treatment and (d) with KI.

Upon completion of the annealing, a transparent blue colored K(TCNQ) film was obtained.

Infrared resonance (IR) absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the chemical composition of the films made using the described method. The IR absorption spectra were measured using a Nicolet 5DX. The XPS spectra were obtained using a VG Microlab310. Mg  $K\alpha$  ( $E=1253.6$  eV) excitation was used as the source of X-ray radiation. The energy scale of the spectrometer was calibrated by setting the measured C(1s) BE to 284.6 eV. The data were treated by Microcal Origin 5.0.

For electrical characterization, two layers of aluminum (Al) were additionally evaporated before and after the preparation of K(TCNQ) thin film to form a stacked structure on glass substrate. The Al layers in the test structure served as the electrodes.

For photochromic characterization, a YAG laser system was used, with 532 nm wavelength, 10 ns width of pulse, 35  $\mu$ J power and a spot diameter of approximately 3 mm.

Raman spectroscopy is used to validate the charge-transfer mechanism in the vibration energies of molecules before and after color change of the K(TCNQ) films due to the irradiation of the laser. The Raman spectra were measured using Dilor Labram1B.

### 3. Results and discussion

#### 3.1. Chemical and structural characterization

To compare the chemical composition of the films, IR spectra of a TCNQ film and three slightly different K(TCNQ) films are obtained (Fig. 1). A typical IR spectrum of TCNQ film prepared using the same method as the K(TCNQ) films but without the potassium source

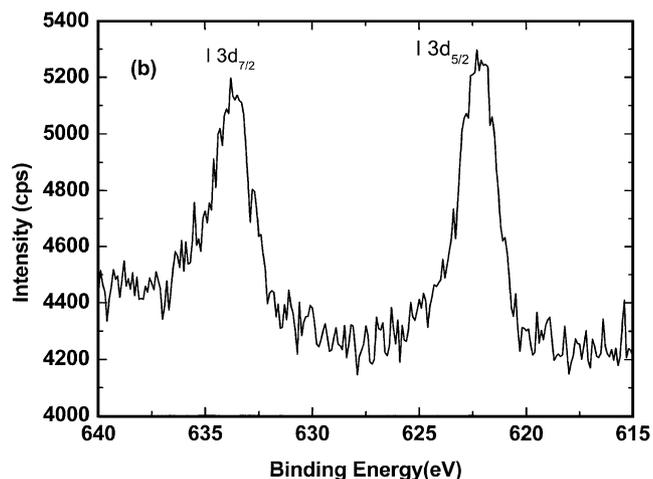
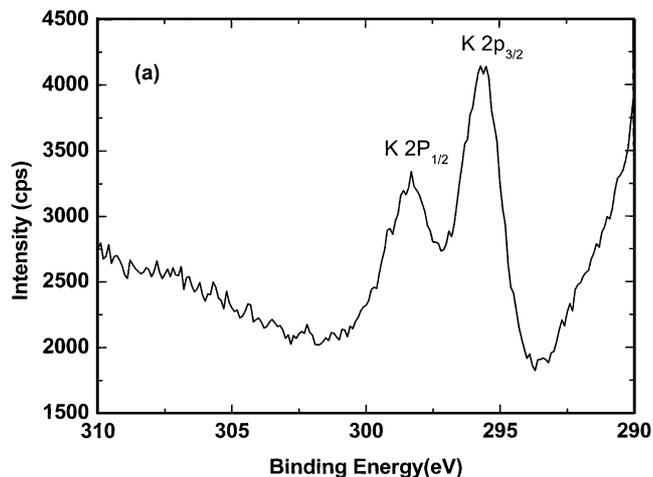


Fig. 2. XPS spectra of (a) K and (b) I in K(TCNQ) thin films using the KI source.

is shown in Fig. 1a. The IR spectra from the samples of as-evaporated K(TCNQ) film using a KOH source, vacuum annealed K(TCNQ) film using a KOH source and as-evaporated K(TCNQ) film using a KI source are shown in Fig. 1b, c and d, respectively.

The four absorption peaks of TCNQ (Fig. 1a) at 3049.6, 2221, 1543 and 863  $\text{cm}^{-1}$  were all disappeared in the other three spectra (Fig. 1b–d). The IR spectra peaks of the K(TCNQ) thin films in Fig. 1b–d match exactly with that of bulk K(TCNQ) materials reported by other researchers [10,11]. These spectra are evidences of the successful formation of K(TCNQ) molecular structure.

In Fig. 1b and c, an OH absorption peak (3377.7  $\text{cm}^{-1}$ ) is apparent in the K(TCNQ) films prepared with the KOH source, but not in that prepared with the KI source (Fig. 1d). The annealing helped to reduce the amount of OH, as the absorption peak weakened, but did not completely eliminate the OH from the film (Fig. 1c).

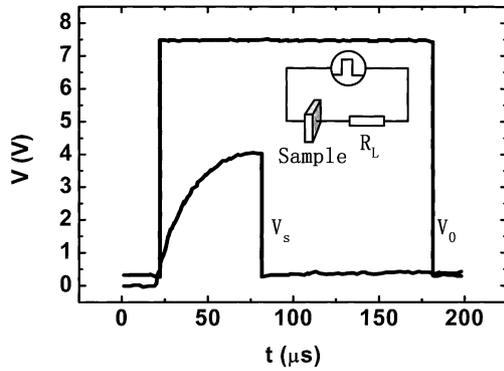


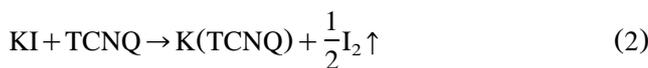
Fig. 3. Switching effect of the K(TCNQ) thin film from high-resistance state to low-resistance state at room temperature. The inset shows the test circuit diagram with the  $R_L$  as the current-limiting resistor and the square wave generator.

The XPS spectra of the K(TCNQ) thin films prepared using KI source (Fig. 2) shows an I peak indicating the existence of I atoms in the film, even though no iodine (I) bonding was observed in the IR spectrum (Fig. 1d). According to the quantitative analysis of the XPS spectra, the K to I ratio in the sample is:

$$\frac{n_K}{n_I} = \frac{I_K/S_K}{I_I/S_I}$$

Here,  $I_K$  and  $I_I$  are the areas enveloped by the strongest spectral line (which means the number of photoelectrons) of K and I, respectively;  $S_K$  and  $S_I$  are the atom sensitive factors of K and I, respectively. The K to I ratio in the sample is calculated with the described formula, it is approximately 10:1.

Therefore, we conclude that the K(TCNQ) films we prepared contain small amounts of  $H_2O$  or I depending on the potassium source. These species might be absorbed on the specimen surface or in the film as impurities, but not forming bonds with the K(TCNQ) molecules. Hence, the following solid state replacement reactions of Eqs. (1) and (2) are thought to have taken place during the film preparations for the KOH source and KI source, respectively:



### 3.2. Electrical characterization

The electrical tests were done while the K(TCNQ) specimens were either at room temperature or heated to

approximately 120 °C using the circuit shown in Fig. 3a. Fig. 3b shows the voltage,  $V(t)$ , across the test structure, i.e. Al/K(TCNQ)/AL, at room temperature after a single voltage pulse. The initial rise of  $V(t)$  is an indicative of capacitance effect. What is interesting is that once the voltage across the film reaches certain threshold ( $\sim 4$  V in this case), a sudden drop of the film resistance from a high state of  $\sim 10^7 \Omega$  to a low state of  $\sim 10^2 \Omega$  is observed. The duration of the switch is only a few hundredths of a millisecond. The film will stay at low-resistance state unless there is an external excitation, such as an electrical field or heat. For example, after the specimen was heated to approximately 120 °C, the low-resistance state switched back to high-resistance state. This is different from that of a single crystal bulk sample [5], but similar to that of other metal-(TCNQ) thin films [1–3]. It is possible that the negative resistance effect observable at an increased temperature compared to the bulk crystal is unique to thin film samples.

$I$ – $V$  curves of the K(TCNQ) film in the test circuit can be obtained by measuring the voltage across the film and the current passing through the current-limiting resistor,  $R_L$ . A hysteresis-like  $I$ – $V$  curve was observed with a 30 M $\Omega$   $R_L$  (Fig. 4a). While maintaining the K(TCNQ) film at 120 °C, by gradually increasing the supply voltage,  $V_0$ , the voltage across the film,  $U_x$ , slowly increased, the current through the film,  $I$ , also increased (Fig. 4a, Path ‘1’). When  $U_x$  reached a threshold (typically 2–4 V), the resistance of the K(TCNQ) film switched from high-resistance state to

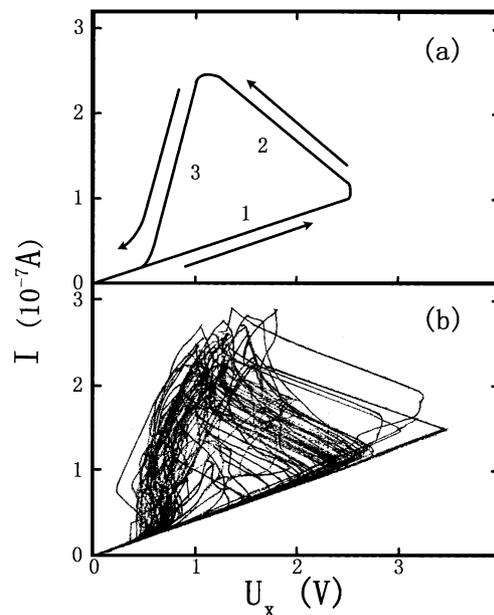


Fig. 4.  $I$ – $U$  curves of the K(TCNQ) thin film at 120 °C (a) hysteresis-like loop at 120 °C (b)  $I$ – $U$  curves of the K(TCNQ) thin film at 120 °C after 100 times repeat.

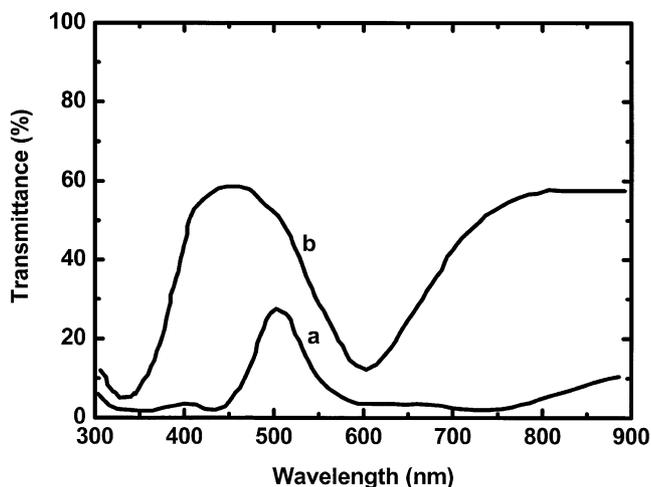


Fig. 5. Transmission spectra of K(TCNQ) film (a) before and (b) after laser irradiation.

low-resistance state, i.e. a negative resistance effect appeared, and the  $I$  increased with the  $U_x$  slowly decreasing (Fig. 4a, Path '2'). Finally, if we lowered the  $V_0$  to zero, the  $U_x$  also came back to zero (Fig. 4a, Path '3'). This process can be repeated many times. A 100-time repetition of the  $I$ - $V$  curve is shown in Fig. 4b.

### 3.3. Optical characterization

Like other metal-(TCNQ) films [2,3], the K(TCNQ) films also exhibit the photochromic property. The transmission spectra of the K(TCNQ) film before and after the laser (632.8 nm wavelength) irradiation are shown in Fig. 5a and b, respectively. After the laser irradiation, the color of the K(TCNQ) film at the irradiated spots was changed from dark blue to yellow. Considerable transmittance differences between spectra before and after irradiation at the 650 and 405 nm wavelengths are observed, comparing Fig. 5a with b. This property could potentially make the K(TCNQ) film suitable for storage media applications, such as currently available red-light DVD or upcoming blue-light DVD storage media.

The Raman spectra of TCNQ and K(TCNQ) films are shown in Fig. 6. After the color change, the characteristic peak of TCNQ<sup>0</sup> was observed, indicating the laser irradiation neutralized some TCNQ molecules in the K(TCNQ) thin film. These Raman spectra are in agreement with Yoshikawa et al. have been reported [12].

If we use a laser power greater than 3 mW and limit the irradiation time to less than 10 s, the irradiated spot becomes 'bright', like the 'write' process of optical storage. Once the irradiation time was increased, e.g. to longer than 30 s, either there was no 'bright' spot at all,

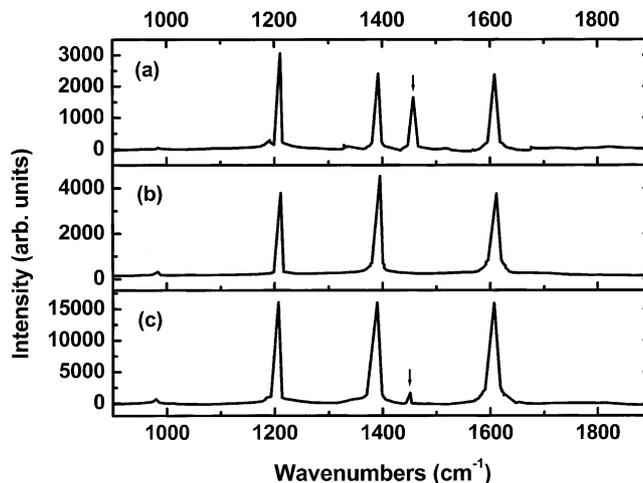


Fig. 6. Raman spectra of (a) TCNQ film, K(TCNQ) film (b) before and (c) after color change.

or the original 'bright' spot disappeared, similar to the 'erase' process of optical storage. The process from 'dark' to 'bright' of K(TCNQ) film is a photochromic process. The reversal process from 'bright' to 'dark' is induced by heat. Fig. 7 is a photo of K(TCNQ) thin film showing a pattern of 'bright' lines generated by moving the sample under the irradiation of the 632.8 nm laser with 3 mW power. The laser beam spot size was  $\sim 3 \mu\text{m}$ , but the lines were wider than that due to the vibration of the sample holder during the experiment. With an optical microscope, we observe that the color of the 'bright' spots and lines is yellow and the color of other 'dark' areas is blue (Fig. 8).

Like Ag(TCNQ) [1,2] and Cu(TCNQ) [3], we believe that the electrical and/or optical bistable prop-

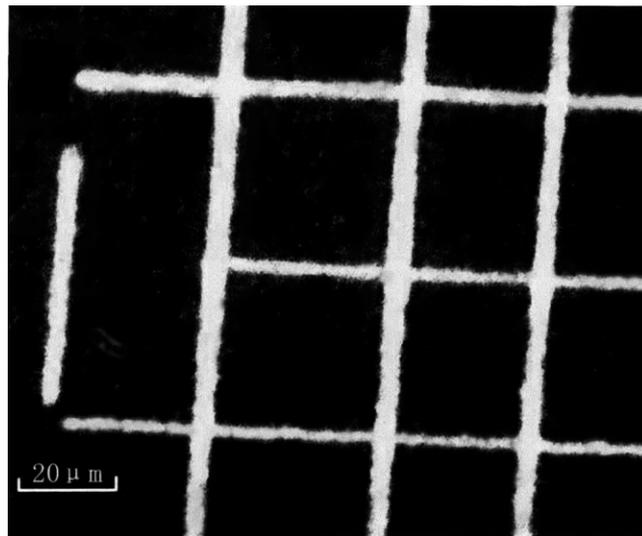


Fig. 7. An optical photograph pattern on the K(TCNQ) thin film produced by the 632.8 nm laser.

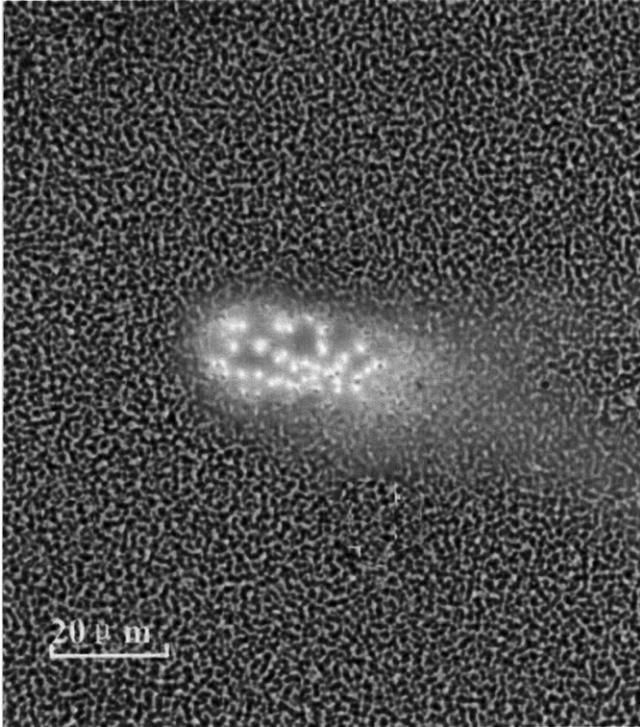
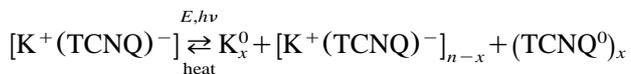


Fig. 8. An optical photograph of the K(TCNQ) thin film showing photochromic effect. The color of the sample in the center of the image changed from blue to yellow under 632.8 nm laser irradiation for less than 10 s.

erties of K(TCNQ) films are a result of the following process:



On the left hand side of the reaction, the K(TCNQ) film is at a high-resistance state (blue colored film). On the right hand side, however, the K(TCNQ) film is at a low-resistance state (yellow colored film). The film transition from a high-resistance state (blue) to a low-resistance state (yellow) occurs when an external optical/electrical excitation is introduced. The film can return to original state by heating it to 120 °C or above. These are the same phenomena observed in other charge-transfer complexes, such as Ag(TCNQ) and Cu(TCNQ) [1–3].

#### 4. Conclusion

We have successfully prepared K(TCNQ) thin films using PVD coupled with solid state chemical replacement reaction. It is shown that the K(TCNQ) thin films produced using the method described in this article have the negative resistance effect at room temperature to as high as 120 °C.

The photochromic effect of the K(TCNQ) thin films was also discovered and described in detail. It is shown that the K(TCNQ) thin films would have potential applications of optical storage.

The method described in this article for preparing organic charge-transfer thin films is not limited only to make K(TCNQ) thin films, it also clears a way for preparing other thin films of highly reactive alkali-metal and TCNQ complexes, e.g. Na(TCNQ) thin films.

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