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Observation of microwave conductivity in copper iodide films and relay effect in the dye molecules attached to CuI photocathode

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Abstract

Microwave conductivity and two channels of recombination process were observed in the CuI films. Spin orbital splitting resulted in split in the valence band of CuI. The dye molecules attached to the CuI film act as an electron mediator in addition to the sensitization process under back wall-mode illumination.

Keywords: Microwave conductivity of thin CuI films; Relay effect of dye molecules

1. Introduction

Copper iodide has aroused much attention due to occurrence of filled d^{10} shells in addition to the s^2p^6 shells, excitonic properties, different crystallographic phases (cubic, wurtzite and zincblend), semiconductivity and positive spin orbital pining of the valance band [1–4]. The low temperature γ-CuI is known as a p-type semiconductor with a band gap of 3.1 eV. The energy difference of $\Gamma_{15,2}$ and $\Gamma_{1,2}$ valleys at Γ point corresponds to the band gap excitation. The upper-most valance bands, $\Gamma_{15,2}$ and $\Gamma_{12,1}$ of CuI, is derived from the $3d$ states of copper atoms and $5p$ of iodine atoms [5]. We have clearly observed microwave conductivity in thin CuI films and split of the electronic bands at room temperature. Dye molecules attached to the CuI film act as an electron mediator in addition to the sensitization process under back wall-mode illumination.

2. Experimental

Sintered CuI pellets were prepared by sintering compressed powder (obtained from Nacalai Tesque, 99.9%) pellet at 200 °C for 30 min at N_2 atmosphere. CuI films were prepared on various substrates (Si, quartz substrates, TiO_2 films, conducting glass and glass substrates) by exciting a sintered CuI pellet by fundamental laser beam (excitation wavelength—308 nm, repetition rate—2 Hz, pulse width—240 mJ/pulse) with an incident angel of 45° in vacuum. The background pressure was maintained as 2×10^{-5} Torr (see Ref. [6] for more details). The resulted films were characterized by X-ray diffraction from the films (X-ray diffractometer-Jeol), optical spectroscopy (UV/VIS/NIR spectrometer-Jasco V570) and energy dispersion spectrometry (scanning electron microscope: Hitachi S3000H). Conductivity of the films was measured by four-probe technique. In addition, CuI films were excited with a forced laser beam (Nd:YAG wavelength of 266 nm, pulse with of 20 ns) through the air/film interface while directing microwave radiation (8–12 GHz) to the sample. Transient of reflected

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microwave conductivity signal was measured. More details of this technique have been described elsewhere [7]. Photoelectrochemical measurements of CuI electrodes sensitized with iodate of methyl violet 6B were also carried out in I^-/I_3^- ($I^-:I_3^- = 1{:}10^{-5}$) redox-electrolyte with respect to standard calomel electrode under monochromatic irradiation. All measurements were carried out at room temperature unless specially mentioned.

3. Results and discussion

CuI thin films (on glass substrates) exhibited a higher microwave conductivity compared to the powder. Transient of microwave-photoconductivity of the film is shown in Fig. 1. As is shown, two channels of recombination of electrons and holes were observed. Fast decay in microwave conductivity is correlated with band-to-band relaxation of electrons and slower decay is due to traps levels [7], probably due to the non-reacted copper ions in the CuI film. Recombination of photo-generated electron–hole pairs in copper defects is a known phenomenon [8]. The existence of excess copper in the film was confirmed by EDS technique and the ratio of Cu to I was found to be 10:9.85.

X-ray diffractograms of deposited films (on quartz substrates) and CuI powder are represented in Fig. 2. The intense peak at 25.4° indicates that the deposited

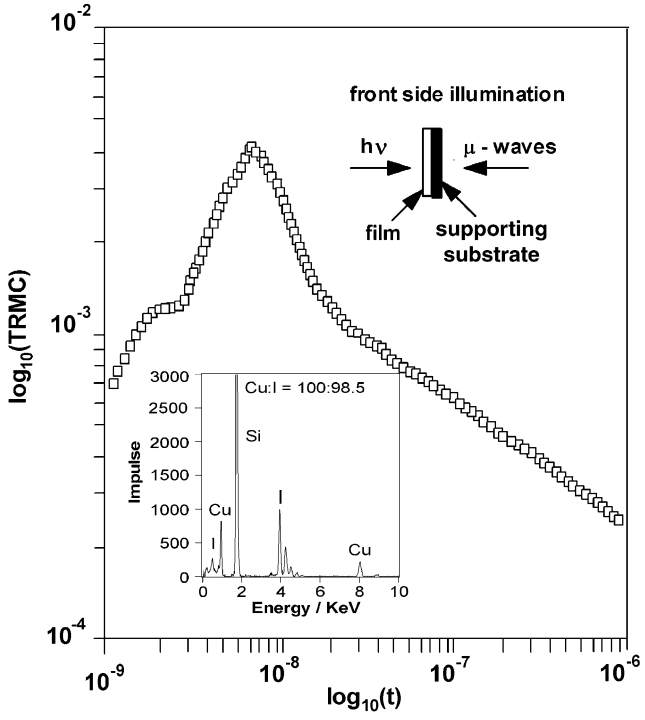

Fig. 1. Transient microwave-photoconductivity of the CuI film (on glass). The insert represents the EDAX diagram of the CuI film (on the silicon substrate).

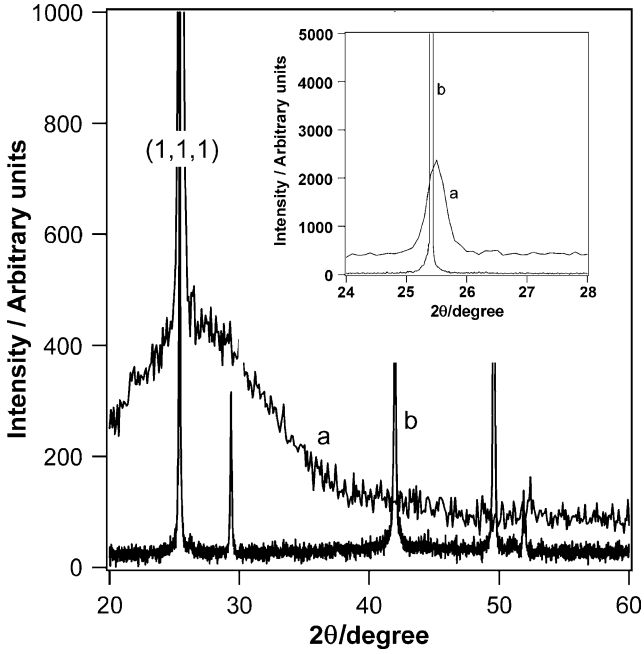

Fig. 2. X-ray diffractogram of: (a) deposited films (on quartz substrate) and (b) CuI powder.

films are highly (1,1,1) oriented. Growth of thin films with a preferred orientation and a shift of the peak position are specific features for thin films. However, weaker peaks belonging to other lattice planes are also observed at higher angles. These characteristic peaks are slightly shifted to higher angles compared to that of polycrystalline samples (inset of Fig. 2). The shift of peak position to higher angles may be due to impurities and/or contraction of adjacent layers (caused by tensile stress) in the thin films compared to that of polycrystalline sample [9]. The average grain size (d_g) of the film was evaluated by the Debye–Scherrer's equation ($d_g = K\lambda/\beta \cos\theta$), [10] by applying the (1,1,1) peak and was evaluated as 25 nm. Formation of grains with nano-scale was clearly observed from an atomic force microscope.

The absorption spectra of CuI powder (after conversion of diffuse reflectance spectrum by Kubelka–Munk equation) and the film (on glass substrates) are shown in Fig. 3. Only band-to-band transient was observed for polycrystalline CuI powder (curve a). Whereas thin CuI films (on quartz substrates) exhibited different properties compared to that of polycrystalline powder. The fundamental band gap of CuI is evaluated as 3.1 eV from the onset of TUPAC plot (not shown in the text). However, in addition to band gap excitation, several transients at high energies were observed at 402 and 333 nm (curve b) for thin CuI films. The energy difference between peaks at wavelengths 333 and 402 nm is 700 meV and close to the previously reported value for spin orbit splitting of highest valance band ($\Gamma_{15,2}$) of CuI [4]. Electron transients in higher energies

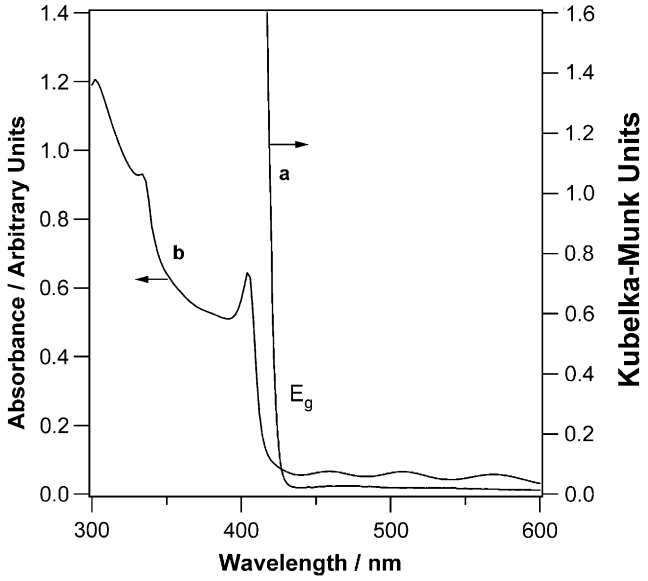

Fig. 3. Absorption spectra of CuI (a) powder and (b) film (on quartz substrate).

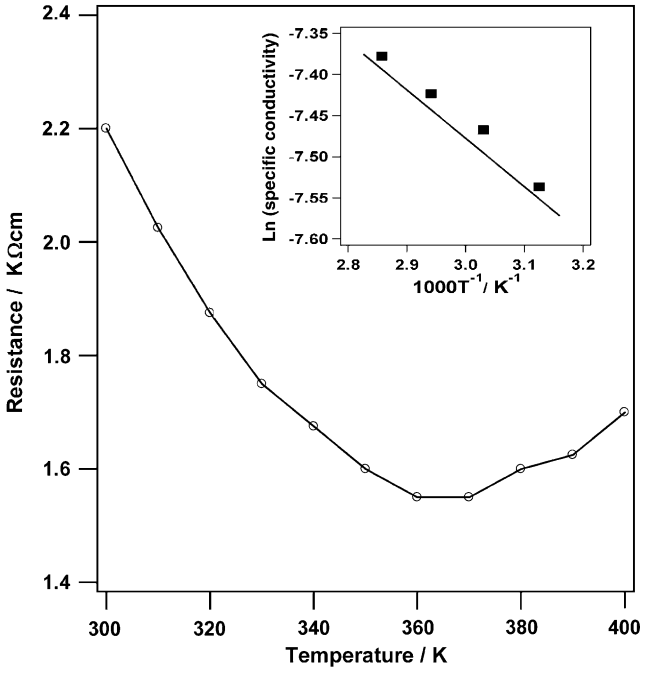

Fig. 4. Variation of resistance with temperature for CuI film (on glass), insert represents the variation of specific conductivity (σ) with temperature (T) as a plot of $\ln(\sigma)$ vs. T^{-1}.

than band gap have been observed in GaAs and Ge [11,12]. These films exhibited sheet resistance of 2.2 kΩ cm at room temperature. This value is greater than that observed for CuI films prepared by the RF-DC magnetron sputtering as well as from an acetonitrile solution [13,14]. We have studied the variation of resistance with temperature for the CuI films (on glass). As is shown in Fig. 4, a decay of resistance of the film was observed with an increase in the temperature ($<100\,^{\circ}$C), which is due to the negative temperature coefficient of resistance (caused due to change of free carrier concentration). The resistance of the film increased with temperature that exceeded 365 K. This unusual feature may be due to phonon scattering at the grain boundaries [15]. The hopping conduction between grains, carrier depletion of the film due to polarization and formation of copper oxide could interfere with the conductivity measurements. However, we are not in a position to prescribe the contribution of the hopping conduction between grains and/or the polarization effect on the conductivity measurements. The activation energy of the CuI films was evaluated as 36.7 meV from the gradient of $\ln(\sigma)$ vs. T^{-1} (where σ and T are the specific conductivity and temperature, respectively) that shown as the insert of the Fig. 4. This value is less than the thermal energy (kT, where k is the Boltzman constant) at room temperature. Small activation energy can be attributed to the migration of copper interstitials [16]. Thermal activation of electrons from the valance band acceptor levels results in holes in the valance band, which helps in increasing the conductivity of the film.

The IPCE spectra of dye|CuI|ITO (ITO: conducting glass) under front wall-mode illumination (via electrolyte|dye interface) and back wall-mode illumination (via ITO|CuI interface) are shown in Fig. 5. Relatively higher peak at 408 nm was observed under back wall illumination with the wavelength shorter than 500 nm. At these wavelengths only CuI get excited and an electron–hole is generated in the conduction band and

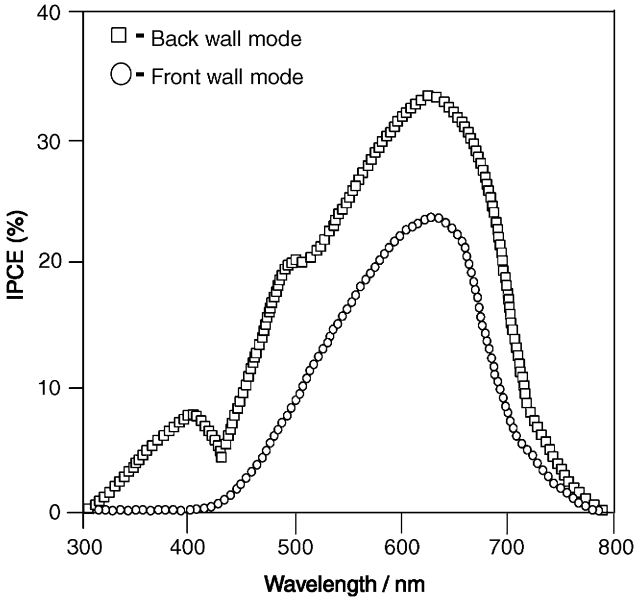

Fig. 5. The IPCE spectra of dye|CuI|ITO under different modes of illumination: (a) front wall and (b) back wall. A cationic dye (iodate of methyl violet 6B) was used for sensitization purposes.

valance band, respectively. The electrons in the conduction band tunnel into the electrolyte via the dye molecules for participating in the redox reaction,

$$\mathrm{CuI} + h\nu(\lambda < 500\,\mathrm{nm}) \rightarrow \mathrm{CuI}(e_{\mathrm{CB}} + h_{\mathrm{VB}}),$$
$$e^-_{(\mathrm{CB\ from\ CuI})} + D \rightarrow D^-,$$
$$4D^- + 2I_3^- \rightarrow 4D + 6I^-. \quad (1)$$

However, only sensitization occurred at illumination with wavelengths higher than 500 nm under both the illumination modes. Sensitization process on CuI films have been thoroughly discussed elsewhere [17,18]. Different kinetics at TiO_2|dye|CuI electrode under back wall-mode illumination clearly indicates that there is a possibility that the dye molecules attached to the electrode act as a mediator in the charge transfer process.

4. Conclusion

Higher microwave conductivity and split of electronics bands are observed in the CuI films. Sensitized CuI cathode exhibited different kinetics under different modes of illumination.

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