

Preparation and Application of Semiconductor-Polymer Composites

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Synopsis

Copper sulfide-polymer composite was prepared by depositing copper into porous polyolefine film with a method of electroless plating and sulfurizing the copper. The composite was an n-type semiconductor and useful as a component of p-n junction device and as a gas detector. The method was also useful for the preparation of silver sulfide-, nickel sulfide-, and cobalt sulfide-polymer composites.

INTRODUCTION

Many metal sulfides are interesting semiconductors in the field of photoelectronics but have low mechanical strength and low flexibility. In order to improve the disadvantages, CdS-polymer film was prepared by dispersing CdS powder into polymer matrix.¹ The film, however, had low electric conductivity. Yamamoto et al.² obtained CdS-polymer composite of higher electric conductivity by mixing CdS powder with DMF solution of polymer, spreading the mixture on a glass plate, and removing DMF.

The present authors found a new method of preparing CuS-polymer composite by depositing copper into porous polyolefine film and sulfurizing the copper. The preparation and application of the composite is described.

TABLE I
Property of Hipore

Matrix	HP-1000	HP-2000	HP-3000
Membrane thickness (μm)	100	100	100
Porosity (%)	55	70	90
Mean pore diameter (μm)	0.05	0.50	0.70
Maximum pore diameter (μm)	0.10	0.80	1.20
Air permeability (s/100/cc)	1500	230	10
Tensile strength (kg/cm^2)	35	40	150
Electric conductivity (S/cm)	$> 10^{-12}$	$> 10^{-12}$	$> 10^{-12}$

TABLE II
Composition of the Solution for Electroless Plating

Plating metals	Sensitizing solution		Activating solution		Electroless plating solution	
Cu	SnCl ₂ H ₂ O	30 g/L	AgNO ₃	1 g/L	CuSO ₄ 5H ₂ O	20 g/L
	Aqueous ammonia	5 mL/L	Aqueous ammonia	5 mL/L	HCHO	60 mL/L
	HCl (concd)	25 mL/L			NaOH	10 g/L
					Na ₂ SO ₄	26 g/L
					K ₂ tartarate	46 g/L
Ag	SnCl ₂ H ₂ O	30 g/L	AgNO ₃	1 g/L	AgNO ₃	45 g/L
	Aqueous ammonia	5 mL/L	Aqueous ammonia	5 mL/L	Aqueous ammonia	60 mL/L
	HCl (concd)	25 mL/L			NaOH	4.0 g/L
					Glucose	4.5 g/L
Ni	SnCl ₂ H ₂ O	30 g/L	PdCl ₂ 2H ₂ O	3 g/L	NiSO ₄	30 g/L
	Aqueous ammonia	5 mL/L	HCl (concd)	5 mL/L	NaPH ₂ O ₂	10 g/L
	HCl (concd)	25 mL/L			Na ₂ succinate	10 g/L

EXPERIMENTAL

Preparation of CuS-Polymer Composite

All reagents used are of reagent grade unless otherwise described. Porous polyolefine films are Hipore film HP-1000, HP-2000, and HP-4000 (Asahi Chemical Industry Co. Ltd.), specifications of which are shown in Table I.

For the preparation of the composite, the film was cleaned with acetone. In order to deposit metal into the porous film, the conventional method of electroless plating was adopted. The film was dipped into sensitizing solution, activating solution, and plating solution successively. Composition of each solution is shown in Table II. For sulfurizing the metal deposited, each of carbon disulfide solution of sulfur, dimethylsulfoxide (DMSO) solution of sulfur, dimethylformamide (DMF) solution of sulfur, and aqueous solution of hydrogen sulfide was tested. Immediately after the sulfuration, the film was washed with solvent and dried in vacuum.

Evaluation of Composite Films

For X-ray diffraction analysis and electron microscopy with X-ray microanalysis, X-ray diffraction apparatus RAD III of Rigaku Denki and scanning

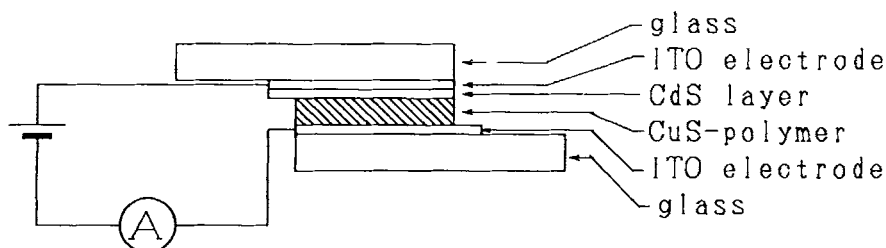


Fig. 1. p-n Junction cell.

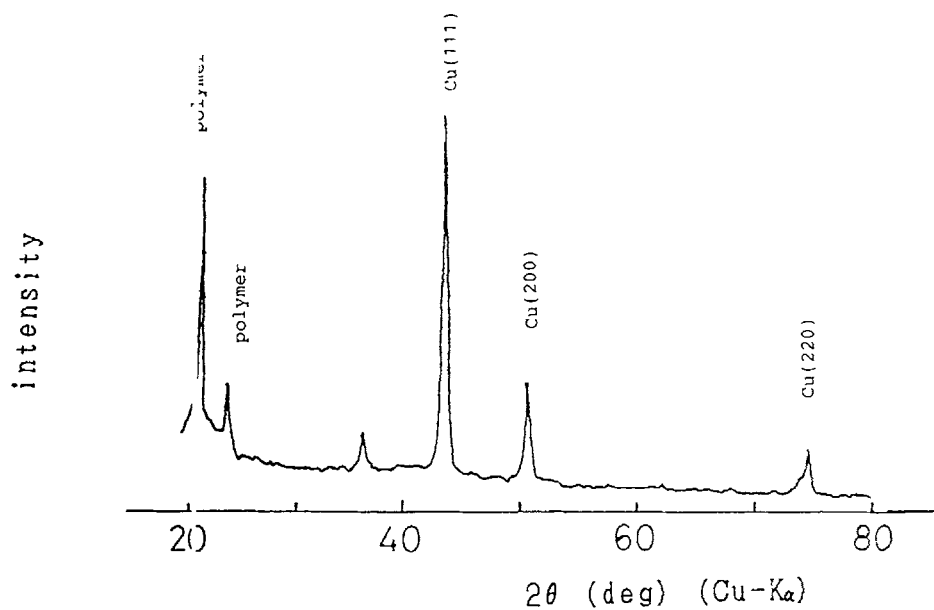
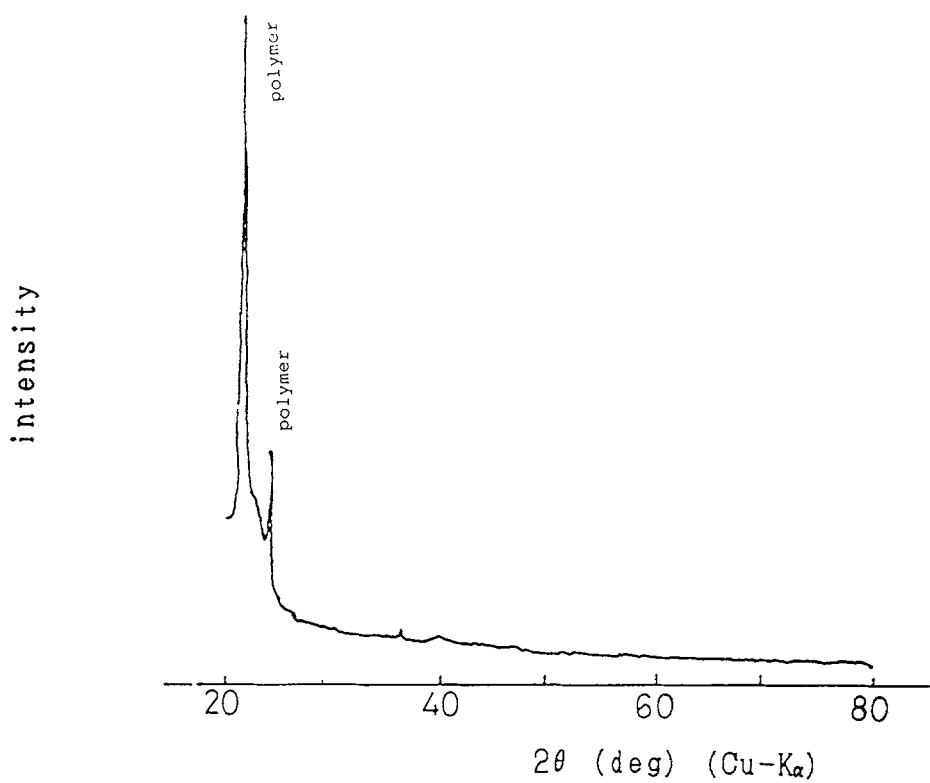


Fig. 2. X-ray diffraction pattern of various samples. (a) Hipore 2000, (b) Cu-Hipore 2000, and (c) CuS-Hipore 2000 (CuS content 35%).

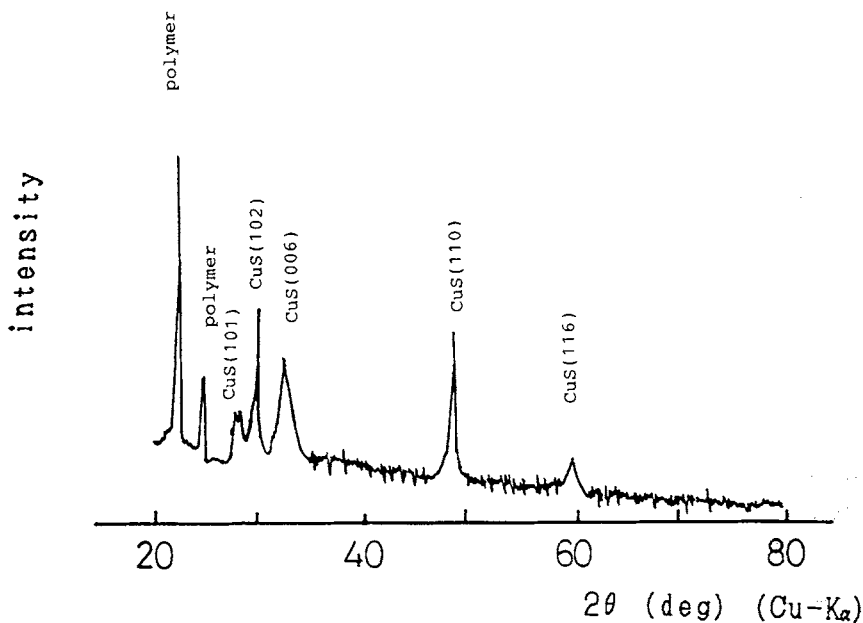


Fig. 2. (Continued from the previous page.)

electron microscope JXA-733 of Nippon Denshi were used respectively. Electric conductivity and mobility of the carrier were measured according to Van der Pauw's method.³ By this Hall effect measurement, we know if the carrier is hole or electron.

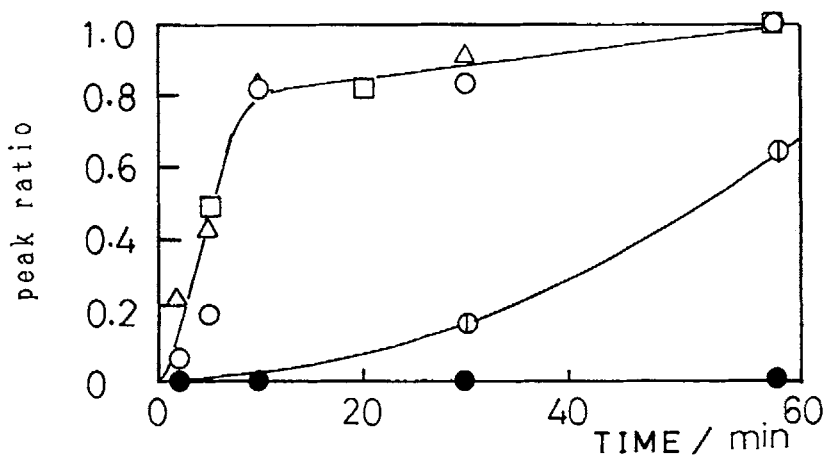


Fig. 3. Change of degree of sulfuration with time for various sulfuring solutions: (○) DMSO (sulfur concentration 3 mM); (△) CS₂ (sulfur concentration 3 mM); (□) DMF (sulfur concentration 3 mM); (●) Na₂S (S²⁻ concentration 3 mM); (⊙) H₂S (S²⁻ concentration 41 mM).

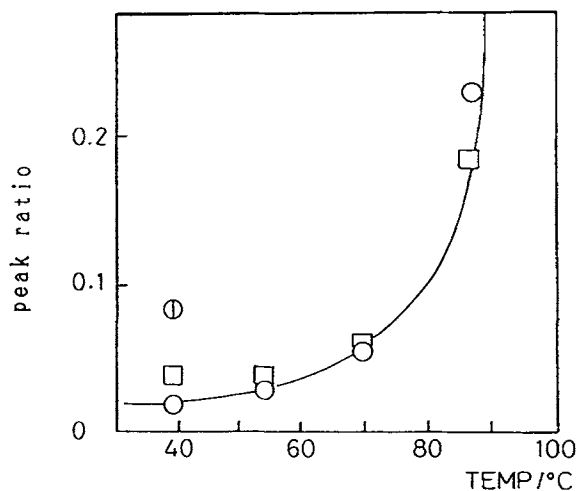


Fig. 4. Effect of temperature on degree of sulfuration: (○) DMSO; (□) DMF; (⊙) CS₂, where sulfur content is 3 mM.

Examination of Composite Films as p-n Junction and Gas Detector

The CuS-polymer composite film on an ITO glass plate and CdS layer on an ITO glass, which was prepared by plating CdS on an ITO glass,^{4,5} were pressed together between two glass plates as shown in Figure 1. The junction cell obtained was used for the current-voltage measurement.

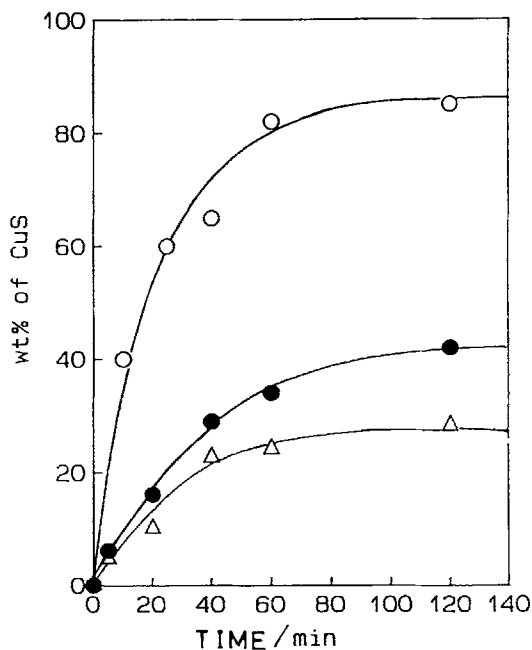


Fig. 5. Change of CuS content with time: (○) cellulose; (●) HP-2000; (△) HP-1000.

Also, the CuS-polymer film of 2.5×1.5 cm fixed on a glass plate was placed into a glass vessel containing gas to be examined. Electric resistance of the film in the vessel was measured at 100°C .

RESULTS AND DISCUSSION

In Figure 2, the X-ray diffraction pattern of Hipore 2000, Cu deposited Hipore 2000, and CuS-Hipore 2000 composite obtained by sulfurizing the Cu deposited

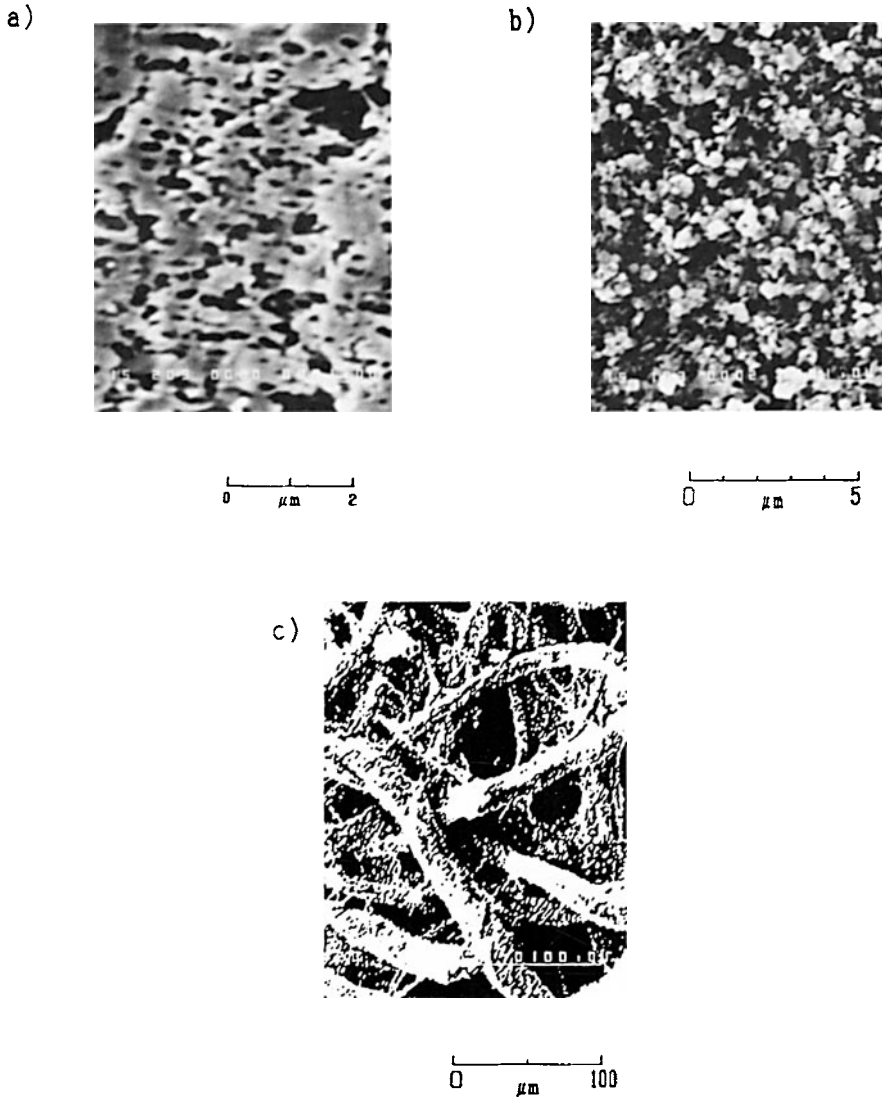


Fig. 6. SEM pictures of various samples: (a) Hipore 2000 ($\times 1000$), (b) CuS-Hipore 2000 ($\times 1000$), (c) CuS-cellulose ($\times 400$), where CuS content is 35% for (a) and (b) and 40% for (c).

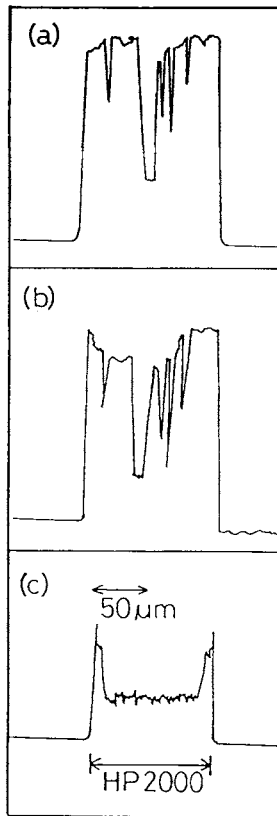


Fig. 7. Distribution of elements through CuS-Hipore 2000 film. (a) Cu, (b) S, (c) Ag, where CuS content is 35%.

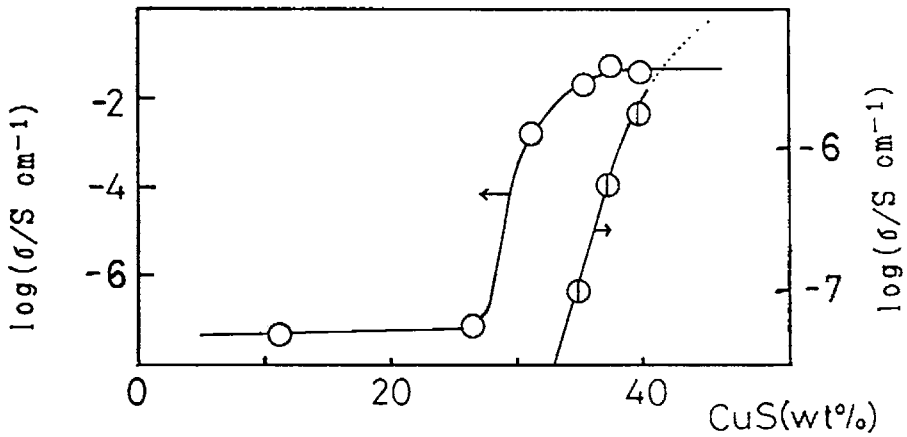


Fig. 8. Change of electric conductivity CuS-Hipore 2000 with CuS content: (○) on the surface; (⊙) through the film.

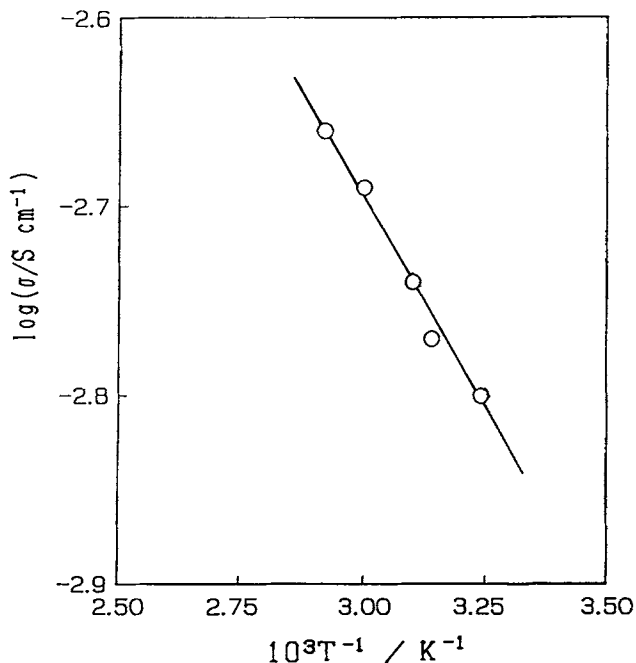


Fig. 9. Temperature dependence of electric conductivity of CuS-Hipore 2000.

Hipore 2000 is shown respectively. Sharp peaks specific to Hipore 2000 are observed at 21.3° and 24.9° in Figure 2(a), those specific to Cu at 43.0° (111), 50.2° (200), and 74.1° (220) in Figure 2(b), and those specific to hexagonal CuS at 47.9° (110), and 27.7° (101) in Figure 2(c). Degree of sulfuration was followed by measuring the ratio of the peak of CuS (110) to that of Cu (111). The result is shown in Figure 3, where the peak ratio is normalized in such a way that the ratio is 1 at sulfuration time of 3 h. From the figure, it is obvious that the sulfuration by DMSO, DMF, and CS_2 solution of sulfur proceeds rapidly but that by aqueous solution of Na_2S hardly proceeds. On the other hand, the sulfuration by H_2S gas proceeded gradually where X-ray diffraction peak due to Cu_2S was also observed. Figure 4 shows the effect of sulfuration temperature on the degree of sulfuration which is expressed by the peak ratio as described above. It is obvious that the higher the temperature the higher the degree of sulfuration both in DMSO and DMF. In CS_2 the sulfuration at higher tem-

TABLE III
Electric Properties of CuS/Polymer Membranes

	HP-2000	Cellulose paper	Pellet
CuS content (wt %)	35	38	100
Conductivity (S/cm)	0.00102	0.000104	0.15
Carrier	p-type	p-type	p-type
Mobility (cm^2/Vs)	0.024	0.0031	4.0

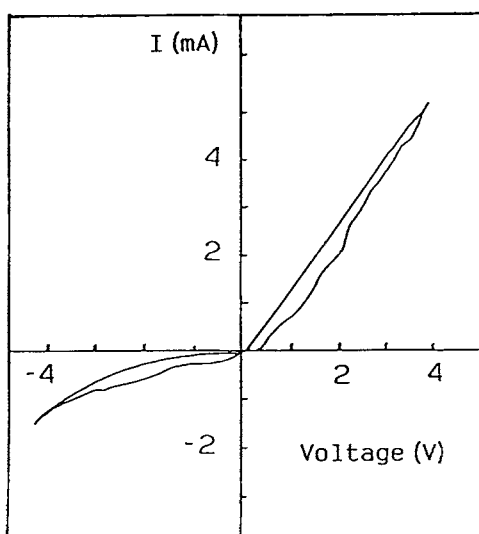


Fig. 10. I - V curve for p-n junction consisting of CuS-Hipore 2000-polymer and CdS layer.

perature was not carried out because of low boiling point of the solvent. Also, sulfuration at temperatures higher than 100°C caused the deterioration of the film.

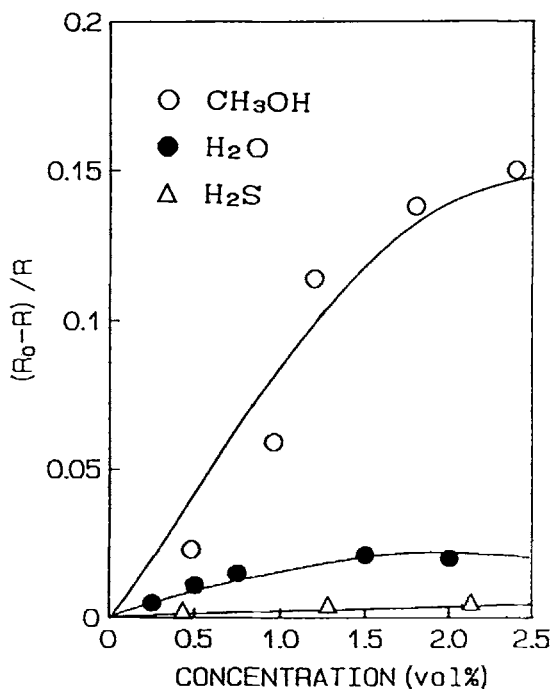


Fig. 11. Change of electric resistance of CuS-Hipore 2000 with concentration of CH₃OH, H₂O and H₂S.

TABLE IV
Electric Conductivity of Metal Sulfide/HP-2000

Metal sulfide	Content (wt %)	Conductivity (S/cm)
CuS	35	1.8×10^{-1}
Ag ₂ S	30	$> 1 \times 10^{-9}$
NiS	29	9.5×10^{-6}
CoS	20	3.2×10^{-5}

Change of CuS content with plating time is shown in Figure 5, where the CuS content increases with time below about 60 min and reaches to a saturated value. For comparison, the result on sulfurized cellulose film is shown, where cellulose paper of Advantech is used. Scanning electron microscopic (SEM) pictures of films are shown in Figure 6, where the CuS-Hipore 2000 composite film shows almost homogeneous distribution of CuS in Figure 6(b) but the CuS-cellulose composite film shows still porous structure on the surface as shown in Figure 6(c). Results of X-ray microanalysis (XMA) of cross-section of the CuS-Hipore 2000 film is shown in Figure 7. Here, both Cu and S distributes densely on the surface and coarsely inside of the film. Also, Ag distributes similarly but more homogeneously, which is incorporated into the film in the activation process.

Change of electric conductivity of the CuS-Hipore 2000 with CuS content is shown in Figure 8, the conductivity on the surface increases rapidly at CuS content of about 30% and that across the film at CuS content of about 35%. This may be due to the formation of conducting pass of CuS grains. This result agrees with that of Yamamoto et al.² Electric conductivity at low CuS content seems to be due to the small amount of Ag incorporated in the activation process. Temperature-dependence of electric conductivity on the surface of the CuS-Hipore 2000 containing 35 wt % of CuS is shown in Figure 9. The dependence is expressed by the following Arrhenius equation,

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (1)$$

where activation energy E_a is 0.86 eV. The dependence is characteristic to the property of semiconductor.

Hall effect measurement was carried out for CuS-Hipore 2000, CuS-cellulose and CuS pellet, where CuS pellet was prepared by precipitating CuS from CuSO₄ solution with H₂S, drying the precipitate and pressing it at 400 kg/cm². All of the samples were found to be p-type. Carrier mobility and electric conductivity are shown in Table III.

In Figure 10, I-V curve of the p-n junction cell consisting of CuS-Hipore 2000 and the CdS layer is shown. Obviously the cell works as a rectifying cell. Change of electric resistance of the CuS-Hipore 2000 with concentration of CH₃OH, H₂O and H₂S gases is shown in Figure 11. The change is small for H₂O and H₂S but appreciable for CH₃OH. Thus, use of the CuS-polymer film as a detector for CH₃OH is promising.

Preparation of metal sulfide-polymer composite was examined for Ag, Ni, and Co. The sulfuration was easy for Ag as it was for Cu. However, the sulfuration for 10 h at 80°C was required for Ni and Co. Electric conductivity of the composite for the metal sulfides is shown in Table IV.

The present method of preparing metal sulfide-polymer composites is very simple but seems to be applicable to various fields.

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