The Electrical and Physical Properties of CuS– and CdS–Polyacrylonitrile Composite Films Prepared by Using the Organosol Method

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Synopsis

Electrical and physical properties of the CuS- and CdS-introduced polyacrylonitrile (PAN) films were studied. Electrically conducting PAN film was prepared by introducing CuS and CdS by the organosol method. Electrical surface conductivity of CuS- and CdS–PAN composite film prepared by the organosol method was 10^{-1} and 10^{-5} S/cm, respectively. Temperature dependence of surface conductivity for CuS–PAN composite film was investigated. The *IV* characteristics and time dependence of conductivity of samples were observed. The conduction mechanism of CuS- and CdS–PAN composite film was mainly electronic. Electrical properties of the CuS- and CdS–PAN composite film were mainly governed by the CuS and CdS crystal formed in the PAN film. Temperature dependence of surface conductivity of the heat-treated CuS–PAN composite film was also investigated. Results show that the electrical properties of the sample were varied slightly according to annealing temperature. Tensile strength and modulus of CuS- and CdS–PAN composite film were slightly decreased than original PAN film, but this decrease was not prevented utilization in electronic devices.

INTRODUCTION

Some semiconducting metal sulfides (MS) are now used as photoconductor, phosphors, electrodes of photogalvanic cells, catalysts, etc.[1] CuS and CdS are useful materials among metal sulfides since they show interesting physical properties such as electric conductivity, photoconductivity, and fluorescence.[2-6] However, their practical uses are sometimes restricted due to their nonmiscibility in solvents and difficulties in moulding them.

Recently, authors[7-10] reported that Cu_xS-treated PET and nylon 6 film have a semiconducting property. The electrical semiconducting property of the Cu_xS-treated film is considered due to the Cu_xS network on the surface of the film. However, only a thin layer of Cu_xS is formed on the surface of the film.

In this work, the semiconducting polyacrylonitrile (PAN) film consisting of CuS- and CdS–PAN composite film can be prepared by a new organosol method to improve the volume conductivity. The surface and volume conductivity of the CuS–PAN composite film were 10^{-1} S/cm, which is lower by an order of 10^{12} than that of the original PAN film. Because the physical properties of the CuS- and CdS–PAN composite film were similar to those of the original film, this fact suggests new ways to utilize CuS- and CdS–PAN composite film in electronic devices.

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EXPERIMENTAL

Materials and Reagents

Polyacrylonitrile (Hanil Synthetic Fibers Co., Ltd) was used without purification. Cupric acetate, cadmium iodide (Junsei Chemical Co.), thioacetamide (Aldrich Chemical Co.), and *N,N*-dimethylformamide (DMF) were used G.P. grade. H_2S was used in the gas state.

Preparation of CuS–PAN Composite Film

The preparative process of CuS-PAN composite can be devided to three stage as follows (Fig. 1):

1. PAN was dissolved in 0.2 M/L DMF solution of cupric acetate. PAN/DMF solution concentration is 20%.
2. Thioacetamide (CH_3CSNH_2) was dissolved in DMF (0.2 M/L).
3. The latter solution was added to the former solution, and then the solvent of CuS–PAN organosol was vaporized in a vacuum oven.

Organosol means the stable sol state of metal compound in organic solvents.

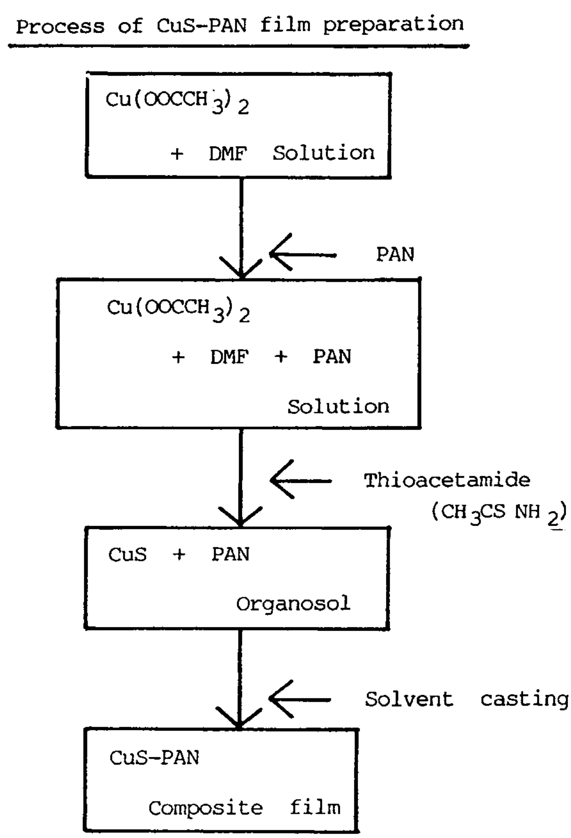


Fig. 1. Schematic diagram of the process of CuS–PAN composite film preparation.

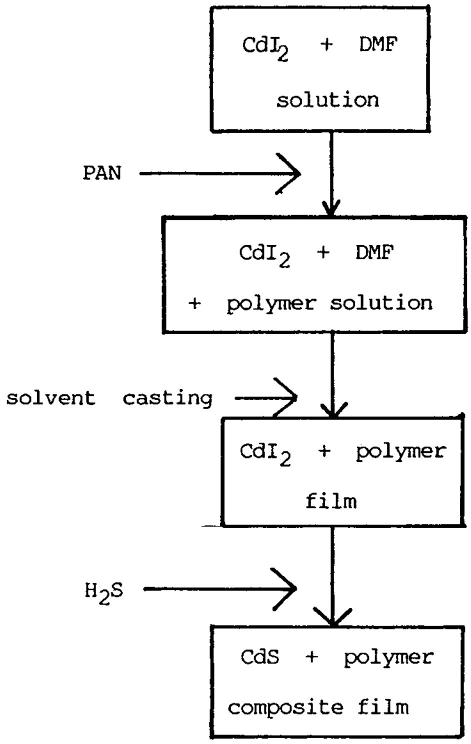


Fig. 2. Schematic diagram of the process of CdS–PAN composite film preparation.

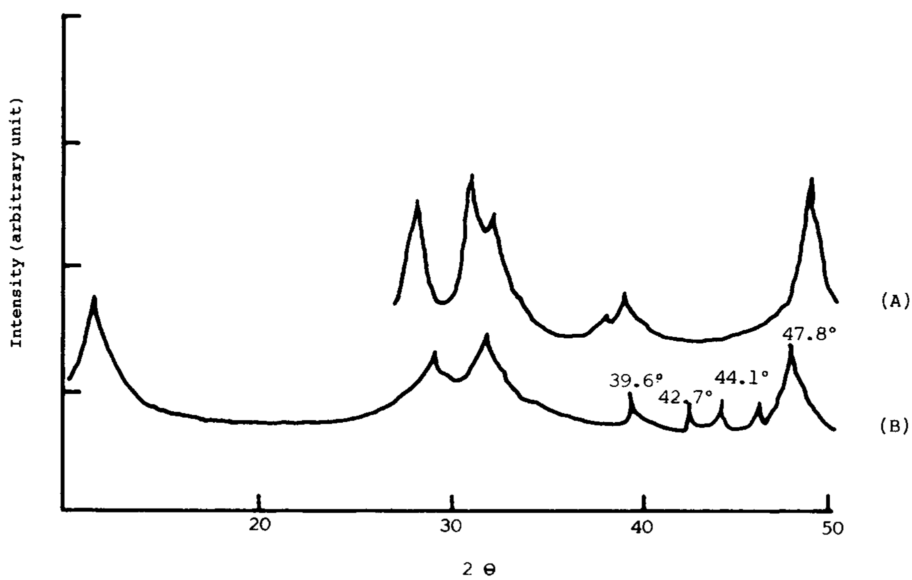


Fig. 3. X-ray diffraction intensity curve of (A) CuS powder and (B) CuS–PAN film.

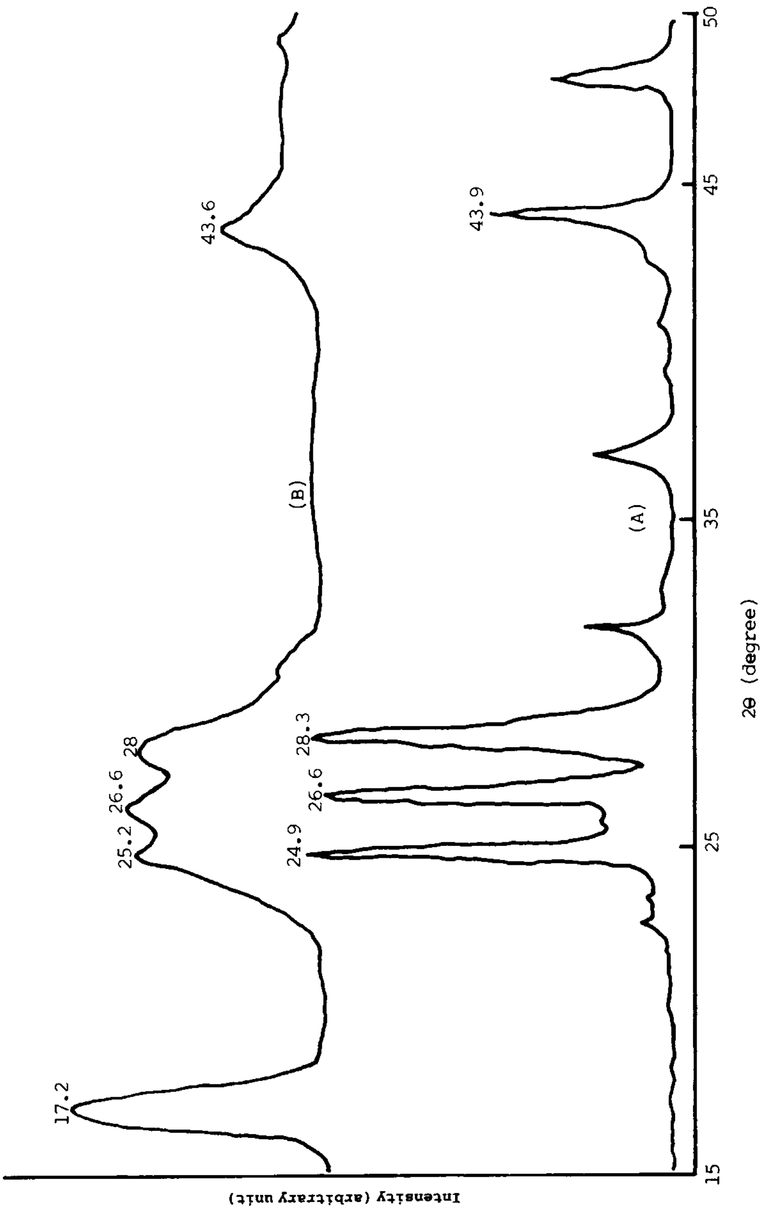
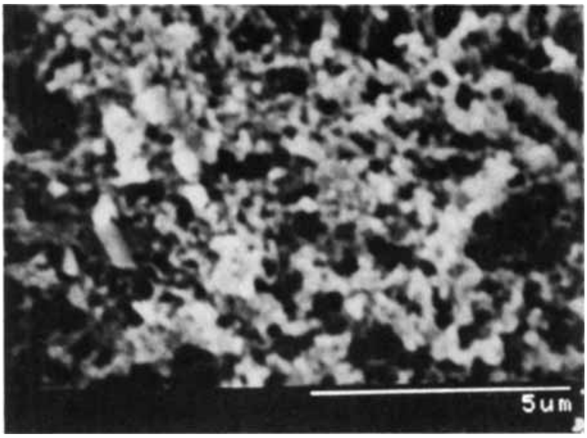
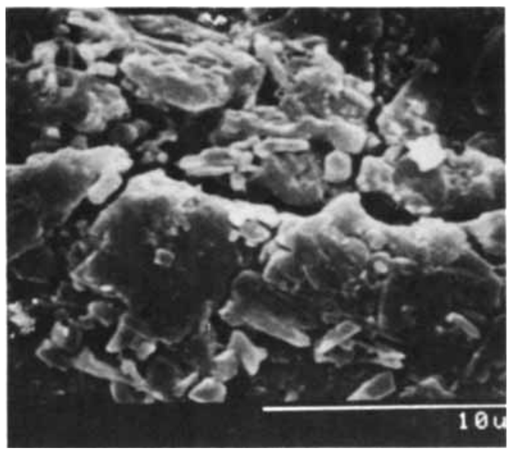


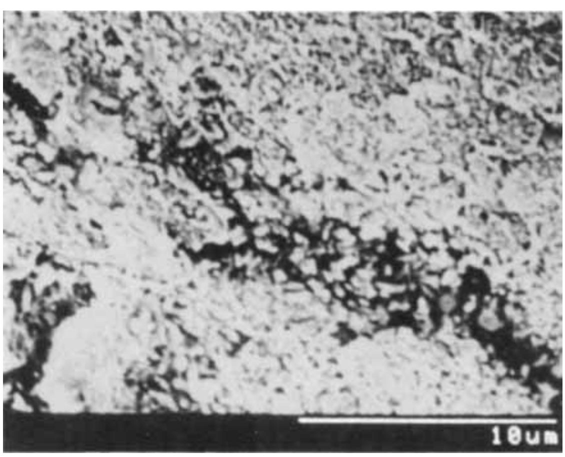
Fig. 4. X-ray diffraction intensity curve of (A) CdS and (B) CdS–PAN.



(A) X 5000

(B) X 5000





(C) X 5000

Fig. 5. SEM for surface and fracture of CuS–PAN film.

Preparation of CdS–PAN Composite Film

Figure 2 shows the schematic diagram of the process of CdS–PAN composite film preparation. After PAN, cadmium iodide was dissolved in DMF, and this solution was vaporized in a vacuum oven. And then excess dry H_2S gas was added to the polymer film containing cadmium iodide at room temperature.

Polymer Characterization

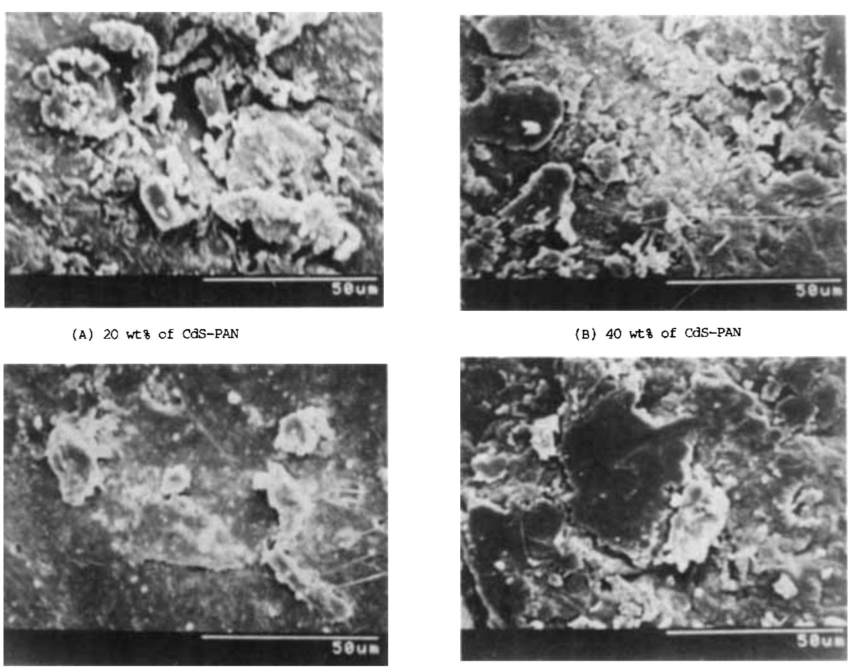
To identify the introducing of CuS onto PAN film, the X-ray diffraction intensity profiles of Cu_xS powder and CuS–PAN film were examined with Ni-filtered CuK_α radiation (35 kV × 20 mV) (Rigaku D/MAX, Japan). The morphology of the CuS- and CdS–PAN film was investigated with an Hitachi S-510 scanning electron microscope.

Temperature Dependence of Conductivity

The conductivity of the CuS–PAN composite film was measured by the four-probe method with an ampere meter (Keithley 179A TRMS Mutimeter) and potentiometer (Keithley 617 electrometer). And the conductivity of the original PAN film was measured by the two-probe dc technique with Keithley 617 electrometer at room temperature up to 200°C. The temperature dependence of conductivity in respect to annealing was also investigated. Annealing temperature was 90, 120, and 150°C.

IV Characteristics

Current–voltage (*IV*) characteristics were measured at a given temperature by applying dc voltage for 30 min. The conduction current was measured with



(A) 20 wt% of CdS-PAN (B) 40 wt% of CdS-PAN (C) 60 wt% of CdS-PAN (D) 80 wt% of CdS-PAN

Fig. 6. SEM for CdS–PAN film surface.

a Keithley 617 electrometer, and dc voltage was supplied with a stabilized dc power supply (ED 245B).

Time Dependence of Conductivity

Time dependence of conductivity was investigated at a given temperature under the applied voltage of 200 mV for up to 60 min. All experiments were carried out at vacuum of 10^{-1} torr to avoid artificial effects (oxygen, moisture, etc.).

Mechanical Properties

Tensile strength and initial modulus of the original PAN, CuS-, and CdS-PAN composite film were measured with Tensilon/UTM-4-100 (Toyo Baldwin Co.) at a crosshead speed of 4 mm/min.

RESULTS AND DISCUSSION

Polymer Characterization

Figure 3 shows the X-ray diffraction spectra of CuS powder (A) and CuS-PAN composite film (B) prepared by the organosol method. Figure 4(B) ex-

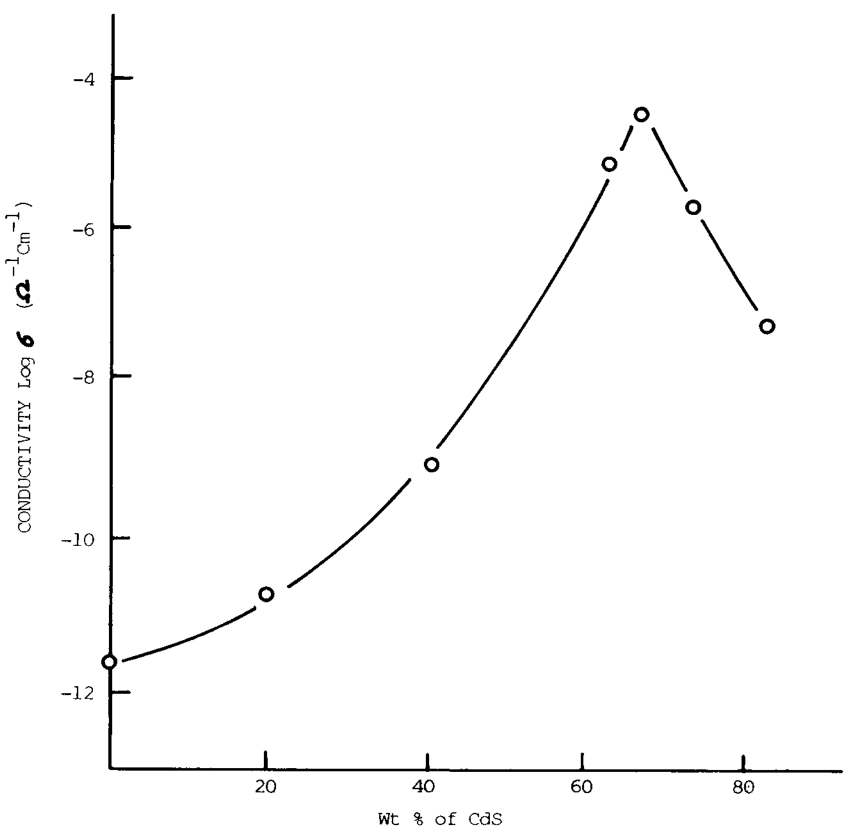


Fig. 7. Dependence of electrical conductivity (O) of CdS-PAN on the weight percent of CdS (measured at 25°C).

hibits peaks near 47.8, 44.1, 42.7, and 39.6°, which were known as typical peaks for CuS crystal.[11] Figure 4 shows the X-ray diffraction spectra of CdS powder (A) and CdS-PAN composite film (B). Figure 4(B) exhibits peaks near 35.2, 26.6, 28, and 43.8°, which were known as typical peaks for CdS. These findings can be explained by the fact that CuS and CdS were introduced in the PAN film as expected.

Figure 5 exhibits micrographs for surface (A, B) and fracture (C) of CuS–PAN composite film. Figure 5(A), the micrograph for upper surface of casting film, exhibits many pores, which is considered to be formed by solvent casting. Figure 5(B), the micrograph for bottom surface, exhibits brain-like crystals[11] that clump together irregularly. Figure 5(C) exhibits many CuS crystals similar to surface micrographs. Therefore, CuS crystal is introduced to the inner part of film as well as the film surface. The surface and bulk conductivity should be the same.

Figure 6 exhibits micrographs for the surface of CdS–PAN composite film. CdS crystal was dispersed uniformly up to 60 wt % of CdS, but CdS was dispersed nonuniformly and disorderly in 80 wt % of CdS. Therefore, the electrical conductivity of CdS–PAN composite film was steeply decreasing in the 80 wt % of CdS (Fig. 7). Electrical conductivity of the CdS–PAN composite film is 10^{-5} S/cm for 60 wt % of CdS but is 10^{-7} S/cm for 80 wt % of CdS.

Electrical Conductivity of MS–PAN Composite Film

Figure 8 shows the dependence of electrical conductivity of CuS–PAN composite film on the weight percent of CuS measured at room temperature. Elec-

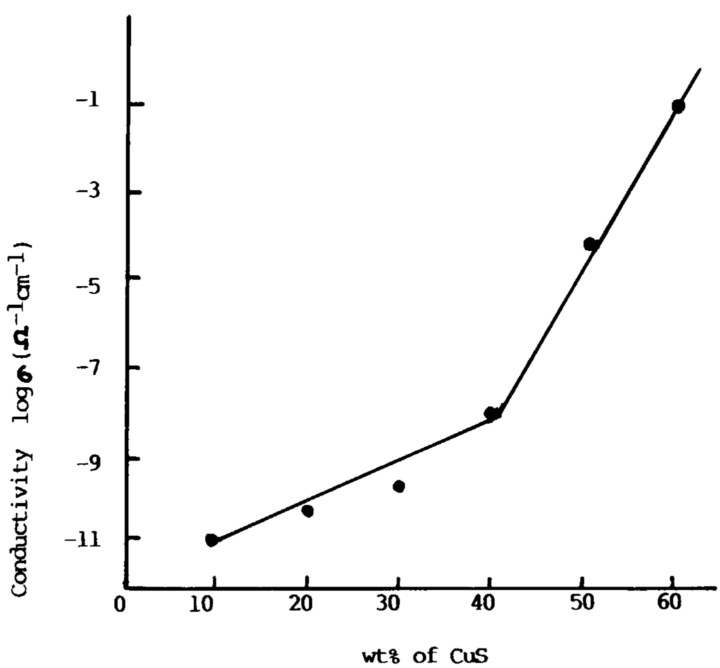


Fig. 8. Dependence of electrical conductivity (●) of CuS–PAN composite on the weight percent of CuS in the composite measured at 25°C.

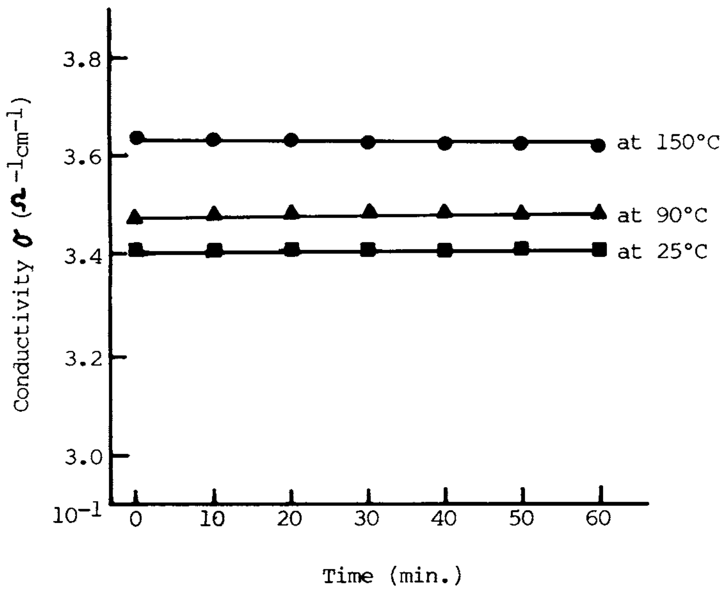


Fig. 9. Time dependence of surface conductivity for CuS–PAN composite film at various temperature.

trical conductivity of CuS–PAN composite depended on its composition and steeply increased in 40 wt % of CuS. Formation of an electrical conducting channel by contact of highly dispersed copper sulfide explains this result. The sharp increase of electrical conductivity with increase in weight percent of CuS in the CuS–PAN composite resembles the sharp increase of conductivity with increase in carbon content in carbon–polymer composites.[12]

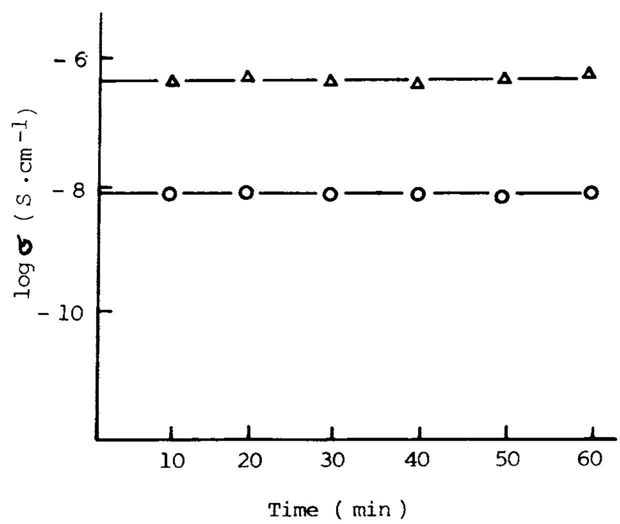


Fig. 10. Time dependence of conductivity for CdS–PAN under constant applied voltage (1.5 V): (○) 45 wt %, (△) 55 wt % of CdS.

Conduction Mechanism of CuS–PAN Composite Film

In order to estimate the conduction mechanism, the electric current was measured as a function of time under constant voltage. If the ionic conduction is dominant, the current would decrease with applied time as the ionic carrier are eventually purged from the system.

Figures 9 and 10 show the time dependence of conductivity for CuS–PAN and CdS–PAN composite, respectively. Therefore, as seen in Figs. 9 and 10, the electronic conduction is the main process in MS–PAN film.

In order to support this fact, *IV* characteristics were also examined. Figures 11 and 12 show the *IV* characteristics of CuS–PAN and CdS–PAN composite, respectively. It was found that the current was proportional to the applied voltage. That is, the conduction is approximately ohmic. These results strongly suggest that the electronic conduction is the main process in MS–PAN composite film.

The electrical conducting properties of the CuS–PAN and CdS–PAN composite film is considered due to a CuS and CdS network on the surface and inner part of the film.

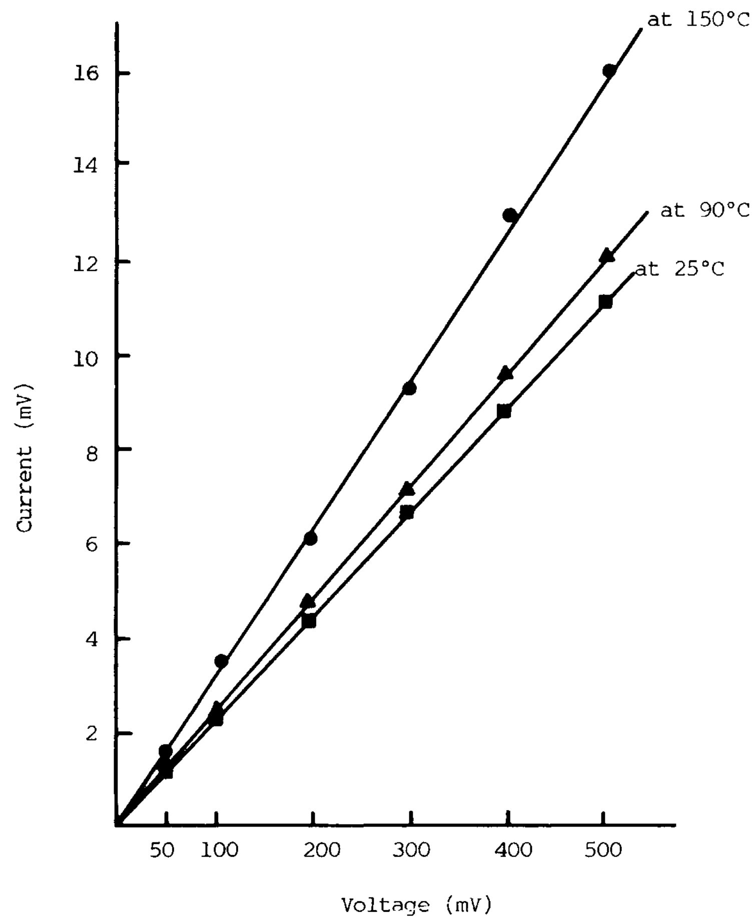


Fig. 11. Dependence of current on applied potential for CuS–PAN composite film.

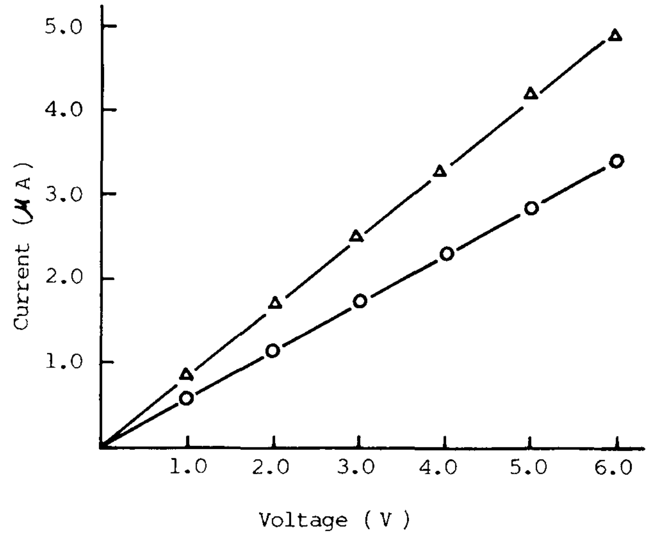


Fig. 12. Dependence of current on applied potential for CdS–PAN: (○) 45 wt %, (△) 55 wt % of CdS.

Temperature Dependence of Conductivity

Figure 13 shows the temperature dependence of the conductivity of CuS–PAN composite film measured by the four-probe method. It can be seen that conductivity is constant up to 90°C and increases above this temperature. It is reported[13–16] that an abrupt change in the conductivity curve at about 90°C is assigned to the transition from the γ phase to β phase of CuS. And this behavior is very similar to the characteristic of electrical behavior on the CuS crystal.

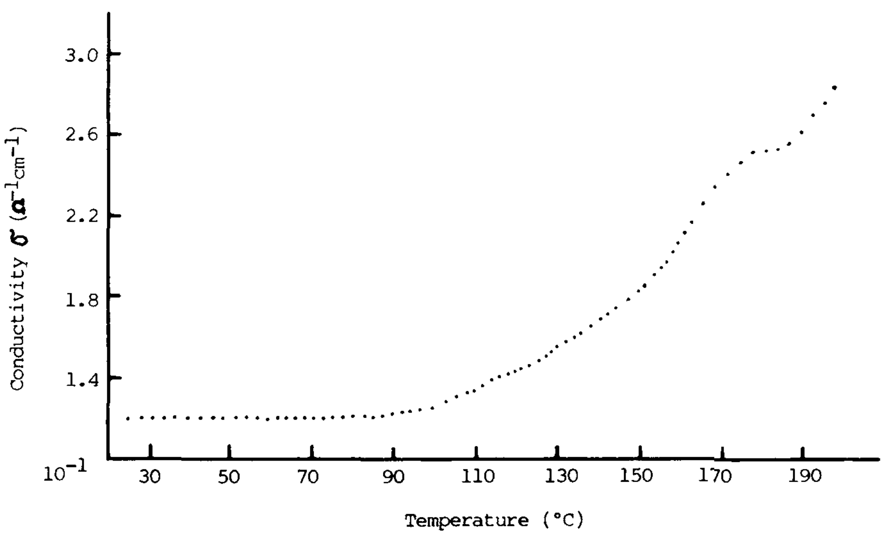


Fig. 13. Temperature dependence of surface conductivity for CuS–PAN composite film.

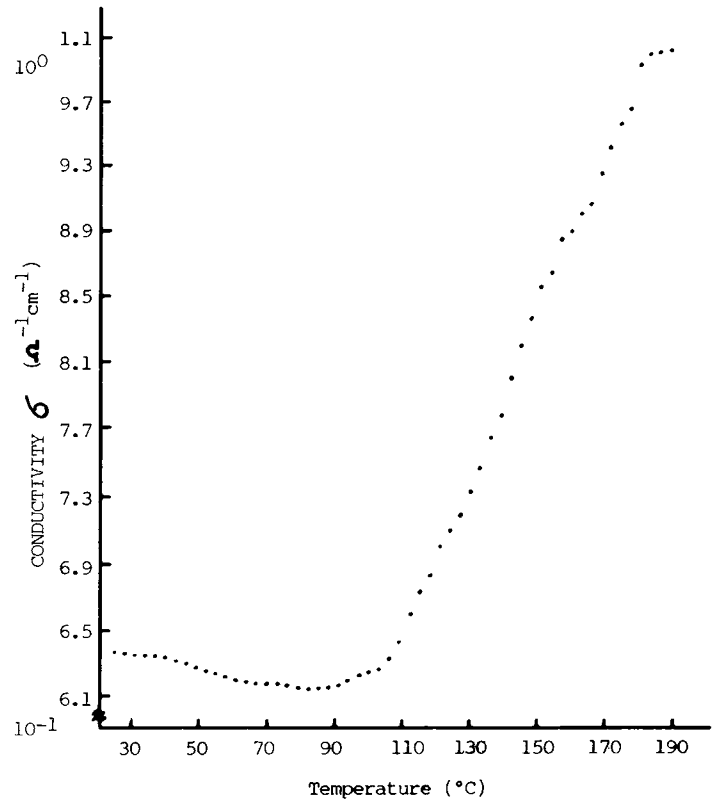


Fig. 14. Temperature dependence of surface conductivity for CuS–PAN composite film (heat treatment at 90°C).

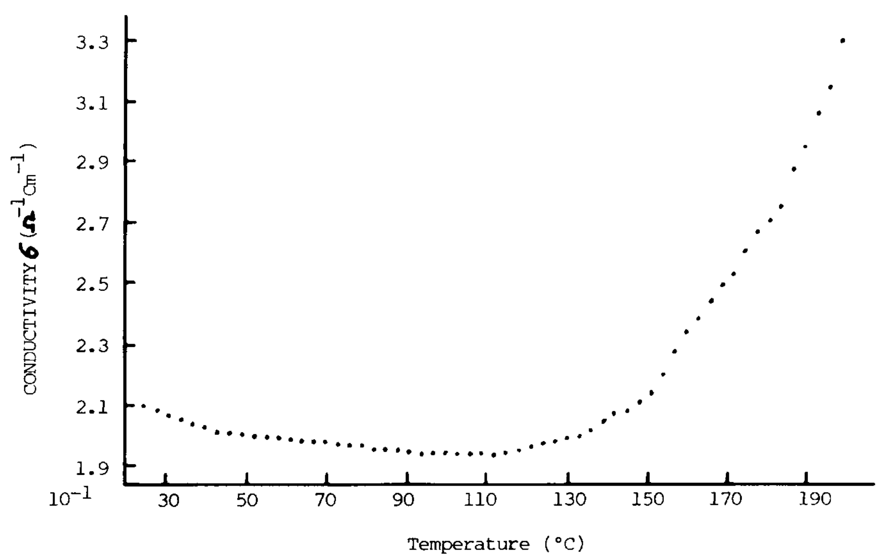


Fig. 15. Temperature dependence of surface conductivity for CuS–PAN composite film (heat treatment at 120°C).

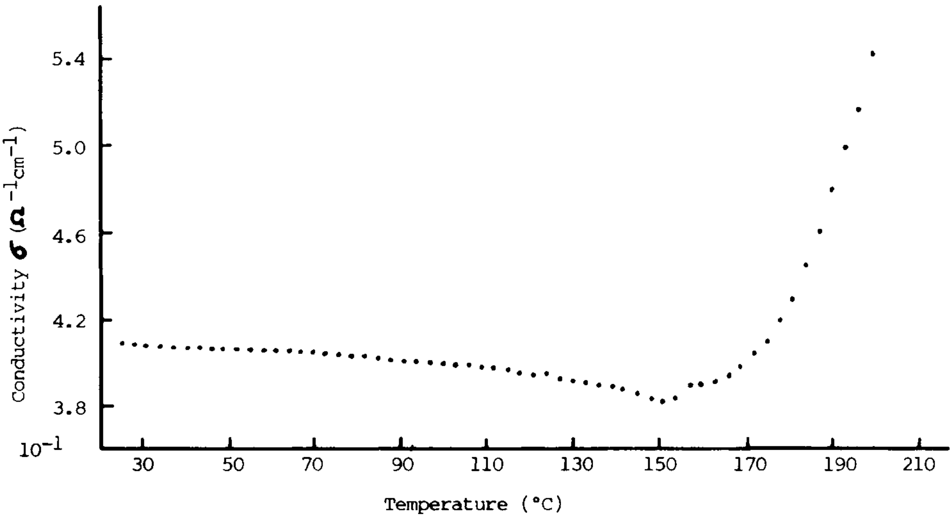


Fig. 16. Temperature dependence of surface conductivity for CuS–PAN composite film (heat treatment at 150°C).

Figures 14–16 show the temperature dependence of conductivity in respect to the annealing sample at 90, 120, and 150°C, respectively. Temperature dependence of conductivity on the heat-treated CuS–PAN composite film is similar to that of CuS–PAN composite film, but temperature change in the conductivity curve is different according to annealing temperature. However, the difference between the heat treatment at the three temperatures studied is rather marginal. Furthermore, the variation of conductivity with temperature for three heat-treated samples is very small, and the conductivity is in the same order, that is, 10^{-1} S/cm. A more detailed analysis of the effects of heat treatment on the conductivity is now in progress in our laboratory.

Mechanical Properties

Table I shows the tensile strength and initial modulus of original PAN film and CuS–PAN composite film. Tensile strength and modulus were constant up to 30 wt % CuS and decreased with an increase of the weight percent of

TABLE I
Tensile Strength and Modulus of CuS–PAN Composite Film

Sample	Tensile strength (MPa)	Tensile modulus (MPa)
Original (PAN)	44.81	1296.3
CuS–PAN film (10 wt %)	42.26	1111.8
CuS–PAN film (20 wt %)	39.75	1074.7
CuS–PAN film (30 wt %)	37.45	1025.8
CuS–PAN film (40 wt %)	22.93	893.2
CuS–PAN film (50 wt %)	12.13	707.5

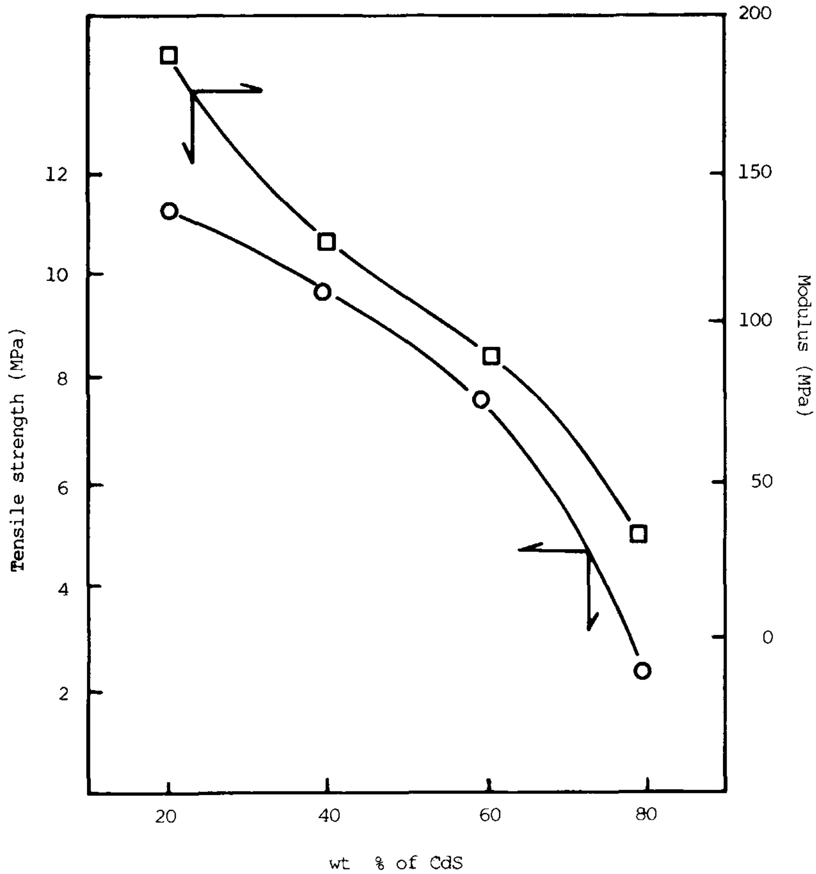


Fig. 17. Dependence of modulus and tensile strength of CdS–PAN film on the weight percent of CdS.

CuS at more than 40 wt %. But this does not prevent its utilization in electronic devices.

Figure 17 shows the dependence of modulus and tensile strength of CdS–PAN composite film on the weight percent of CdS. Modulus and tensile strength were decreased with an increase of the weight percent of CdS, and steep decreasing at 60 wt % CdS. This is coincident with the SEM micrograph (Fig. 6). Therefore, CdS–PAN film was utilized in electronic devices up to 60 wt % CdS content.

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References

1. N. B. Hannay, *Semiconductors,* Reinhold, New York, 1959.
2. H. K. Henish, *Electrochemiluminescence,* Perganon, Oxford, 1962.
3. G. Beghi, *Performance of Solar Energy Converters: Thermal Collectors and Photovoltatic Collectors and Photovoltaic Cells,* Reidel, Dordrecht, Holland, 1983.
4. B. R. Nag, *Electron Transport in Compound Semiconductors,* Springer, Berlin, 1980.

5. R. K. Willardson and A. C. Beer, *Semiconductors and Semimetals,* Academic Press, New York, 1966, 1967, 1968, 1975, and 1980.

6. S. M. Sze, *Physics of Semiconductor Devices,* Wiley, New York, 1981.

7. J. I. Park, E. Y. Kang, S. S. Im, and J. W. Kim, *J. Korean Soc. Text. Eng. Chem.,* **22,** 48 (1985).

8. S. G. Lee, E. Y. Kang, and S. S. Im, *Polymer (Korea),* **10,** 165 (1986).

9. E. Y. Kang, E. J. Chung, and S. S. Im, *J. Appl. Polym. Sci.,* **33,** 317 (1987).

10. S. S. Im and E. Y. Kang, *J. Appl. Polym. Sci.,* **35,** 475 (1988).

11. R. D. Engelken and H. E. McCloud, *J. Electrochem. Soc.,* **132,** 567 (1985).

12. K. Miyasaka and K. Watanabe, *J. Mater. Sci.,* **17,** 1610 (1982).

13. E. Hirahara, *J. Phys. Soc. Jpn.,* **2,** 211 (1947).

14. E. Hirahara, *J. Phys. Soc. Jpn.,* **6,** 428 (1951).

15. S. Miyatani, *J. Phys. Soc. Jpn.,* **11,** 1059 (1956).

16. K. Okamoto and S. Kawai, *Jpn. J. Appl. Phys.,* **12,** 1130 (1973).

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