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Effects of plasma pre-treatment on surface properties of fabric sputtered with copper

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Abstract

Purpose – In this study, the polyester fabrics were treated with low temperature plasma before Cu sputtering. The effect of oxygen gas plasma pre-treatment on the surface structures, electrical properties, and mechanical properties of samples was investigated. The paper aims to discuss these issues.

Design/methodology/approach – A laboratory direct current (DC) magnetron sputter coating system was used to deposit the nanoscale copper (Cu) films onto the surface of polyester plain fabric at room temperature.

Findings – The crystal structure of the sputtered copper films did not show any obvious change on the O_2-plasma-treated fabric, but the surface roughness and surface particle size increased significantly. Improvement in electrical properties of copper films was closely related to the deposition time. The tensile test results indicated that the mechanical properties of the plasma-treated polyester fabrics were also improved after copper coating.

Originality/value – The research reports on the functional textiles, and the experiment results and analysis are original. There is a great potential to commercialize such functional textiles.

Keywords DC magnetron sputtering, Copper film, Electrical, Oxygen gas plasma, Tensile

Paper type Research paper

1. Introduction

Nanoscale copper thin film is an ideal functional material with high conductivity and good resistance to electromigration, which can be used in advanced electronic devices. Recently, various techniques have been employed to prepare nanoscale copper films,

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including chemical vapor deposition (CVD), physical vapor deposition (PVD), sol-gel process, pulsed laser deposition, and magnetron sputtering (Purica *et al.*, 2002; Khranovskyy *et al.*, 2009; Myong and Lim, 2003; Martinez *et al.*, 1997; Sakai *et al.*, 2008; Richter *et al.*, 2009; Valle *et al.*, 2004; Ali *et al.*, 2006). Among these techniques, magnetron sputtering has attracted a great deal of interest because of simple and clean process (Sakai *et al.*, 2008). Moreover, plasma treatment techniques are usually considered environmentally friendly processes which can be used to modify material surface in order to offer better adhesion between the substrate and thin films.

Therefore, this paper studied the effect of low temperature O_2 plasma pre-treatment on the structural, electrical characteristics of copper films prepared at different sputtering time, as well as the effects on the tensile properties of the fabrics. The electrical stability of the fabrics sputtered with copper films was also discussed.

2. Experimental

2.1 Preparation of materials

100 percent white polyester plain fabric of 75 g/m^2 with warp and weft yarn density of 16 tex × 16 tex was used. The fabric was first immersed in acetone solution for 30 min with ultrasonic washer to remove any oil or impurities that might be scattered on the fabric surface randomly during the manufacturing processes. Then they were washed twice with deionised water and dried at 50°C in a drying oven. The dried samples were cut into a size of 20 × 20 cm^2 for sputter coating.

2.2 Plasma pre-treatment

Plasma pre-treatments of polyester fabrics were carried out by low temperature plasma apparatus HD-1A manufactured by Zhongke Changtai Plasma Technology Co., Ltd (Changzhou, China), which is a radio-frequency (13.56 MHz) etching system. Oxygen was used for the treatment at the flow rate of 0.3 LPM (litre per minute) with a power of 70 W. Each sample was treated at 30 Pa for 3 min.

2.3 Sputter coating

A laboratory direct current (DC) magnetron sputter coating system JZCK-420B (Shenyang, China) was used to deposit copper thin films. A high purity copper (Cu) target (99.999 percent) with a diameter of 10 cm was mounted on the cathode, and the fabric sample was placed on an anode with one side facing the target. The distance between the target and the fabric sample was 60 mm. Argon (99.99 percent) was used as the bombardment gas. Prior to the deposition, the target was discharged in argon gas for about 5 min to remove impurities on its surface and sputtering chamber was pumped to achieve a base pressure of 5.0×10^{-4} Pa. To avoid the deformation of the fabric sample caused by high temperature, water-cooling was used to control the temperature of the fabric sample during the sputtering process. Meanwhile, the sample holder was rotating at a speed of 100 rpm to ensure copper particles uniformly deposited on the fabric sample. According to previous experimental analysis, the sputtering pressure was set at 0.2 Pa with the power of 120 W. The coating time was set at 5, 10 and 15 min, respectively, in this study.

2.4 Characterization

The surface morphology of the untreated and O_2-plasma-treated substrates was observed under a scanning electron microscopy (SEM; HITACHI SU1510 (Japan)) at a magnification of 4,000 × to reveal the surface features. All the samples were coated with gold prior to SEM testing.

The sputtered Cu film on the untreated (as-deposited) and plasma pre-treated polyester fibers (plasma treated) were analyzed using the atomic force microscopy (AFM; Model: CSPM 4000 from Benyuan Co., Ltd (Guangzhou, China)) in contact mode. The surface scan of 5 μm × 5 μm was carried out for the surface analysis and the scanning frequency was adjusted to 1.2 Hz. All samples were scanned at room temperature.

The crystalline phase of copper films was examined by X-ray diffraction patterns (XRD; Model Y500 from Dandong Co. Ltd) with Cu-K radiation.

2.5 Electrical and mechanical properties

The electrical properties of copper films were characterized by resistivity analysis, which was measured by SZT-2A four-point probe tester made by Tongchuang Technology Co., Ltd (Suzhou, China). In order to minimize the deviations brought by the unevenness of the fabric sample surface, the resistivity of each sample was measured ten times, and then the average values were used.

Tensile properties of fabrics were measured on a HD 026NS type fabric electronic tensile strength tester (Hongda Textile Instrument, Nantong, China). The sample size was $20 \times 20\ cm^2$ and they were fixed in a holder with the distance of 100 mm, the speed of stretching tension was set at 100 mm/min. The warp and weft of samples were measured ten times, respectively, and the average values were used. The tensile strength and elongation at break were measured and compared.

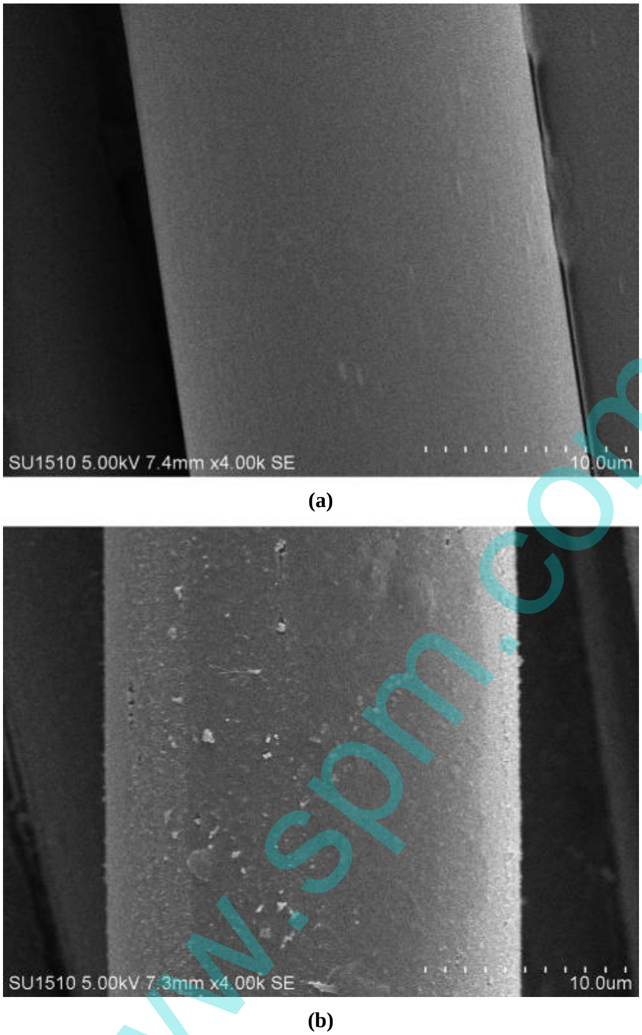
3. Results and discussion

3.1 Surface morphology

The SEM images clearly reveal the effect of the plasma pre-treatment on the surface morphology, as shown in Figure 1. It can be observed from the SEM images that the untreated polyester fiber had smooth surface free from damages. On the other hand, some visible pitting aggregate structures formed on the O_2-plasma-treated polyester fiber surface. The pitting of O_2-plasma-treated fiber surface can be attributed to the etching effect caused by the bombardment of the oxygen plasma species on the fiber surface. As a result, the surface of fiber became rougher.

The AFM images illustrate the surface structures of the polyester fibers sputtered with Cu for different deposition time with or without plasma pre-treatment. These images show that sputtering time had a significant influence on the morphology and microstructure of the sputtered copper films on the fiber surfaces. The surface grain size increased significantly as sputtering time increased from 5 to 15 min, as presented in Table I. A longer sputtering time provided surface adatoms with higher mobility to diffuse, thus increasing the surface grain size of the sputtered film on the fibers (Li *et al.*, 2009; Kim *et al.*, 2006).

Figure 2(d)-(f) shows the surface features of the fibers which were pre-treated with O_2 plasma and then deposited with Cu for different sputtering times. Compared to those in Figure 2(a)-(c), the surface morphology of the sputtered film on the plasma pre-treated fibers did not show obvious change. However, the calculated surface grain



Notes: (a) Untreated; (b) O_2-plasma treated

Figure 1.
SEM images of polyester fibers

Table I.
Particle size, RMS roughness of the sputtered Cu film on the untreated and plasma pre-treated polyester fibers

	Deposition time (min)	Particle size (nm)	RMS roughness (nm)
Untreated fiber	5	85.8	3.31
	10	105.2	6.97
	15	135.5	9.59
Plasma treated	5	129.4	14.6
	10	156.1	15.3
	15	162.7	18.5

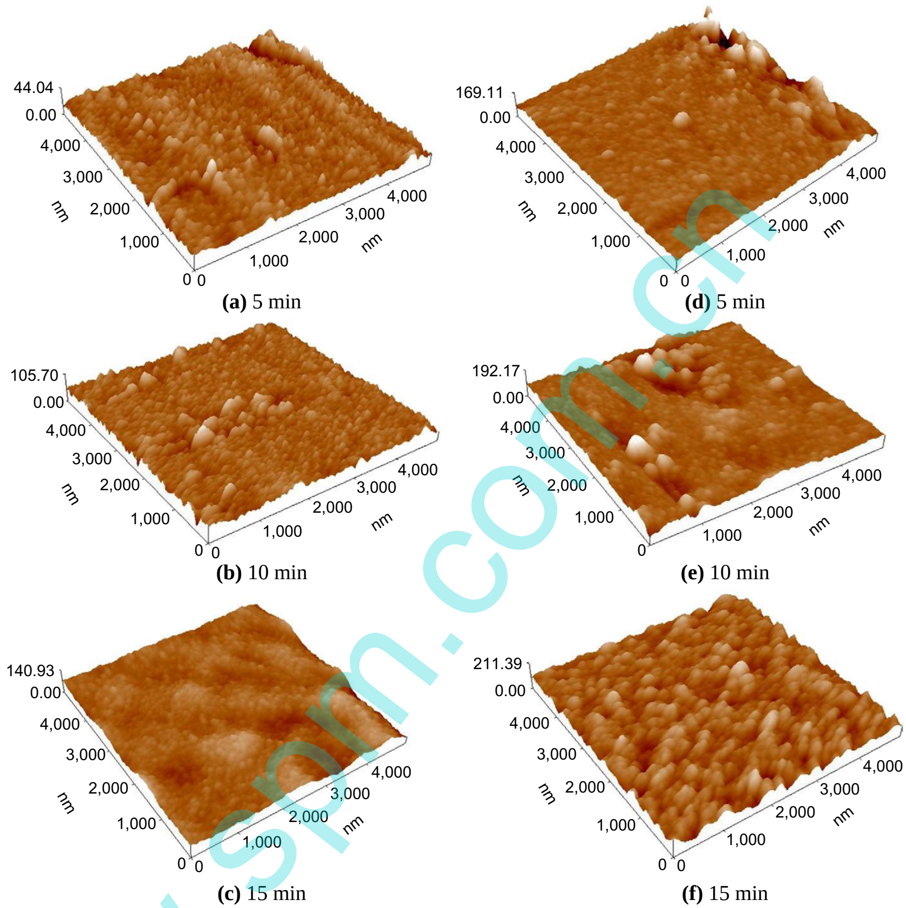


Figure 2.
AFM images of the as-deposited fiber surface: (a) 5 min coating, (b) 10 min coating, (c) 15 min coating; and plasma pre-treated: (d) 5 min coating, (e) 10 min coating, (f) 15 min coating

size of the Cu film formed on the O_2-plasma pre-treated fibers showed slight increase. This phenomenon can be attributed to the etching effect, leading to uneven growing of the deposited particles on the etched surface. The formation of activated oxygen radicals on the plasma pre-treated fiber surface contributed to the rearrangement of the sputtered Cu atoms. Therefore, the surface grain size of the Cu film formed on the plasma pre-treated fibers appeared larger than that of the untreated fibers.

It was also found the plasma pre-treatment affected the surface roughness of film deposited on the polyester fibers, as indicated in Table I. Table I shows that the root mean square (RMS) roughness of the sputtered Cu films on the untreated polyester fibers increased from 3.31 to 9.59 nm as the sputtering time increased from 5 to 15 min. The rougher film was attributed to growth of the deposited particles due to the longer sputtering time, as shown in Figure 2(a)-(c). The O_2 plasma pre-treatment obviously modified the surface of the fibers as revealed in Figure 1, which also contributed to the increase in surface roughness of the sputtered Cu fibers, as shown in Table I.

The surface roughness of the sputtered Cu films on the plasma pre-treated polyester fibers increased from 14.6 to 18.5 nm as the sputtering time increased from 5 to 15 min.

3.2 XRD analysis

Figure 3 shows the XRD spectra of the sputtered Cu film on the untreated and plasma pre-treated polyester fibers. The XRD spectra indicate that (111) was the predominant orientation of the Cu thin film at a diffraction angle (2θ) near 43°. For the deposited film on untreated polyester fibers, the (111) peak position slightly shifted toward the higher diffraction angle compared to the sputtered Cu film on the plasma pre-treated polyester fibers. The decreased 2θ value was attributed to oxygen atoms diffusing into the copper films. The crystallinity of copper films was not influenced by plasma pre-treatment, which was explained that the relaxation of the residual strain occurred in the film when the sputtering process was completed.

3.3 Electrical properties

The electrical properties of Cu sputtered polyester fabrics were also investigated. The resistivities of the fabrics sputtered with Cu without plasma pre-treatment and with plasma pre-treatment plotted against the sputtering time is shown in Figure 4. It is clearly revealed that the increase in sputtering time resulted in obvious decrease in resistance. The resistance was 25.3, 16.5 and 13.9Ωcm as the sputtering time changed

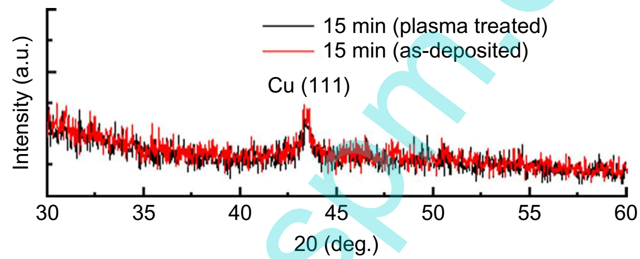


Figure 3.
XRD spectra of the as-deposited (red line) and the oxygen plasma pre-treated (black line)

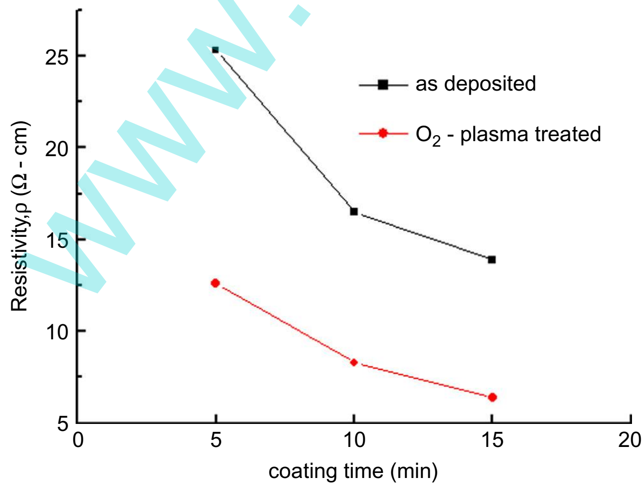


Figure 4.
Effect of sputtering time on the electrical resistance

from 5 up to 15 min. This phenomenon can be attributed to the growth of the deposited film on the fiber surfaces (Harper *et al.*, 1999). The growth of grain sizes with sputtering time led to reduction in grain boundary scattering due to charge carriers, thus increased the mobility for the obtained films (Lee *et al.*, 2004), and eventually reduced the film resistivity (Harper *et al.*, 1999). The resistivities of all the samples with plasma treatment was below 13 Ωcm, indicating the improved conductivity of the plasma pre-treat fabrics. It is believed that plasma pre-treatment improved the adhesion of the sputtered Cu particles to the fiber substrate, thus led to the better conductivity.

The conductive stability of the copper films was also investigated by measuring the resistivity of film exposed in air for different times. It is clearly revealed that the resistance was gradually increased as the exposure time extended. This was attributed to the oxidation effect of the sputtered film when it was exposed to air. It is also found that films deposited on the plasma pre-treated fabrics showed smaller increase in resistance compared to the film deposited on the untreated fabrics when exposed to air, as shown in Figure 5. Plasma pre-treatment improved the growth of the sputtered Cu particles on the fiber surfaces, which led to the formation of larger grain clusters on the fibers, as presented in Table I. Larger grain sizes on the plasma pre-treated fabrics provided less surface area when it exposed to air, leading to the reduced oxidation effect (Oh *et al.*, 2007).

3.4 Tensile properties

The results of tensile tests are listed in Table II. It can be seen that the tensile strength and elongation at break for original polyester fabrics increased both in warp and weft

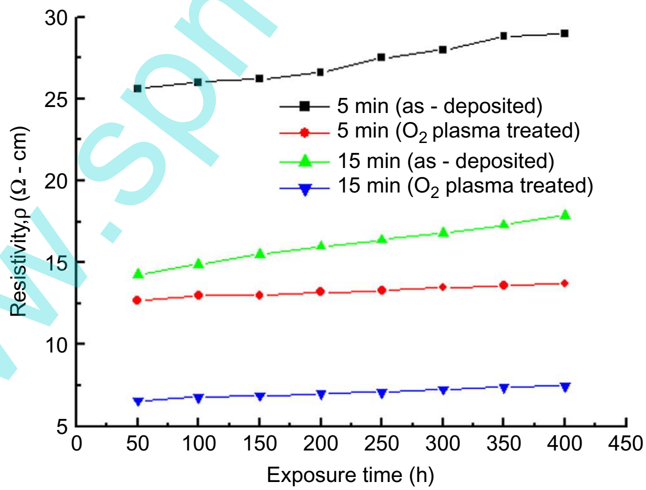


Figure 5.
Effect of exposure time on the electrical resistance

Table II.
Tensile property of the original, as-deposited and the plasma-treated polyester fabrics

	Deposition time (min)	Tensile strength (N) Warp	Tensile strength (N) Weft	Elongation at break (%) Warp	Elongation at break (%) Weft
Original	0	152.4	133.2	20.1	19.3
As-deposited	15	160.2	135.8	21.4	19.5
Plasma treated	15	163.8	136.6	22	19.8

directions after copper deposition. The tensile strength of 15 min copper-coated polyester fabric was significantly larger than that of original sample in warp and weft direction. However, there was only a slight increase in elongation at break for 15 min copper-coated polyester fabrics. The reason was that copper particles deposited on the fabrics also required some force, which led to the increase in breaking strength and elongation at break when the fabrics are stretched by an external force.

The effect of O_2-plasma pre-treatment on the tensile strength and elongation at break for copper-coated polyester fabrics is also shown in Table II. Table II indicates that there was a slight increase in tensile strength and the elongation at break. The plasma treatment improved the adhesion between the sputtered film and the fibers, which contributed to the increase in tensile strength and the elongation at break. Moreover, the increased surface roughness of the plasma-treated fibers also contributed to the increase in tensile strength and the elongation at break due to the increased fiber friction.

4. Conclusions

This study demonstrated the effects of O_2 plasma pre-treatment on properties of the copper films deposited by DC magnetron sputtering on polyester fabric with different sputtering times. The O_2 plasma pre-treatment did not significantly change the crystallinity of the deposited copper films, but increased its surface roughness and surface grain size. The O_2 plasma pre-treatment improved the adhesion between the sputtered film and the fiber surface, leading to the improved surface conductivity. It was found that the O_2 plasma pre-treatment reduced the aging effect. The copper-coated polyester fabrics are promising materials for anti-static, electromagnetic shielding and other applications.

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