Two-photon photo-voltaic spectroscopy on wannier excitons in Cu_2O

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Two-photon excitation spectra of photo-voltaic effects and relevant excitonic emissions of a naturally grown single crystal of Cu_2O have been studied at 77 K and 2 K. The photo-voltaic have been detected under local excitation at a macroscopical distance apart from the electrodes. The participation of the yellow series excitons in the generation of the photo-voltaic signal has been descussed.

The correlation between photo-electric effects and relevant optical absorption in semiconductors had been a central interest of Prof. E.F. Gross and his colleague since the beginning of 1950 s [1,2]. They found hydrogenic absorption lines of excitons in Cu_2O and verified the concept of Wannier excitons experimentally.

Application of laser technology to solid state spectroscopy triggered new progress in exciton physics. A pioneering challenge to observe the two-photon absorption spectrum of the excitons in Cu_2O was the milestone [3], and the clear demonstration was established later on [4]. It was demonstrated there that the *s*- and *d*-excitons in the yellow series are excited selectively by two-photon processes. Corresponding *p*-excitons are excited by one-photon transitions as widely known.

The participation of excitons in photoconduction and photo-voltaic effects has been discussed in [5,6]. These phenomena have been utilized to detect the ballistic propagation of the excitons, that has been interpreted as a manifestation of the superfluid phase of paraexcitons [7].

The aim of our experiments is to develop a new method to study the dynamical aspect of the excitons. The principle of the method is a simple applicaton of linear photo-voltaic spectroscopy to two-photon excitation regime. Simultaneous observation of the excitation spectra of relevant exitonic emissions is also performed.

1. Experiments

A naturally grown single crystal was used as a sample. A rectangular plate of $6 \times 2.6\,mm^2$ on side of a [100] plane and of about 1 mm thickness was used. One electrode of $2.5 \times 2.5\,mm^2$ size was set at one side of the sample and the other electrode of the similar size was located at just opposite side. Electrodag was used to from the contacts. The sample was immersed in liquid N_2 or superfluid He.

A color center laser (Solar CF-151M) pumped by a *Q*-switched Nd : YAG laser was used as a lihgt source for the two-photon excitation. The pulse width and the repetition were ~ 50 ns and ~ 400 Hz, respectively. One-photon excitation was performed by monochromatized light from a Xe lamp. Emissions from the sample were observed by a standard system for spectroscopy. Photo-voltaic signal was measured by a digital voltmeter (Advantest R6452). Optical and electric signals recorded simultaneously by a computer.

2. Results and discussion

Figure 1 shows examples of photo-voltaic spectra obtained by one-photon excitation at 77 K (*a*) and 2 K (*b*). General shapes of the spectra were consistent with the photo-conduction spectra [2] and the photo-voltaic spectra [8]. Relevant energies of the excitonic structures are shown in the figure.

It should be noticed that voltaic effects reaching — 2 V in the dark are present at 2 K. Large amount of the dark-voltaic signal quickly diminished to the level shown in Fig. 1 *b* when the sample was irradiated by light. A striking phenomenon observed characteristically at 2 K was a very slow recovery of the signal after interrupting the light irradiation.

Recently, it was found that $I-V$ character and relevant electroluminescence of the sample used here are strongly influenced by the irradiation of light [9]. The origin of the photo-induced diminution of the dark voltaic effects should be correlatively clarified revering researches on transport phenomena of carriers in low temperature [10].

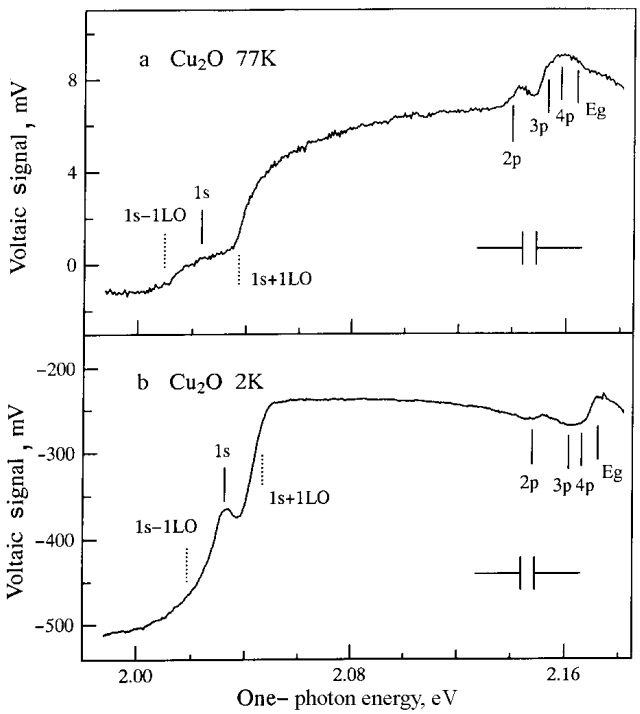

Figure 1. Photo-voltaic spectra at of Cu_2O 77 K (*a*) and 2 K (*b*).

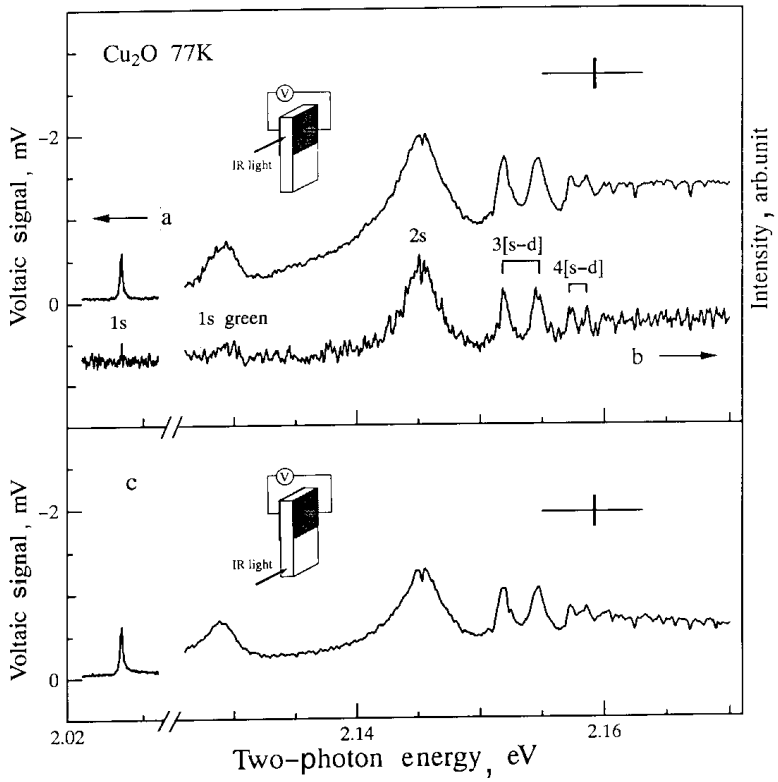

Figure 2. Photo-voltaic spectra (a), (c), and excitation spectrum of $X_0-\Gamma_3^-$ band (b) at 77 K. The insets show respective configurations of light irradiation.

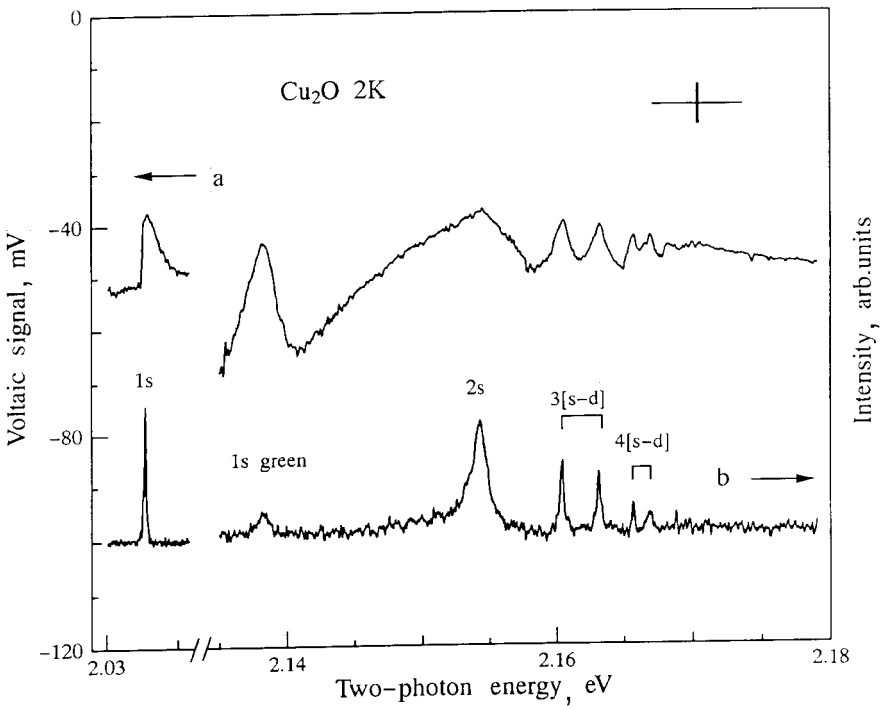

Figure 3. Photo-voltaic spectra (a), (c), and excitation spectrum of X_0 (b) at 2 K.

Figure 2, *a* shows an example of two-photon photo-voltaic spectra at 77 K when the incident laser beam of ~ 0.3 mm diameter passes through a central region of the crystal sandwiched by the electrodes. The excitation density was $\sim 500\,\mathrm{kW/cm^2}$ at the maximum. Fig 2, *b* shows an excitation spectrum of the 1 LO phonon-assisted 1 s ortho-exciton emission $(X_0-\Gamma_3^-)$. The excitonic structures are clearly resolved. The energy of each structure in the spectra corresponds to relevant $[s-d]$-exciton energy as labeled in the figure[1]. These facts show that the excitons participate in the generation of the photo-voltaic signal.

Figure 2, *c* shows a similar photo-voltaic spectrum when the location of the laser beam was shifted ~ 3 mm apart from the edge of the electrodes as shown in the inset of the figure. Almost similar spectrum with similar intensity was obtained. This fact shows that the remote generation of the excitons gives clear effects of the generation to photo-voltaic signal.

The participation of the ortho-excitons in such phenomenon should be ruled out except for their polaritonic propagation, because their lifetime is observed to be in order of nsec [13]. The contribution of diffusive propagation of the para-excitons may be also ruled out taking account of their diffusion length at 77 K [14]. One possibiblity is free carrier generation at local centers influenced by the excitons as implied from the fact obtained by the excitation spectrum of free holes [15]. However, the diffusion length of free holes is roughly estimated to be only $\sim 100\,\mu$m at 77 K from the hole mobility with appropriate lifetime [16]. It is worth investigating the mechanism of this long-range effect comparing with that of the ballistic propagation [7].

Figure 3, *a* is an example of two-photon photo-voltaic spectra under the remote excitation at 2 K. Fig. 3, *b* is the excitation spectrum of the resonance emission of the ortho-excitons (X_0). Each excitonic structure in Fig. 3, *a* corresponds with relevant structures in Fig. 3, *b*. In this case, the excitonic effects appear as the diminution of the signals as seen in the case of 1 s exciton generation by one-photon excitation.

Finally, a few comments are given for the two-photon photovoltaic spectrum around the 1 s yellow exciton resonance at 2 K. As witnessed in Fig. 3, the photo-voltaic spectrum shows broadening toward high energy side comparing with the sharp structure of the excitation spectrum of the emission. The fact clearly suggests that the mechanism of the generation of photo-voltaic signal is different from that of emissions. The high energy wing may be due to the ortho-excitons of large kinetic energy really produced by coherent scattering of acoustic phonons. They may not contribute to the X_0 emisions before relaxation. On the other hand, the coherent excitation of the ortho-excitons makes coherent resonance scattering dominant [17] and carrier generation suppressed.

[1] The assignements for the excitonic structures are different in literature [4,11]. The structure of the highest energy in a family of the same principal quantum number showed the largest diamagnetic shift suggesting the *s*-dominant nature [12].

3. Conclusion

We have demonstrated two-photon photo-voltaic spectroscopy to study the photo-carrier generation mediated by the yellow series excitons in Cu_2O. With the simultaneous observation of the excitonic emissions, it is revealed that excitons participate in giving rise to the photo-voltaic effects. Remarkable photo-voltaic signal is observed even under remote generation of excitons. The dark-voltaic effect is present at 2 K and is found to be remarkably influenced by light irradiation. The present method is promising to investigate exciton-mediated generation of free carriers and their dynamical feature.

Acknowledgments

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