Applied Surface Science 255 (2009) 8430–8434

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Electroless copper plating on 3-mercaptopropyltriethoxysilane modified PET fabric challenged by ultrasonic washing

Yinxiang Lu [a,b,*]

[a] Department of Materials Science, Fudan University, Shanghai 200433, China
[b] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

ARTICLE INFO

Article history:
Received 18 March 2009
Received in revised form 23 April 2009
Accepted 27 May 2009
Available online 6 June 2009

Keywords:
Poly(ethylene terephthalate) fabric
Electroless plating
3-Mercaptopropyltriethoxysilane
Ultrasonic washing
Shielding effectiveness

ABSTRACT

Electroless deposition of Cu on poly(ethylene terephthalate) (PET) fabric modified with 3-mercaptopropyltriethoxysilane was investigated. Morphology, composition, structure, thermal decomposing behavior of copper coating PET fabric after ultrasonic washing in water for 1 h were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, X-ray photoelectron spectroscopy (XPS), Raman spectrometer, X-ray diffraction (XRD), and thermogravimetric analysis (TG), respectively. Copper plating on modified fabric has good adherence stability and high electric conductivity before and after ultrasonic washing, while copper coating fabric without modification is easily destroyed during the washing process, which leads to the textile changing from conductor to dielectric. As the copper weight on the treated fabric is 28 g/m^2, the shielding effectiveness (SE) is more than 54 dB at frequency ranging from 0.01 MHz to 18 GHz.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Conductive textiles, which are coated with aluminum, copper, silver and nickel, are an important kind of materials for preventing electromagnetic interference [1–4]. Conductive fabrics coated with different metals have been used in many electronic instruments in a variety of manufactured forms such as fabric tape or foam gaskets. There are many reports on metallization techniques, including sputtering and chemical vapor deposition (CVD) [5,6]. However, these methods require high-temperature treatment, which is not appropriate for textile substrates. Electroless plating method is widely used in microelectronics, radio-electronics, and aerospace techniques [7–9]. It allows us to obtain uniformly thick coatings on the articles of any profiles of metallic, dielectric and semiconducting materials and gives us the possibility to regulate physical–chemical properties of the coatings (such as electrical conductivity, chemical, mechanical and magnetic properties) in a wide range [10,11]. Electroless deposition of Cu has the significant merit of lower cost, fast deposition, and formation of good membranes at low temperature. In addition, Cu is suitable for wet processes since its oxidation–reduction potential (ORP) is electropositive [12,13]. Electroless copper plating is currently used to manufacture conductive fabrics [14].

Electroless plating on fabrics is normally carried out by multistep processes which included: scouring, rinsing, etching, rinsing, sensitization, rinsing, activation, electroless plating, rinsing and drying. In order to gain high adhesive metallic coating, the textiles should be etched by $KMnO_4$ or H_2SO_4. Even then, the metallic layer is intrinsically adsorbed to the fabrics by weak van der Waals force, which means physical adsorption. The metallic coating layer is easily destroyed by mechanical or ultrasonic washing [15].

To overcome this problem, we have developed a technique of electroless deposition of Cu on PET fabric modified with 3-mercaptopropyltriethoxysilane [16]. This process can reduce the number of steps and control the adsorption of Cu by utilizing interactions between the copper and the modified PET substrate. The interfacial interactions could improve the deposition conditions, such as deposition rate and the thin film properties, such as adhesion, surface morphology, and electrical conductivity. Then morphology, composition, structure, thermal decomposing behavior and electromagnetic property of copper coating PET fabrics after ultrasonic washing were clarified by means of scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, X-ray photoelectron spectroscopy (XPS), Raman spectrometer, X-ray diffraction (XRD), thermogravimetric analysis (TG) and shielding effectiveness (SE) measurement.

* Correspondence address: Department of Materials Science, 220 Handan Road, Fudan University, Shanghai 200433, China. Tel.: +86 21 65642871; fax: +86 21 65642871.
E-mail address: yxlu@fudan.edu.cn.

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.05.148

2. Experimental

2.1. Pretreatment of PET fabric

Polyethylene terephthalate (PET) fabrics (60×40 count/cm^2, 80 g/m^2, taffeta fabric) were used as substrates. The surface area of each specimen is 500 (25×20) cm^2.

PET fabrics were ultrasonically cleaned in acetone and ethanol, respectively, for 5 min and dried at 60 °C for an arbitrary length of time, and weighed.

The cleaned fabrics were dip-coated with the acetone solution of 1 vol% (3-aminopropyl)trimethoxysilane and heated at 125 °C for 30 min to form a silica-like layer. Then the fabrics were irradiated in air by UV-light for 30 min. The UV-light used in this work emits primarily at 185 nm.

The fabrics with the silica-like surface layer were immersed in an anhydrous toluene solution containing 1 vol% 3-mercaptopropyltriethoxysilane for 2 h, then rinsed with toluene, ethanol and water, respectively. The resulting fabrics were heated at 125 °C for 30 min in air to remove residual solvent, and weighed.

2.2. Electroless plating of PET fabric

One clean, untreated PET fabric (Sample 1) and another pretreated PET fabric (Sample 2) were put into the same neutral aqueous solution without catalyst. The composition of electroless bath and the operating conditions were listed in Table 1. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or HCl to a final value of 7. After plating, the samples were carefully rinsed with distilled water, ethanol and dried in an oven for 1 h at 50 °C, and weighed. Finally, the samples were ultrasonically washed (Ultrasonic cleaner, DL-120A, China, Zhisun Co., Ltd.) in water for 1 h, rinsed with ethanol, dried in an oven at 50 °C for 1 h, and weighed again.

2.3. Characterization of PET fabric

Scanning electron micrographs (SEM) were obtained using Philips XL 30 electron microscope. The samples were deposited on a sample holder with a piece of adhesive carbon tape. The chemical composition of the copper deposit was determined using energy dispersive X-ray (EDX) analysis attached to the SEM. X-ray diffraction (XRD) patterns of PET fabrics (2θ ranges from 10° to 95°) were recorded at room temperature with scanning speed of 0.15° min^{-1} using Cu Kα radiation (λ = 0.154 nm) from a 40 kV X-ray source (Rigaku D/max-γB) and diffracted beam monochromator, operated at 100 mA. Raman spectrums were characterized by Raman spectrometer (LabRam-1B, France, JY Co., Ltd.). Thermogravimetric analyses (TG) were performed on a Mettler Toledo TGA/SDTA851 analyzer in air with a heating rate of 5 °C/min, from 30 to 800 °C. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI 5000C ESCA system with Mg Kα source at 14.0 kV and 25 mA. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The surface resistance R_s was measured by a four-point probe (BD-90). R_s is considered to be the resistance of a square sample. The units of R_s are commonly expressed as ohms-per-square or Ω/□. Spectrum analyzer (Agilent 8563E) and signal generator (HP 8648C and Agilent 83732B) were combined to measure the shielding effectiveness of PET fabric (25 cm × 20 cm). The coaxial transmission line method as described in ASTM D 4935-99 was used to test the electromagnetic interference shielding effectiveness of the conductive fabrics.

Table 1
Composition and operation conditions of electroless plating.

Chemical	Concentration (g/L)
$CuCl_2{\cdot}2H_2O$	9
H_3BO_3	6
$C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$ (EDTA$Na_2{\cdot}2H_2O$)	18
$C_2H_{10}BN$ (DMAB)	7
pH	7
Temperature (°C)	60
Time (h)	4

3. Results and discussion

3.1. SEM analysis

The morphology of copper-coated fabrics after ultrasonic washing was studied by scanning electron microscope (SEM). Fig. 1(a) shows that the copper deposits on the untreated PET fabric (Sample 1) were loose and the surface was very rough, which resulted in dark-brown copper deposits. As shown in Fig. 1(b), the deposits became more compact and smoother on modified fabric (Sample 2). The color of the deposits also had a corresponding improvement, changing from dark-brown to copper-bright. The bright appearance of the deposits usually indicates better mechanical and electrical properties. Fig. 1(c) is the EDX spectrum of Sample 2. It indicates that the coating is composed of Cu, and other possible ingredients, such as B, N, are invisible.

3.2. Adherence stability analysis

The significant difference in adherence stability of these two coatings (Samples 1 and 2) was detected when the samples were ultrasonically washed in water for 1 h; the weight of the samples in every procedure was shown in Table 2.

The modification process added trace amount weight (approximately 6–10 mg) to the PET fabric; after 4 h plating in the same solution, 1.411 g Cu was deposited on Sample 2, however, there is only 0.998 g Cu deposited on Sample 1. It is possible that the –SH modified surface can catch Cu^{2+} ion from the bath more quickly than the untreated one. Following the Cu^{2+} adhering to the surface is reduced, Cu is continuously deposited and metallized to form uniform thin films by autocatalysis. Table 2 also shows that the weight loss of Sample 1 is about 0.195 g after ultrasonic washing, but little change is happened to Sample 2. We think it is due to the strong Cu–S bond which links the plating film and the modified substrate tightly. For Sample 1, there is only weak van der Waals force which interacts between the copper layer and the untreated PET fabric, so the slack copper coating is easily shelled off by ultrasonic washing.

3.3. XPS analysis

In order to identify surface composition of electroless copper film, XPS measurement was employed to test Sample 2. The XPS spectra of copper plating are shown in Fig. 2. In XPS spectra, peaks at 933 eV, 121 eV and 75 eV are ascribed to Cu 2p, Cu 3s and Cu 3p, respectively. The result clearly shows that Cu element exists as Cu^0, which is also proved by EDX spectrum.

3.4. Raman analysis

Raman spectra of untreated (a), (3-aminopropyl)trimethoxysilane treated following by UV irradiated (b), and 3-mercaptopropyltriethoxysilane modified (c) PET fabrics are indicated in Fig. 3. A peak at 1729 cm^{-1} is attributed to carbonyl (C=O) stretching vibration, and a peak at 1614 is ascribed to phenyl ring stretching vibration. The C–H stretching vibration due to methylene group is observed at 1466 cm^{-1}, the aromatic >C=C< stretching vibration

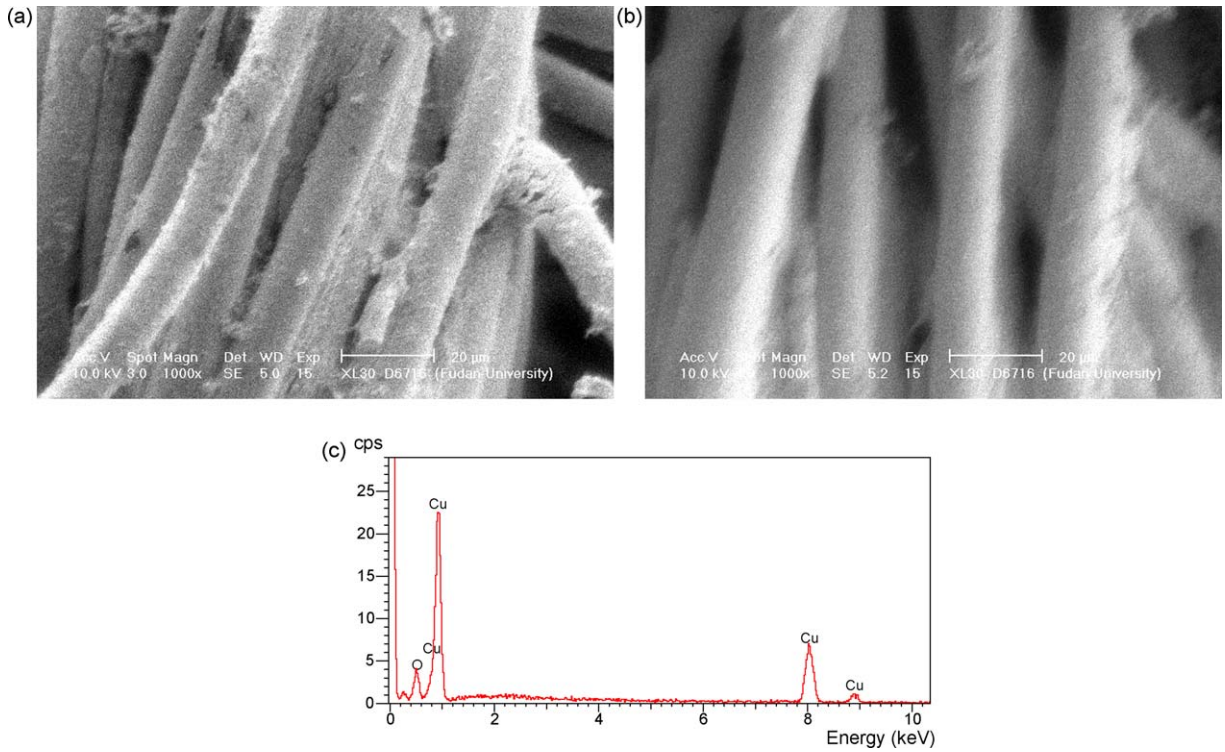

Fig. 1. SEM photos of copper plating PET fabrics after ultrasonic washing (a) Sample 1, (b) Sample 2 and (c) EDX spectrum of Sample 2.

is observed at 1288 and 1365 cm^{-1}. A peak at 1187 cm^{-1} belongs to ester (C(O)–O) stretching vibration. Phenyl ring breathing vibration is revealed at 1002 cm^{-1}. Comparing the three curves, untreated substrate (a) has minimal peaks, substrate (b) has additional peaks at 1098, 920 and 854 cm^{-1}, which contribute to –C(O)N<, Si–O–Si stretching vibration and Si–O cross-linking ring breathing vibration. Curve (c) is similar in shape with (b) except its peak intensity is stronger. Unfortunately, hydroxyl group (–OH) and mercapto group (–SH) are invisible in (b) and (c), respectively. Raman spectra of copper plating fabric (Sample 2) are shown in Fig. 3(d), all the peaks for organic groups in Fig. 3(c) are covered, which indicate a compact metal coating.

3.5. XRD analysis

XRD patterns for PET fabrics (Sample 2) before and after plating are shown in Fig. 4. The strong diffraction peaks at $2\theta = 17^\circ$, 22° and 25° are characteristic peaks of 3-mercaptopropyltriethoxysilane modified PET fabrics. The peaks that appeared at $2\theta = 43^\circ$, 50°, 74°, and 90° represent (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of copper, respectively. The copper oxide phase was not detected in the deposits. According to results of XPS analysis, the copper plating is composed of Cu^0; it is consistent that no peaks of other compositions can be seen in XRD patterns. Comparing XRD patterns shown in Fig. 4(a) and (b), the characteristic peak intensity of the plated PET substrate is decreased obviously. The result shows that the covering degree of copper plating is compact.

Table 2
Weight of PET fabrics.

	Before plating (g)	After plating (g)	After washing (g)	Weight loss (g)
Sample 1	4.036	5.034	4.839	0.195
Sample 2	4.042	5.453	5.438	0.015

3.6. TG analysis

To study thermal stability of PET fabrics (Sample 2) before and after plating, thermogravimetric analysis (TG) was performed under air atmosphere at heating rate of 5 °C/min. TG curve in Fig. 5(a) includes two well defined weight loss steps which are attributed to 250–430 and 440–540 °C, respectively. The first 87% weight loss of 3-mercaptopropyltriethoxysilane modified PET fabrics corresponds to its decomposition and disconnection of chain. This indicates that decomposition reaction of PET fabrics starts from 250 °C, and with temperature increasing, decomposition is gradually translated to ruleless disconnection of chain, ending at 430 °C. The second weight loss in the range of 440–540 °C is probably due to volatilization of organic fraction, mainly in form of CO, CO_2 and other gases. At 540 °C, the remainder of the

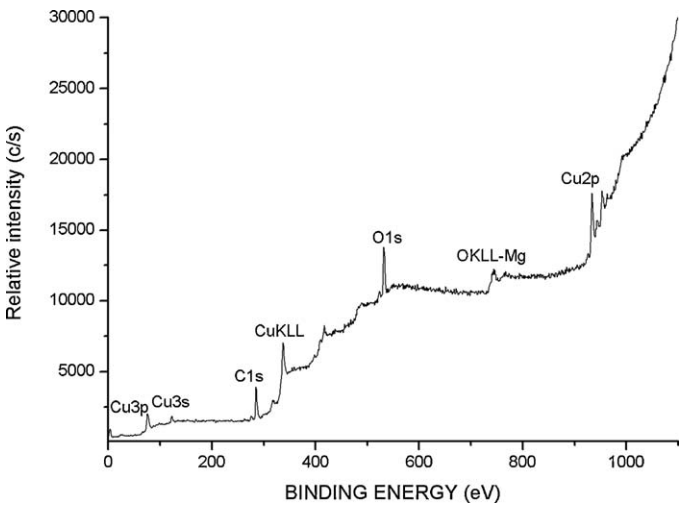

Fig. 2. XPS spectra of copper plating on modified PET fabric (Sample 2).

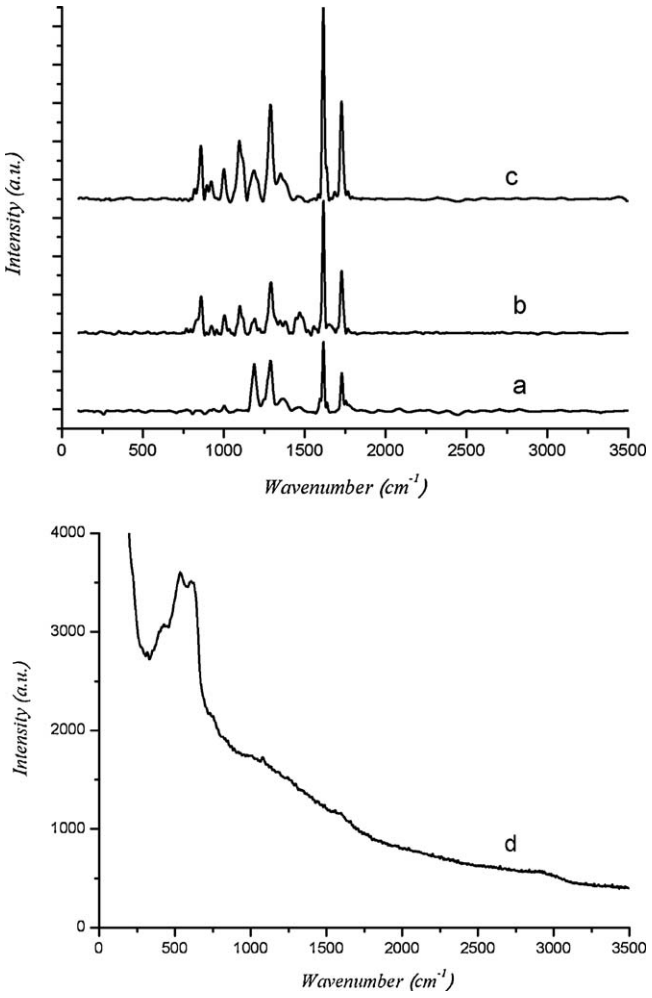

Fig. 3. Raman spectrum of PET fabrics (a) untreated, (b) (3-aminopropyl) trimethoxysilane treated and UV irradiated, (c) 3-mercaptopropyltriethoxysilane modified and (d) after copper plating and ultrasonic washing (Sample 2).

contents is less than 0.5%. The result illuminates that the decomposition of PET fabrics before plating is much complete. In Fig. 5(b), there are also two weight loss steps as shown in Fig. 5(a). It is the reason that copper plating cannot volatilize

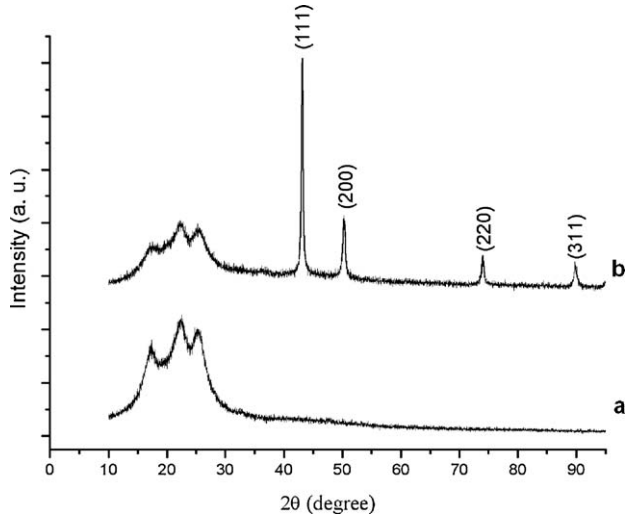

Fig. 4. XRD spectra of PET fabrics (a) 3-mercaptopropyltriethoxysilane modified and (b) after copper plating and ultrasonic washing (Sample 2).

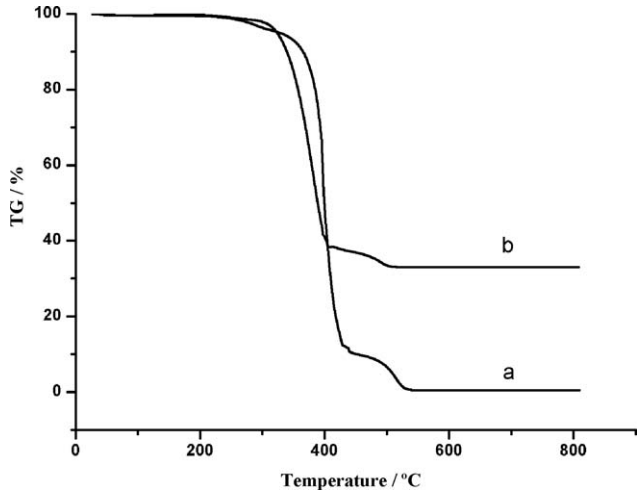

Fig. 5. TG curves of PET fabrics (a) 3-mercaptopropyltriethoxysilane modified and (b) after copper plating and ultrasonic washing (Sample 2).

during the temperature range. As shown in Fig. 5(b), the remainder contents is more than 33% at 500 °C, so it can be deduced that the weight contents of copper plating reaches about 26% in the plated PET fabric, since copper plating is oxidized at high-temperature under air atmosphere, the result is coincident with the data shown in Table 2.

3.7. Surface resistance and shielding effectiveness

According to Table 2, after electroless plating, the copper weight on the fabric is 19.96 g/m^2 for Sample 1, and 28.22 g/m^2 for Sample 2. As we know, the surface resistance of copper-coated fabrics is related to the weight of copper coating on the fabrics. So the surface resistance for these two samples is 0.14 and 0.06 Ω/□, respectively, as showing in Table 3.

After ultrasonic washing in water, Sample 1 changed into dielectric, while Sample 2 remained excellent electric conductivity. According to the Schelkunoff theory [17], better conductivity of the fabrics leads to higher shielding effectiveness (SE). The SE of Sample 2 was more than 54 dB (SE > 99.999%) at frequency ranging from 0.01 MHz to 18 GHz (Fig. 6). The result shows that the plated PET fabric has good shielding effectiveness and can be used in some special application, such as advanced electronic products and national defense field.

From the morphological, mechanical and electrical properties of the copper coating on PET fabrics, it can be concluded that silane modification is an efficient way to promote these qualities. PET fabrics cannot be directly modified by 3-mercaptopropyltriethoxysilane in this experiment. Similar compounds, e.g. mercaptopropyltrimethoxysilane, can react with the hydroxyl (–OH) groups on the surface of the glass slides [18]. And hydroxyl (–OH) groups can be linked to the surface of PET substrate by treating with (3-aminopropyl)trimethoxysilane and UV irradiation[19]. After silane modification, mercapto (–SH) groups are covered on the surface of PET fabrics. The existence of Si and S atoms on the fabrics was proved by the EDX analysis (Fig. 7). It is known that mercapto groups can absorb metal particles in solution, and form sulfur-metal bonds which enhance the adhesive power between the

Table 3
Surface resistance of copper coating PET fabrics.

	After plating (Ω/□)	After washing (Ω/□)
Sample 1	0.14	Dielectric
Sample 2	0.06	0.06

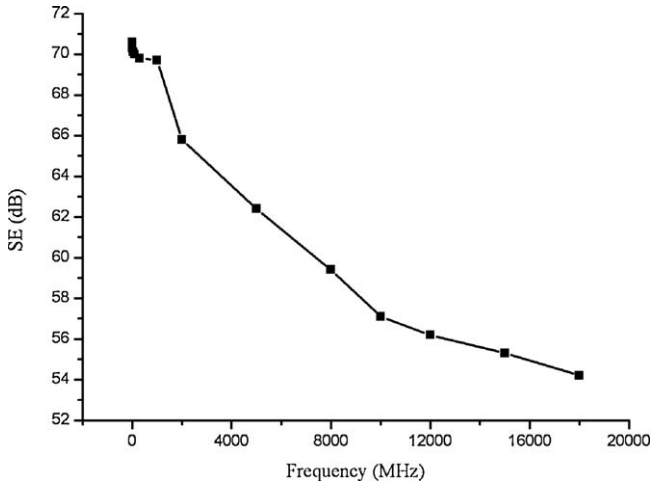

Fig. 6. Shielding effectiveness of copper plating PET fabric after ultrasonic washing (Sample 2).

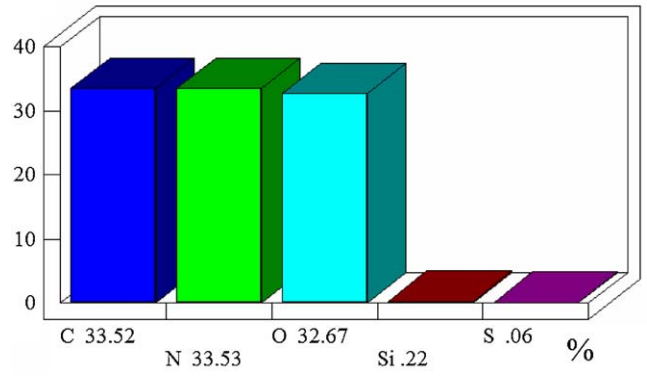

Fig. 7. EDX analysis of silane modified PET fabrics (mean value: atomic %).

metal layer and substrate [18]. The theory was applied to this work, and excellent copper coating layer was obtained.

4. Conclusions

Copper coating with good adherence stability and high electric conductivity was successfully fabricated on 3-mercaptopropyltriethoxysilane modified PET fabrics by electroless plating technique. EDX and XPS spectra show that the coating is composed of Cu^0. Compared with the substrate before plating, the peak intensity of the plated PET fabric in XRD decreases obviously; Raman spectra indicate that PET substrate has been modified by substituted silanes before plating; and peaks for modified substrate are disappeared after plating, which confirms that the copper coating is compact. TG curves of PET fabrics before and after plating present two weight loss steps, which are distributed in 250–430 and 440–540 °C, respectively. Contrasted with the 3-mercaptopropyltriethoxysilane modified copper plating fabrics, copper coating without modification loses weight greatly during the ultrasonic washing process, which leads to the metallic fabric changing from conductor to dielectric. As the copper weight on the modified fabric is 28 g/m^2, the SE of copper-coated fabrics is more than 54 dB at frequency ranging from 0.01 MHz to 18 GHz.

Acknowledgements

This work was supported by National Natural Science Foundation of China (no. 60701014) and Shanghai Leading Academic Discipline Project (no. B113).

References

[1] J. Voyer, P. Schulz, M. Schreiber, Electrically conductive flame sprayed aluminum coatings on textile substrates, J. Therm. Spray Techn. 17 (5–6) (2008) 818–823.
[2] H.C. Chen, K.C. Lee, J.H. Lin, M. Koch, Comparison of electromagnetic shielding effectiveness properties of diverse conductive textiles via various measurement techniques, J. Mater. Process. Tech. 192 (2007) 549–554 (Sp. Iss. SI).
[3] H.B. Wang, J.Y. Wang, J.H. Hong, Q.F. Wei, W.D. Gao, Z.F. Zhu, Preparation and characterization of silver nanocomposite textile, J. Coat. Technol. Res. 4 (1) (2007) 101–106.
[4] S.Q. Jiang, C.W. Kan, C.W.M. Yuen, W.K. Wong, Electroless nickel plating of polyester fiber, J. Appl. Polym. Sci. 108 (4) (2008) 2630–2637.
[5] J. Scholz, G. Nocke, F. Hollstein, A. Weissbach, Investigations on fabrics coated with precious metals using the magnetron sputter technique with regard to their anti-microbial properties, Surf. Coat. Tech. 192 (2–3) (2005) 252–256.
[6] A.L.M. Reddy, F.E. Amitha, I. Jafri, S. Ramaprabhu, Asymmetric flexible supercapacitor stack, Nanoscale Res. Lett. 3 (4) (2008) 145–151.
[7] J.R. Rohan, G. O'Riordan, J. Boardman, Selective electroless nickel deposition on copper as a final barrier/bonding layer material for microelectronics applications, Appl. Surf. Sci. 185 (3–4) (2002) 289–297.
[8] R. Haug, U. Behner, C.P. Czaya, H.Q. Jiang, S. Kotthaus, R. Schuetz, C.P.O. Treutler, Low-cost direct chip attach: comparison of SMD compatible FC soldering with anisotropically conductive adhesive FC bonding, IEEE Trans. Electron. Pack. 23 (1) (2000) 12–18.
[9] J.E. Gray-Munro, B. Luan, L. Huntington, The influence of surface microchemistry in protective film formation on multi-phase magnesium alloys, Appl. Surf. Sci. 254 (9) (2008) 2871–2877.
[10] T. Osaka, M. Yoshino, New formation process of plating thin films on several substrates by means of self-assembled monolayer (SAM) process, Electrochim. Acta 53 (2) (2007) 271–277.
[11] V. Tsakova, How to affect number, size, and location of metal particles deposited in conducting polymer layers, J. Solid State Electr. 12 (11) (2008) 1421–1434.
[12] J.C. Bradley, J. Crawford, K. Ernazarova, M. McGee, S.G. Stephens, Wire formation on circuit boards using spatially coupled bipolar electrochemistry, Adv. Mater. 9 (15) (1997) 1168–1171.
[13] R.R. Pauliukaite, G. Stalnionis, Z. Jusys, A. Vaskelis, Effect of Cu(II) ligands on electroless copper deposition rate in formaldehyde solutions: an EQCM study, J. Appl. Electrochem. 36 (11) (2006) 1261–1269.
[14] R.H. Guo, S.Q. Jiang, C.W.M. Yuen, M. Ng, An alternative process for electroless copper plating on polyester fabric, J. Mater. Sci.: Mater. Elect. 20 (1) (2009) 33–38.
[15] M. Chedid, I. Belov, P. Leisner, Experimental analysis and modelling of textile transmission line for wearable applications, Int. J. Colth. Sci. Technol. 19 (1–2) (2007) 59–71.
[16] K. Viswanathan, H. Ozhalici, C.L. Elkins, C. Heisey, T.C. Ward, T.E. Long, Multiple hydrogen bonding for reversible polymer surface adhesion, Langmuir 22 (3) (2006) 1099–1105.
[17] K. Bernhard, Principles of Electromagnetic Compatibility, Artech House, Dedham, MA, 1979.
[18] Z.-C. Liu, Q.-G. He, P.-F. Xiao, B. Liang, J.-X. Tan, N.-Y. He, Z.-H. Lu, Self-assembly monolayer of mercaptopropyltrimethoxysilane for electroless deposition of Ag, Mater. Chem. Phys. 82 (2003) 301–305.
[19] J. Xiang, P. Zhu, Y. Masuda, K. Koumoto, Fabrication of self-assembled monolayers (SAMs) and inorganic micropattern on flexible polymer substrate, Langmuir 20 (2004) 3278–3283.