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Electroless Copper Sulfide Deposition on the Polyacrylonitrile Films with Chelating Agents and its EMI Shielding Effectiveness

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Summary: In this study, an effective deposition of copper sulfide ($Cu_{x(x=1,2)}S$) on the PAN film was proposed by an electroless deposition method with the reduction agents $NaHSO_3$ and $Na_2S_2O_3 \cdot 5H_2O$ and chelating agents (ethylenediaminetetraacetic acid, EDTA and triethanolamine, TEA). The mechanism of the $Cu_{x(x=1,2)}S$ growth and the electromagnetic interference shielding effectiveness (EMI SE) of the $C_{ux(x=1,2)}S$/PAN films were studied. It was found that the vinyl acetate monomer residue in the PAN substrate would be purged due to the swelling effect by EDTA and TEA solution. And then, the anchoring effect occurred due to the hydrogen bonding between the pits of the PAN substrate and the chelating agent. The swelling degree (S_d) was proposed and evaluated from the FT-IR spectra. The relationship between swelling degree of the PAN films and EDTA concentration(C) is expressed as: $S_d = 0.13 + 0.90 \times e\hat{}(-15.15C_{EDTA})$. And TEA series is expressed as: $S_d = 0.07 + 1.00 \times e\hat{}(-15.15C_{TEA})$. On the other hand, the FESEM micrograph showed that the average thickness of copper sulfide increased from 76 nm to 383 nm when the concentration of EDTA increased from 0.00 M to 0.20 M. Consequently, the EMI SE of the $C_{ux(x=1,2)}S$/PAN films increased from 10~12 dB to 25~27 dB. The GIA-XRD analyzer indicated that the deposited layer consisted of CuS and Cu_2S.

Keywords: chelating agent; copper sulfide; electroless deposition; EMI SE; swelling

Introduction

Scientists recently have paid attention to the thin-film technology due to its wide applications. As device applications are being discovered, the study of thin-film materials is greatly arousing interests of material scientists. This useful technique can be applied to not only electrically conductive materials including graphite but also insulators like plastics, rubber and etc.[1,2]. In this study, with chelating agents, the copper sulfide ($Cu_{x(x=1,2)}S$) layers were electroless plated on the PAN substrate without activation and sensitization procedures. It was very different from commercial electroless plating method, especially when the substrates were non-catalytic or non-conductive. Consequently, the improvement of the EMI SE was effectively and significantly achieved. It has been well known that the adhesion of coating films and substrate is simultaneously related to the complementary effects of roughness, surface energy, surface stabilization reaction

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and the possible formation of covalent bonds at the film-substrate interface. As a consequence, the mechanism with respect to these complementary effects was studied and investigated by the FT-IR spectra determination and the glancing incident angle X-ray diffraction pattern.

Finally, the EMI SE of the $Cu_{x(x=1,2)}S$/PAN films with a variety of coating films by different electroless plating procedures was evaluated.

Experimental Part

Preparations of a PAN Film

The PAN substrates were prepared by casting a film, where the N, N-Dimethylformamide (DMF; NIHON SHIYAKU INDUSTRIES, LTD.) was used as the solvent and the solute was the PAN powder (contained 7% vinyl acetate monomer, VAc), which was kindly supplied by Tong-Hwa Synthetic Fiber Co., Ltd.

Weighted 14.0 g PAN powder and dissolved completely in 50 ml DMF solution to form a transparent and light yellow solution. Then pour the above solution into the shallow container slowly. After the above steps, the PAN solution was dried to form a thin and transparent PAN film in an oven at 45 °C.

Deposition Processes of Electroless Copper Sulfide Layers

All the reagents used in an electroless copper solution were reagent grades and the deionized water was used. The cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was the source of cupric ion; meanwhile, the sodium bisulfate ($NaHSO_3$) and the sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) were reduction agents used in this study.

Besides, various concentrations of EDTA and TEA were added not only as a chelating agent but also a key factor to establish a new approach of electroless plating. The electroless plating time was 60 minutes.

FT-IR Spectra Determinations

The samples for FT-IR determination were prepared by cutting them into about 2.5 cm × 2.5 cm flakes. The spectra were recorded in absorbance with a Jasco 300E FT-IR in a range of 400 to 4000 cm-1 at a resolution of 4.0 cm-1. In order to evaluate the swelling degree (S_d) of the PAN substrates, the PAN substrates were immersed into 0.00 ~ 0.60 M TEA solutions for 60 minutes.

Glancing Incident Angle X-ray Diffraction (GIA-XRD) Patterns

The X-ray diffraction study of the samples was carried out by a MAC Science MXP18 X-ray diffractometer (40 KV, 150 mA) with a glancing incident angle of 0.5 degree and the wavelength of the GIA-XRD source was 1.54 Å (Cu Kα radiation) at a scan rate of 1.0 degree/min.

EMI Shielding Effectiveness (SE) Measurement

Materials in shielding applications were tested for attenuation or reduction of a signal expressed in decibels (dB). The shielding effectiveness was given by $SE = 10\log(P_{in}/P_{out}) = 20\log(E_{in}/E_{out}) = 20\log(H_{in}/H_{out})$, where P is the energy field, E is the electrical field strength and H is the magnetic field strength. In passing through a shield of an Electromagnetic (EM) wave could be separated into three components: $SE = A + R + B$, where A was the absorption, R was the reflection and B was the multiple reflection of EM waves. The flanged circular coaxial transmission line method, ASTM Standard D 4935-99, was used to evaluate the EMI SE. The EMI SE values of $Cu_{x(x=1,2)}S$/PAN films obtained by taking out the background shielding measurement. Since the EMI SE was a voltage dependent below the range of 30 MHz, the test range of frequency in this experiment was from 30 MHz to 1500 MHz.

FE-SEM Micrograph Observations

The surface and cross-section morphologies of the CuS/PAN films were observed by a field emission scanning electron microscope (FE-SEM, JEOL-JSM 6700F). The FE-SEM image was operated at 3.0 kV voltage.

In order to take an examination of surface morphologies, samples were coated with platinum. Nevertheless, for another examination of cross-section morphologies, samples needed to be immersed in liquid nitrogen for 10 minutes and fractured. Afterwards, the fracture surfaces were coated with platinum.

Results and Discussion

Deposition Processes of Electroless Copper Sulfide Plating

The following equations[2] can represent the formation of copper sulfide in this investigation:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad (1)$$

$$S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^- \quad (2)$$

$$S + 2e^-(\text{From reaction(1)}) \rightarrow S^{2-} \quad (3)$$

$$Cu^{2+} + S^{2-} \rightarrow CuS \downarrow \quad (4)$$

The ability of the reduction agent was to gradually release sulfide ions upon hydrolytic deposition in acidic media. The formation of Cu^+ ions could be attributed to the reduction of Cu^{2+} ions by the sulfide ions present in the bath.[3]

With an additive of reduction agents ($NaHSO_3$, $Na_2S_2O_3 \cdot 5H_2O$), the cupric ion was attracted by a nitrile group on the PAN film and was reduced to form a conductive layer on the surface of the PAN. It was because that the $-CN$ functional group of the PAN with one lone pair of electrons could attract the Cu^{++} ion in solutions, and the acrylonitrile group ($-C{\equiv}N$) of the PAN possessed a very high polarity which would also arise from the strong dipole moment of the nitrile groups. The lone pair orbital of nitrogen can engage in hydrogen bonding and electros in the π orbital of the nitrile triple bond which can interact with transition metal ions.[4] Therefore, the PAN film did not have to be sensitized, activated or catalyzed. It was a novel application for all the electroless plating methods.[3]

In this research, TEA was used as not only a chelating agent with cupric ions but an anchor into a PAN substrate. For the electroless deposition bath with the chelating agents, the significant thickness of copper sulfide ($Cu_{x(x=1,2)}S$) layer on the PAN films was essential. The reaction model is shown in Figure 1, and more details will be illustrated in the following contents.

FT-IR Spectra of the PAN Films

The major absorption bands for a PAN film were CH twisting deformation at 1250 cm^{-1}, CH in-plane deformation at 1386 cm^{-1}, CH_2 bending at 1454 cm^{-1}, CN stretching at 2242 cm^{-1}, CH_3 stretching at 2869 cm^{-1}, CH stretching at 2937 cm^{-1}, C=O carbonyl stretching at 1737 cm^{-1} and C=C stretching vibration for VAc monomer at 1662 cm^{-1}. The PAN films we applied contained 7% VAc monomer; therefore, the characteristic peaks of VAc monomer were also found in the spectra shown in Figure 2.

The VAc monomer in the PAN film was released from swollen PAN by EDTA or

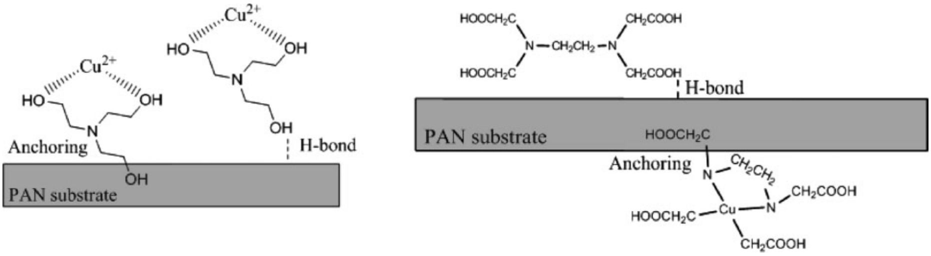


Figure 1.
The hydrogen bonding and anchoring of chelating agents and a PAN film.

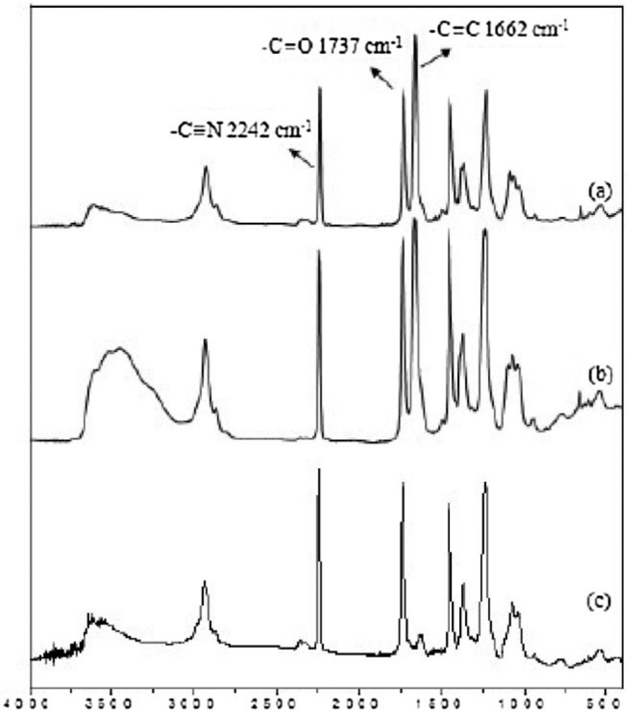
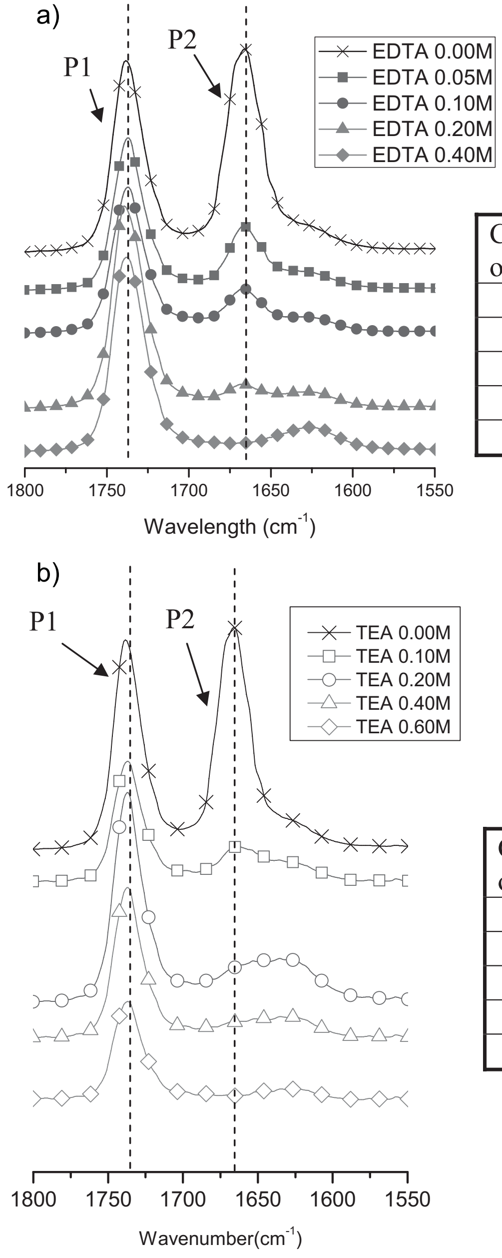


Figure 2.
FT-IR spectrum of (a)Polyacrylonitrile films, (b)PAN films immersed in $NaHSO_3$ and $Na_2S_2O_3$ solution, (c)PAN films immersed in chelating agent solution.

TEA because only the VAc has C=C in the system. The peak area of C=C reduced obviously in FT-IR spectra proved that the VAc monomer released in the EDTA and TEA electroless deposition systems. For this reason, the EDTA and TEA chelating agents will anchor into the PAN substrate due to the left pits formed by purging the residual VAc monomer and the interforce of hydrogen bonding as represented in Figure 1. Furthermore, in order to evaluate the extraction of VAc in the PAN substrate, the peak area was calculated by FT-IR spectra. As P1 & P2 shown in Figure 3, P1 represents the peak area of C=C peak (VAc) and P2 represents the peak area of C=O peak (PAN copolymer). Therefore, the absorption strength of C=C peak (VAc) to C=O peak (PAN copolymer) is adopted to represent the ratio of swelling degree denoted as S_d illustrated in Figure 3(a) & (b). The PAN films were immersed in the reduction agents solution ($NaHSO_3$, $Na_2S_2O_3 \cdot 5H_2O$) with a variety of concentrations of EDTA and TEA solutions, and then the effects of chelating agents on the swelling degree (peak area ratio of P2/P1) of the PAN films are presented in Figure 3. The relationship of the swelling degree (S_d) with respect to the TEA concentration can be fitted in the following equations and shown in the dotted curve in Figure 4.

Glancing Incident Angle X-Ray Diffraction (GIA-XRD) Analyses

By adding TEA into the electroless deposition bath, the GIA-XRD patterns in Figure 5 were superimposed so you can clearly see two peaks appeared at $2\theta = 29.42^\circ$, 31.89°, and 47.90°, respectively. After being compared with the standard JCPDS-ICDD diffraction patterns, the crystalline micro-



Concentration of EDTA (M)	Swollen Degree P2/P1
0.00	1.0494
0.05	0.4894
0.10	0.3885
0.20	0.2058
0.40	0.0953

Concentration of TEA (M)	Peak area P2/P1
0.00	1.0494
0.10	0.3826
0.20	0.2931
0.40	0.1024
0.60	0.0406

Figure 3.
The illustrations of peak area ratio of PAN in (a) EDTA, (b) TEA solutions.

structure of CuS (hexagonal covellite, JCPDS No. 06-0464, a = 3.792, c = 16.344) was verified in the deposition layer. When EDTA was added into the electroless deposition bath, the crystalline microstructures of β-Cu_2S (hexagonal chalcocite, JCPDS No. 31-0482, a = 4.005, c = 6.806), CuS (hexagonal covellite, JCPDS No. 06-0464, a = 3.792, c = 16.344) were verified in the deposition layer.

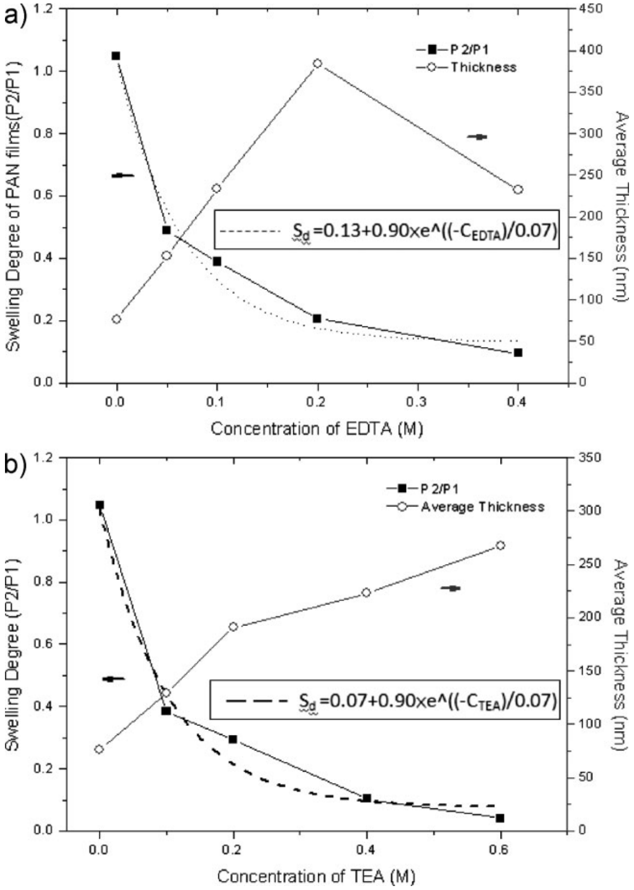


Figure 4.
The swelling degree and thickness of copper sulfide versus concentration of (a)EDTA and (b)TEA.

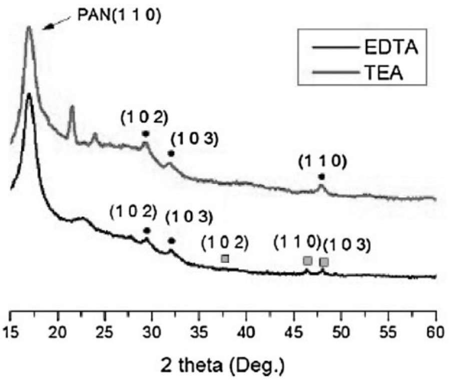


Figure 5.
The GIA-XRD patterns of copper sulfide.

Morphology of the PAN Plated Copper Sulfide

The FE-SEM morphologies of CuS/PAN films prepared in this study were categorized in Figure 6 In this investigation, it was found that the PAN molecular chains were swollen by EDTA and TEA solutions. The VAc monomer existed originally in the PAN film would be purged, and the EDTA anchored into the PAN substrate. It is illustrated in previous section of FT-IR spectra of the PAN films. As a result, the cupric ion chelated with the EDTA on the PAN film. Consequently, the copper sulfide was almost deposited on the PAN film instead of precipitating in the solution. The

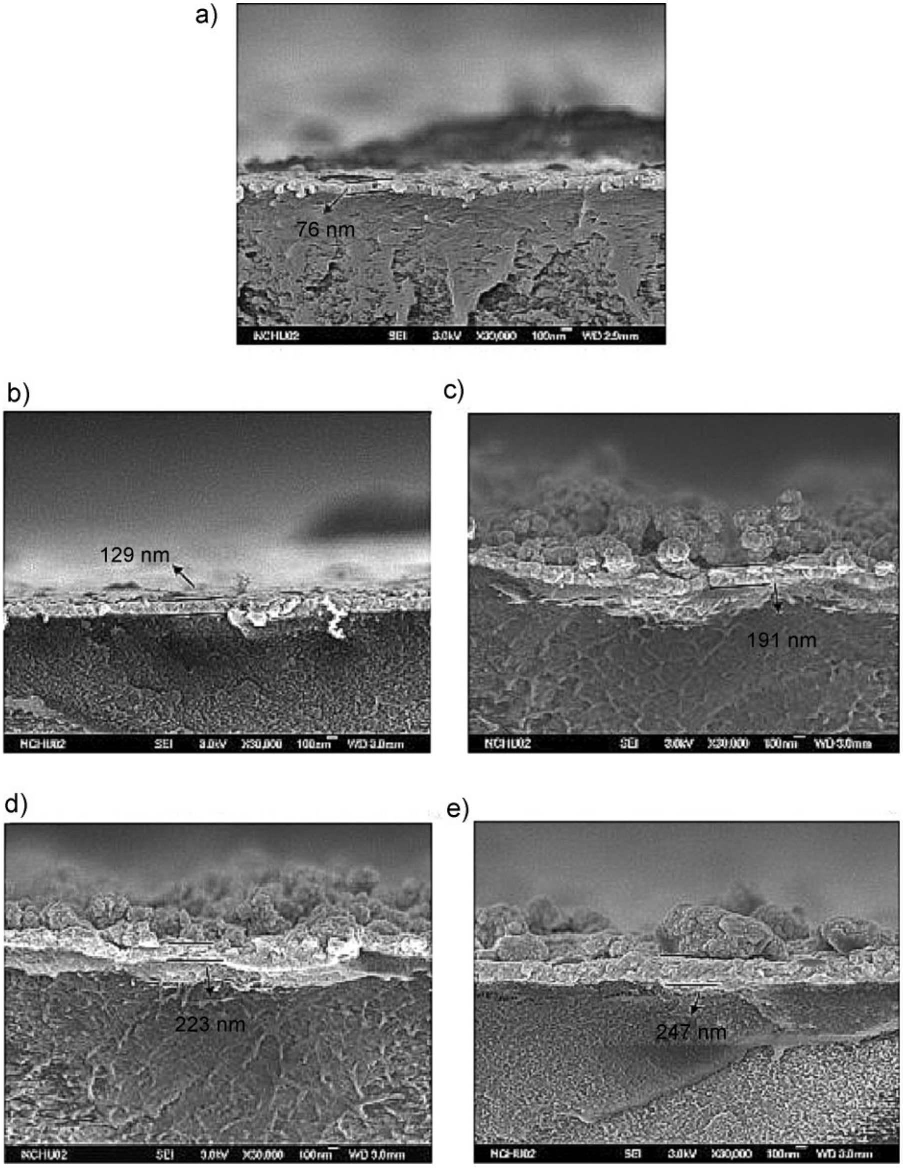


Figure 6.
The cross-section of copper sulfide plated on the PAN films with TEA in the electroless deposition bath.

advantage of EDTA agent was not only to provide the reaction sites but also to accelerate the growth of the copper sulfide layer as indicated in Figure 1 as well as observed in the FE-SEM pictures. Figure 4 shows that the swelling degree related to the anchoring effect is completely governed by the amount of chelating agents and has a saturation value. Nevertheless, the average thickness of copper sulfide coating raised with the increasing of EDTA concentration up to 0.20 M and then decreased due to the over chelating effect.

On the other hand, by adding TEA into the copper sulfide deposition bath, the thickness of copper sulfide can also be observed by the FE-SEM technique. Pictures in Figure 6(a) to (e) are the cross-section views of the CuS/PAN films. According to the illustrations of Figure 6(a), the average thickness of copper sulfide layer is 76 nm. The roughness and irregular surface without the presence of TEA are also evidenced by the cross-section view shown in Figure 6(a). At the plating process, the cupric ion was attracted onto the PAN film due to the polarity of TEA. Consequently, the location of TEA can be indicated as a seed of the reduction site. The different stages of the film growth: incubation/nucleation, growth and terminal phases in the chemical bath deposition have been described by Nair et al. and Lokhande et al. [8–10]. The micrographs in Figure 6(b)

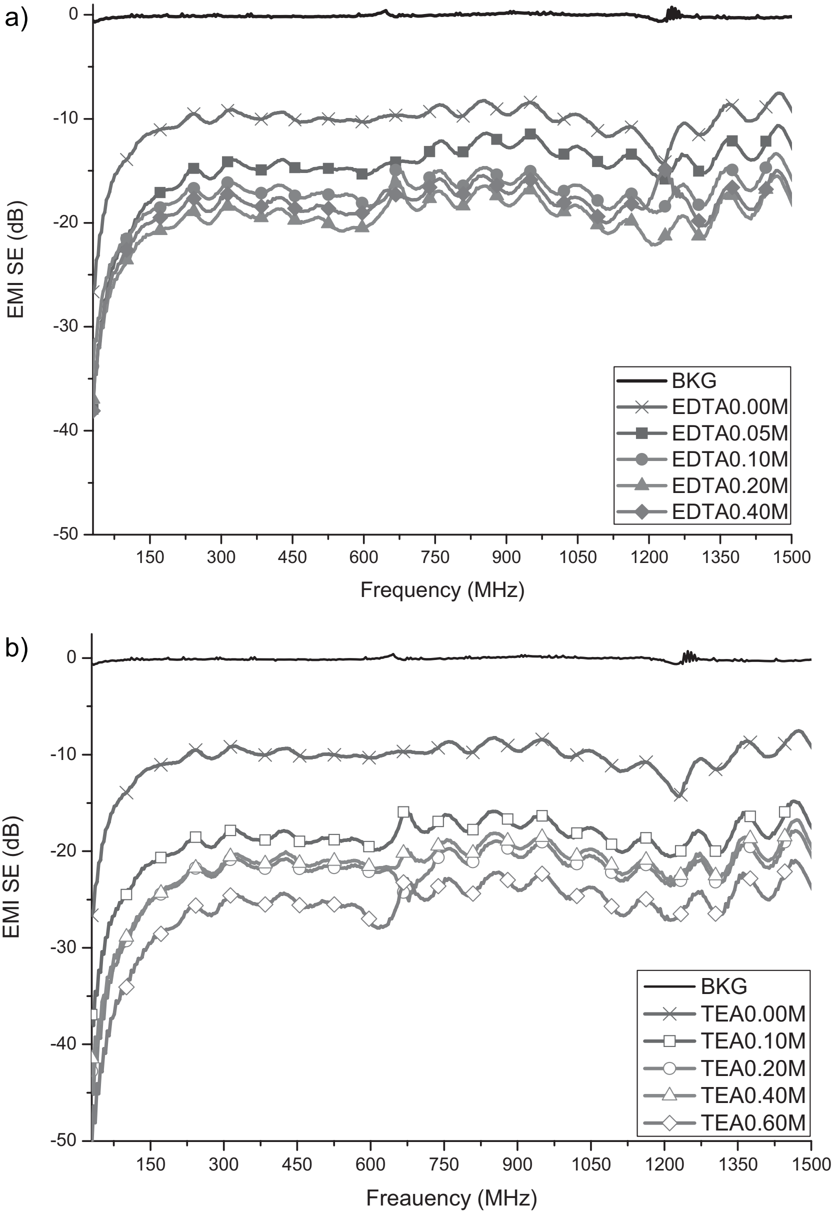


Figure 7.
The EMI SE of $Cu_{x(x=1,2)}S$/PAN films prepared in (a) EDTA and (b) TEA electroless depositions.

to (e) show the average thicknesses of copper sulfide layer plated on the PAN films which increases from 129 nm to 247 nm by adjusting the concentration of TEA as plotted in Figure 4(b). It was also noticed that when the swelling degree (Sd) approached saturation, the thickness of copper sulfide layer would still increase by raising the TEA concentration.

EMI Shielding Effectiveness Measurement

The EMI SE of the $Cu_{x(x=1,2)}S$/PAN films manufactured in this study were measured between 30 MHz to 1500 MHz and plotted in Figure 7(a). The EMI effect is obviously controlled by the thickness of copper sulfide layer. The thickness of copper sulfide affects the EMI SE due to the incident EMI wave reflected by a copper sulfide layer. Jana et al. [11] studied the effect of the thickness of conductive layer of composites on EMI SE, and found that the EMI SE increased and return-loss decreased with the increasing thickness of composites. The EMI SE effect was significantly improved for the $Cu_{x(x=1,2)}$/PAN films by comparing the curves of 0.05 M and 0.00 M EDTA in Figure 6 since the thickness of copper sulfide with 0.05 M EDTA was doubled (153 nm/76 nm). The thickness of the copper sulfide layer reached to a maximum at 0.20 M EDTA and then decreased; therefore, the best electroless plating condition for EMI SE was 0.20 M EDTA.

The EMI SE effect was significantly improved for the CuS/PAN films by comparing the curves of 0.10 M and 0.00 M TEA in Figure 7(b) because the thickness of copper sulfide with 0.10 M TEA is increased (129 nm/76 nm). In addition, the thickness of the copper sulfide layer reached to a maximum at 0.60 M TEA. Therefore, the best electroless plating condition for EMI SE was 0.60 M TEA, and the EMI SE reached 25–27 dB.

Conclusion

In this research, the effective $Cu_{x(x=1,2)}S$ deposition layer on the PAN film was carried out an electroless deposition method with the reduction agents $NaHSO_3$ and $Na_2S_2O_3 \cdot 5H_2O$ and chelating agents (EDTA and TEA). The GIA-XRD identified the crystalline of copper sulfide deposition. EDTA and TEA provided the anchoring effect and were demonstrated by FTIR spectra. They also played a critical role to give the effective deposition layer. The swelling degree (S_d) was described and evaluated by the equation: $S_d = 0.13 + 0.90 \times e\wedge(-15.15C_{EDTA})$. The average thickness of copper sulfide layer increased from 76 nm to 383 nm as the EDTA concentration increased from 0.00 M to 0.20 M. As a result, the EMI SE of the $Cu_{x(x=1,2)}S$/PAN films increased from 10∼12 dB to 20∼23 dB.

In the TEA bath, the swelling degree (S_d) can be also calculated from $S_d = 0.07 + 1.00 \text{ x } e\wedge(-15.15C)$. The average thickness of copper sulfide layer increased from 76 nm to 247 nm while the TEA concentration increased from 0.00 M to 0.60 M. Consequently, the EMI SE of the $Cu_{x(x=1,2)}S$/PAN films reached in between 25 dB and 27 dB.

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