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Semiconducting and Photoelectrochemical Properties of n- and p-Type β-CuCNS

By

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 β -CuCNS, a three-dimensional polymeric solid with interbonded layers is found to have unusual photoelectrochemical and solid state properties. The material becomes p- or n-type depending on whether CNS or Cu is in stoichiometric excess. The n-type is found to be sensitive to the visible spectrum. The methods of preparation of p- and n-type films of β -CuCNS and their photoelectrochemical and solid state properties are discussed.

Es wird gefunden, daß β -CuCNS, ein dreidimensionaler polymerer Festkörper mit Interbindungsschichten, ungewöhnliche photoelektrochemische und Festkörpereigenschaften besitzt. Das Material wird p- oder n-leitend in Abhängigkeit davon, ob CNS oder Cu im stöchiometrischen Überschuß vorliegt. Es wird gefunden, daß die n-leitende Species im sichtbaren Spektrum empfindlich ist. Die Methoden zur Präparation von p- und n-leitenden Schichten von β -CuCNS und ihre photoelektrochemischen und Festkörpereigenschaften werden diskutiert.

1. Introduction

The study of photoelectrochemical properties of semiconductor materials has received a great deal of attention, especially in the context of solar energy conversion [1 to 6]. Materials extensively investigated are binary and ternary compounds [1 to 6]. It is possible that more promising and novel properties are found among unconventional materials with complex structure. In a series of reports we have discussed the properties of CuCNS and its suitability as a material for dye-sensitized photoelectrochemical cells [7 to 10]. The solid CuCNS exists in two polymorphic forms, α -CuCNS with orthorhombic crystals and β -CuCNS that grow as trigonal pyramids [11 to 15]. The β -form is polytypic [14, 15] and consists of 3R and 2H polytypes in synthetic coalescence [14, 15]. The β -structure is composed of layers of a closed-packed network of CuCNS units, the adjacent layers are bonded to each other by strong Cu–S bonds [14 to 15]. Cu and S are tetrahedrally coordinated and the crystal is a three-dimensional polymer [14, 15]. The α and β forms are readily identifiable by the CN stretching frequency in the infrared spectrum which occurs at 2157 and 2173 cm⁻¹, respectively [15].

CuCNS can be easily deposited on copper substrates by immersing them in solutions containing the CNS⁻ ion or by electrolysis. All such deposits are found to consist of the β -form. The polymeric nature of CuCNS with strongly interbonded layers has number of advantages. Films deposited on copper surfaces are generally free from cracks and pin-holes [9], they are firmly affixed to the substrate, and readily adsorb

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other substances (notably those containing a S or CNS ligand). We have found that copper-doped β -CuCNS is n-type and sensitive to the visible spectrum, while the p-type compound which is insensitive to the visible spectrum originates from a stoichiometric excess of CNS. The methods of preparation of n- and p-type β -CuCNS, their photoelectrochemical and solid state properties are described.

2. Experimental

2.1 Method I

a) p-type β -CuCNS: Copper sheets (2 × 5 cm², Aldrich 99.99%) ultrasonically cleaned after anodic polishing in 10% H₂SO₄ were kept immersed in an aqueous solution 0.5 M in KCNS and 0.7 M acetic acid (pH-value \approx 3.5). Propan-2-ol (5 to 10 ml per 100 ml of the solution) was added to keep the surface free from grease. Depending on the duration of immersion, films a few microns to fraction of a millimeter were deposited. b) n-type β -CuCNS: Copper sheets cleaned as in a) were kept immersed in an aqueous solution 0.05 M in KCNS, 0.3 M Na₂SO₃ acidified with acetic acid until pH-value \approx 5 (propan-2-ol added as earlier). Deposition under these conditions was slow. A layer about 10 µm thick was formed in 6 to 8 h. To obtain a film \approx 0.1 mm thick it was necessary to expose the plate to the solution six to eight days, replen-ishing Na₂SO₃ frequently.

2.2 Method II

a) p-type β -CuCNS: An aqueous solution 0.25 M in KCNS, 0.7 M in acetic acid containing propan-2-ol was electrolysed with a copper plate as the anode. The current density was kept at ≈ 2.5 mA cm⁻².

b) n-type β -CuCNS: An aqueous solution 0.25 M in KCNS, 0.01 M in CuSO₄ (containing propan-2-ol) was electrolysed with a copper plate as the cathode. The current density was kept at $\approx 1 \text{ mA cm}^{-2}$.

n-type β -CuCNS films are chocolate brown in colour, those of p-type are white. Both the types are resistant to dilute mineral acids, but readily attacked by alkalis. The electrolytic method of deposition has several advantages. The growth is faster, the thickness of the film is easily controlled, and the level of doping can be adjusted by altering the concentration of CNS⁻ and Cu⁺ ions.

The chemicals used in all experiments were of reagent quality. KCNS (Analar) was further purified by recrystallization.

The chemical composition of the deposits were determined by the following method: Plates were digested in a hot solution of NaOH (0.1 M) for ≈ 1 h to extract CNS in the form of NaCNS. The CNS⁻ ion concentration in the acidified extract was determined spectrophotometrically after addition of FeCl₃. The deposits were also dissolved in saturated KCNS solution (CuCNS is soluble in saturated KCNS) and the copper concentration in the extract was determined by the method described in [16]. The material carefully scraped from thick deposits using an agate razor was also analysed for K, Cu, and other elements by atomic absorption spectroscopy (Hitachi 170-30). The IR spectra of the scraped powder was also obtained (Hitachi 270-50). Photoelectrochemical measurements were carried out under potentiostatic conditions (Hokuto Denko HA-301 potentiostat) using a Pt counterelectrode. Light intensities were measured with an International Light IL 700 radiometer. Photocurrent spectra were ascertained with an Applied Photophysics monochromator and 100 W tungsten filament lamp. Diffuse reflectance spectra were obtained with a Hitachi U-3200 spectrophotometer. The electrolyte used was 0.01 M KCNS. Single crystals and polycrystalline powder of β -CuCNS were also prepared by the methods described in [14] and [11], respectively. The copper-doped β -CuCNS powder was prepared by the following method (method III): Copper sponge (free from oxide) was kept suspended in a solution 0.05 M in KCNS, 0.3 M in Na₂SO₃ acidified with acetic acid (pH-value ≈ 5) for one week. The precipitate was filtered, washed with diluted HNO₃ to remove excess copper, and dried at 110 °C in a current of nitrogen. Attempts to dope CuCNS single crystals with copper were not successful.

The sign of majority charge carriers in single crystals and compressed powder pellets were determined by Hall tests. The electrical conductivity of the materials was measured using a Takeda Riken computing digital multimeter (TR 6877).

3. Results and Discussion

The IR spectra of p- and n-type CuCNS have same structure with an intense band at 2173 cm⁻¹ and a hardly distinguishable maximum in absorption at 2157 cm⁻¹ (Fig. 1), clearly indicating that the polymorphic form deposited on copper is almost entirely the β -form. The chemical analysis and the sign of majority charge carriers in β -CuCNS prepared by different methods are presented in Table I. It is clear that the n- and p-type samples originate from stoichiometric excess of Cu and CNS, respectively. Strongly reducing environment, low concentration of CNS⁻ ions, or

Table 1

Chemical analysis and sign of the majority charge carriers in α -CuCNS prepared by different methods

preparation	analysis	type
method I (a)	Cu (47.6%), CNS (51.8%), K (< 0.5%)	р
method II (a)	Cu (48.9%), CNS (51.2%), K ($\approx 0.6\%$)	p
polycrystalline powder	Cu (48.2%), CNS (50.9%), K ($\approx 0.7\%$)	p
method I (b)	Cu (57.1%), CNS (42.2%), K ($\approx 0.6\%$)	n
method II (b)	Cu (56.0%), CNS (42.8%), K ($\approx 0.1\%$)	n
method III	Cu (58.8%), CNS (40.7%), K ($< 0.5\%$)	n



Fig. 1. IR spectra of CuCNS deposited on copper plates. Absorption maxima at 2173 and 2157 cm⁻¹ corresponds to β and α forms, respectively



Fig. 2. Plot of $\ln \sigma$ vs. T^{-1} for β -CuCNS. \bullet p-type, \circ n-type

electrolytic discharge of Cu⁺ ions at the substrate favour formation of the n-type form. High concentration of CNS⁻ ions or their rapid discharge at the copper substrate yield p-type films. The films of p-type CuCNS change into n-type upon several weeks of storage. This can be understood as resulting from diffusion of copper from the substrate into the film. The polycrystalline powder and the single crystals made by the methods described in the experimental section are p-type. The powder can be changed into n-type by heating (150 °C) with copper dust in a stream of N₂. We have not succeeded in doping single crystals (1 to 2 mm) of β -CuCNS with Cu or growing them under conditions enabling to incorporate a stoichiometric excess of Cu.

The temperature variation of the dc electrical conductivity of p- and n-type materials are indicated in Fig. 2. Distinct differences are seen; in the p-type CuCNS (excess CNS $\approx 2\%$) the conductivity initially increases and then begins to decrease at a relatively low temperature, the thermal activation energy of increase being 0.2 eV. However, in the n-type CuCNS (excess Cu $\approx 9\%$) a rapid increase in conductivity with a higher activation energy ≈ 0.51 eV occurs at ≈ 143 °C and continues until the decomposition temperature (340 °C) is reached. The conclusion we can arrive at from the above observation is that the acceptor impurity levels in the p-type material are located close to the valence band (the decrease in conductivity occurs once they get fully populated), but in the n-type material the donor levels lie well below the conduction band (Fig. 3).



Fig. 3. Energy bands and impurity levels in a) n-type and b) p-type β -CuCNS



Fig. 4. Diffuse reflectance spectra of (a) n-type and (b) p-type β -CuCNS

The diffuse reflectance spectra of the two types (Fig. 4) also support the above conclusion. In the p-type material the sharp absorption edge seen at 345 nm corresponds to a band gap of about 3.6 eV. The n-type material also shows a similar absorption edge located approximately at the same position. In addition two other absorption edge like structures, an intense one at 630 nm (≈ 2.0 eV) and a relatively weak one at 980 nm (≈ 1.3 eV) are also noticeable. Undoubtedly the more intense edge at 630 nm arises as a result of the transitions to the conduction band from the donor impurity (Cu) band. The weaker band originates as a result of the transitions from valence band to the Cu impurity band.

The photocurrent spectra of p- and n-CuCNS in aqueous KCNS are given in Fig. 5. In the case of p-CuCNS the photoresponse is insignificantly small in the visible



Fig. 5. Photocurrent spectra of (a) n-type and (b) p-type β -CuCNS



Fig. 6. Photocurrent-potential (U vs. SCE) curves for (a) n-type and (b) p-type β -CuCNS (visible light)

region, but shows a sharp peak near 340 nm. On the other hand, n-CuCNS responds to visible spectrum and shows three peaks at 340, 648, and 980 nm corresponding to band gap excitation, transitions from the impurity band to the conduction band, and transitions from valence band to the impurity band, respectively. The absorption corresponding to the band gap excitation is weak, because electrons excited from the valence band are also trapped in the impurity band. The most intense peak results from impurity band to conduction band transitions.

The photocurrent-potential curves for the two types of CuCNS electrodes in $\approx 10^{-2}$ M KCNS (pH-value ≈ 7) are displayed in Fig. 6. In the case of the n-type material the onset occurs at -0.78 V versus SCE, whereas in the p-type, the photocurrent becomes zero at -0.64 V versus SCE and the response becomes cathodic upon further decrease of the biasing potential.

CuCNS is chemically stable in acidic media, it also shows a remarkable photostability in aqueous KCNS (aqueous KCNS acts as a redox couple owing to the existence of CNS⁻ as well as (CNS)₂ ions [8]). Fig. 7 shows the development of the photocurrent in an n-type CuCNS photoanode biased -0.03 V versus SCE. The I-Ucharacteristics of the cell are shown in Fig. 8, the energy conversion efficiency is quite small ($\approx 4 \times 10^{-3}$, light source 100 W tungsten filament lamp).



Fig. 7. Time development of the photocurrent in a n-type $\alpha\text{-CuCNS}$ photocathode biased -0.03 V vs. SCE



Fig. 8. *I-U* characteristics of the n-CuCNS/0.1 M KCNS/Pt cell (light source 100 W tungsten filament lamp, biasing voltage -0.03 V vs. SCE)

4. Conclusion

The unusual structural features, photostability, and the possibility of sensitization to the visible spectrum by doping makes β -CuCNS an interesting material which can even find applications in practical devices. The preparation of single crystal films and controlled doping could improve the conversion efficiencies. Unfortunately the heavy doping required for sensitization could also have undesirable effects, the impurities could act as recombination centres.

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