Comparative Studies of Polypropylene Nonwoven Sputtered with ITO and AZO

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ABSTRACT: In this study, the polypropylene (PP) spunbonded nonwoven materials were used as substrates for depositing transparent nanostructures on the fiber surfaces. Magnetron sputter coating technique was used to deposit tin-doped indium oxide (ITO) and aluminum-doped zinc oxide (AZO) films onto the nonwoven substrates. The structures and properties of the deposited ITO and AZO films were investigated and compared using atomic force microscopy, energy-dispersive X-ray (EDX), and electrical and optical tests. The observations by atomic force microscopy revealed the formation of functional nanostructures on the fiber surfaces. EDX analyses confirmed the deposition of ITO and AZO functional films on the PP fibers. It was found that ITO had more compact structures on the fiber surface than AZO under the same sputtering conditions. The transmittance analysis revealed that the nonwoven substrates deposited with nanostructural AZO showed better ultraviolet shielding effect than those coated with ITO in the same thickness. The nonwoven materials coated with ITO had lower electrical resistance than those coated with AZO in the same thickness. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1813–1819, 2009

Key words: coatings; fibers; surfaces; thin films; nanotechnology

INTRODUCTION

Textile industries have been shifting their manufacturing capacities from commodity textiles to technical products. Various forms of new innovative products have been developed to meet the expanding demand for different applications.[1]

For a wide range of applications, it is desirable to produce such textile materials with special surface structures and properties. Textile materials with specific surface structures and properties are also of importance in many technical applications as the surface structures and properties affect abrasion, friction, adhesion, adsorption, and biocompatibility of the materials. However, the surfaces of textile materials are not often ideal for a particular application. Various physical and chemical techniques have been used to modify the surface properties of textile materials.[2,3]

In all of these techniques used, physical treatments have attracted a great deal of attention in recent years because of the environmentally friendly technology. Among them, sputter coating has proven to be one of the most promising techniques for the surface functionalization of textile materials. Sputtering uses a mechanism with a sealing chamber, in which atoms or molecules are ejected from the surface of a target material as a result of collision with high-energy ions. These ejected atoms or molecules have certain kinetic energy and orientation which cause them to condense on the substrate and then form a thin film. Magnetron sputter coating offers advantages such as uniform and compact, stronger bonding between coating and its substrate and environmentally friendly.[4]

Sputter coating has been applied to deposit various functional materials on different substrates.[5–7] Transparent conducting oxides (TCO) produced by sputter coating have also attracted a lot of attention in recent years because they combine attractive properties of high visible transparency with electrical conductivity.[8] Semiconducting transparent thin films have been increasingly used in many industries because of their wide range of applications. Commonly used semiconducting metal oxide thin films include aluminum-doped zinc oxide (AZO)

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and doped indium oxide (ITO) films.[9] In this work, AZO and ITO films were deposited onto the polypropylene (PP) nonwovens by magnetron sputter coating. The surface structures of the deposited AZO and ITO films were investigated and compared using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. The optical transmittance and electrical properties of the TCO-deposited fabrics were also examined by a ultraviolet/visible (UV/Vis) spectrophotometer and four-probe meter.

EXPERIMENTAL

Materials

The spun-bonded PP nonwovens with an area mass of 50 g/m^2 was used in this study. The samples cut from the PP nonwovens were first immersed into acetone solution for 30 min to remove the organic solvent and particles attached to the material. The samples were then further rinsed with deionized water twice and dried at the temperature of 40°C in an oven. The dried samples were used for the deposition of the functional films by sputtering.

Sputter coating

A magnetron sputtering system JZCK-420B was used for the functional coatings. The ITO target had a composition of 97 wt % In_2O_3 and 3 wt % SnO_2, and AZO target had a composition of 97 wt % ZnO and 3 wt % Al_2O_3. Pure argon (99.999%) (Ar) was used as sputtering gas. The target used was mounted on the cathode. The PP spunbonded nonwoven samples were fixed on the sample holder with a distance of 150 mm between the target and the substrate. A base pressure of 5×10^{-4} Pa was used before introducing the high purity argon gas as bombardment gas. To avoid the deformation of the substrate caused by high temperature, water cooling was applied to control the temperature of the substrate during the sputtering process. During the sputtering, the substrate holder was kept rotating at a speed of 100 rpm to ensure the uniform deposition of the functional coating on the surface of the PP substrate. The thickness of the coating was monitored using a coating thickness detector (FTM-V) fixed in the sputtering chamber.

Coating was performed at a pressure of 0.5 Pa with a power of 100 W. Coating thicknesses were made for 20, 50, and 100 nm, respectively.

Comparative studies of coated fabrics

Surface morphology

Scanning probe microscope (SPM) was used to examine the surface morphology. The SPM used in this work was a CSPM4000 AFM (Benyuan, China). Scanning was carried out in the contact mode and all samples were scanned at room temperature in atmosphere. The scanning size was 1000 nm $\times$ 1000 nm, and the scanning frequency was set at 1.0 Hz.

Energy-dispersive X-ray analysis

The environmental scanning electron microscopy (ESEM) Philips XL30 integrated with a Phoenix energy-dispersive X-ray (EDX) detector was used to detect the elemental compositions of the functional nonwovens. The EDX analysis was performed at an accelerating voltage of 20 kV with accounting time of 100 s.

Optical properties

The optical properties of the functional fabrics were measured by UV/Vis spectroscopy. The UV/Vis spectroscopy used was a PerkinElmer Lambda 900. The UV/Vis absorbance spectrum, in this study, was obtained by passing different wavelengths of light ranging from 200 to 600 nm through a nonwoven sample.

Electrical conductivity

The electrical resistivity was measured using a collinear four-probe array. The apparatus used was SX1934 (Baishen Technologies, China). To minimize the deviations brought by the unevenness of textile surface, the resistivity of each sample was measured thrice, and the average values were used.

RESULTS AND DISCUSSION

Surface morphology

The surface morphology of the PP fiber in the nonwoven fabric is clearly revealed by the AFM scan, as presented in Figure 1. It is observed from the AFM scan that the uncoated PP fiber has a relatively smooth surface without any visible particles on the fiber surface. The AFM image demonstrates the periodic stripe-like structures on the fiber surface, which are believed to be formed during the quenching of PP fiber in web-forming process, leading to the orientation of the molecular chains along the fiber axis.[10]

The sputter coatings of ITO significantly alter the surface morphology of the PP fiber, as shown in Figure 2. The sputtered clusters are clearly recognized on the PP fiber surface after the coating of 20 nm ITO, but the rough surface of the strip-like structure is still visible, as indicated in Figure 2(a). The average size of the sputtered ITO clusters is about 18.4 nm analyzed by the AFM Imager

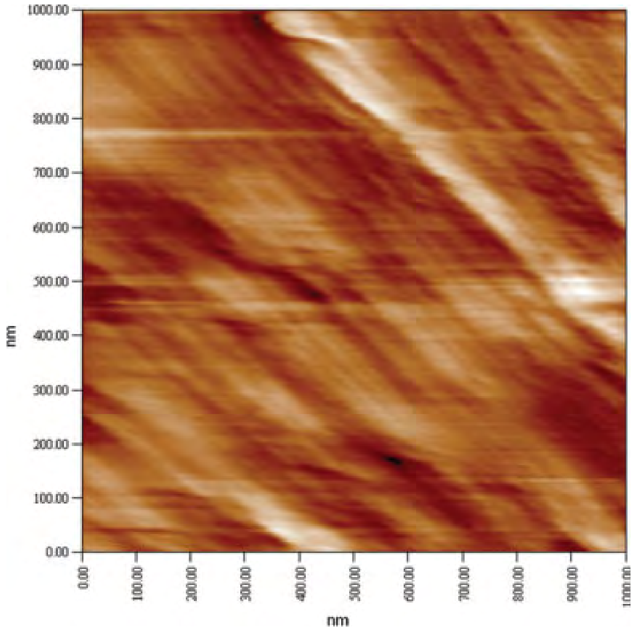

Figure 1 Surface morphology of the original PP fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Software. As the coating thickness is increased to 50 nm, the ITO clusters deposited on the PP fiber surface look compacter and the average size of the sputtered ITO clusters is also increased to about 21.3 nm, as revealed in Figure 2(b). It is clearly recognized from the AFM image in Figure 2(c) that the increased coating thickness from 50 to 100 nm leads to compact distribution of the ITO clusters on the fiber surface. The average size of the sputtered ITO clusters is further increased to 28.5 nm. The growth of the ITO clusters is attributed to the collision and aggregation of the sputtered ITO grains.

The images in Figure 3 reveal the similar phenomenon observed on the PP fibers of the nonwoven coated with AZO. The sputter coatings of AZO also obviously change the surface morphology of the PP fiber. The sputtered clusters are clearly recognized on the PP fiber surface as the coating thickness is 20 nm, but the rough surface of the strip-like structure is also visible, as shown in Figure 3(a). The average size of the sputtered AZO clusters is about 23.8 nm. As the coating thickness is increased to 50 nm, the average size of the sputtered AZO clusters is increased to about 30.2 nm and the strip-like structure is not visible any more, as revealed in Figure 3(b). The average size of the sputtered AZO clusters is further increased to 38.5 nm as the coating thickness is increased to 100 nm. The growth of the AZO clusters is also attributed to the collision and aggregation of the sputtered grains.

The AFM observations reveal that the sputtered AZO clusters form larger aggregates deposited on the PP fibers than those of ITO ones deposited under the same sputtering conditions.

EDX analysis

The surface deposition of functional ITO and AZO films on the PP fibers was confirmed by the EDX analysis, as revealed in Figure 4. The EDX spectrum in Figure 4(a) indicates the dominant composition of carbon (C), reflecting the main composition of the PP nonwoven fibers. Hydrogen (H) is too light to be detected in the EDX analysis.

The surface funtionalization of the PP nonwoven by the sputter coating of ITO is revealed in the EDX spectrum. A significant amount of indium (In) and oxygen (O) on the fiber surface after ITO sputter coating can be seen in the EDX spectrum as presented in Figure 4(b). It can also be observed from the EDX spectrum that the small amount of tin (Sn) is also presented. The amount of C becomes lower compared to that in Figure 4(a). This is attributed to coverage of the ITO nanoclusters on the PP fiber surface.

The introduction of zinc (Zn) and aluminum (Al) can be observed in Figure 4(c) after AZO sputter coating. The high amount of Zn and O in the EDX spectrum indicates the main composition of zinc oxide in the coating. The small amount of Al is also detected, as revealed in Figure 4(c). It is also observed that the amount of C is clearly reduced, which is caused by the deposition of AZO on the PP fiber surface.

Optical properties

The optical properties of the PP nonwoven coated with difference thickness of ITO and AZO films are presented in Figure 5. It shows the transmittance curves of the UV and visible light through the PP nonwoven without and with functional coatings. The original nonwoven shows the transmittance of about 60% in the wavelength range between 300 and 600 nm, indicating the good transmittance of visible light of the uncoated PP nonwoven. The transmittance drops gradually from 60% to about 35% in the wavelength range between 300 and 250 nm.

The UV/Vis spectra reveal the effect of coating thickness on the optical properties of the ITO-coated nonwovens as presented in Figure 5. It is evident that the curves of transmittance show similar pattern in the range between 250 and 600nm. The UV/Vis spectra in Figure 5 also clearly indicates that the average transmittance of the ITO-coated samples over the wavelength range between 450 and 600 nm exceeds 50%, which is very close to that of the original nonwoven, revealing the transparent property of the ITO and AZO coatings in visible light range.

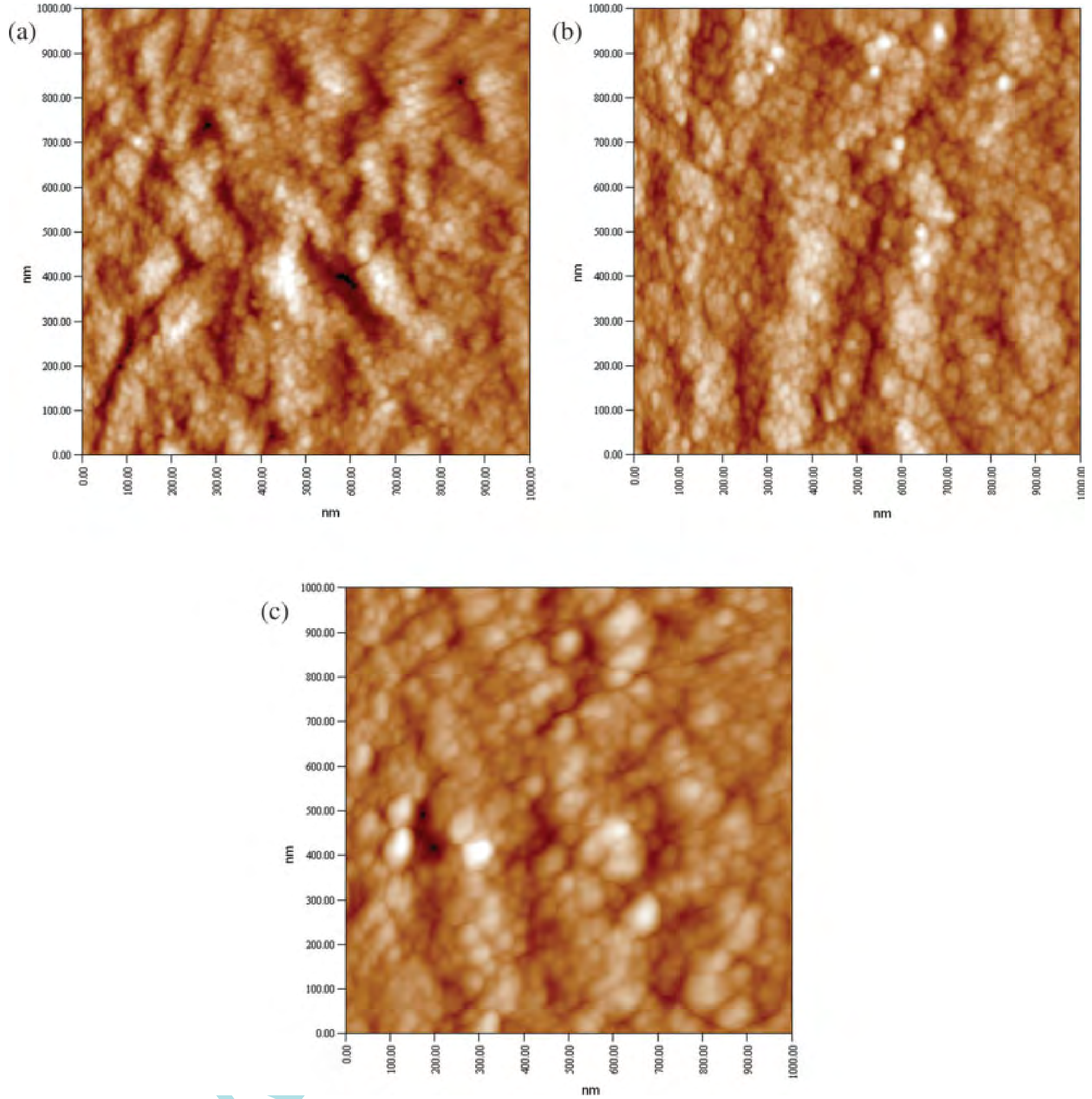

Figure 2 Surface morphology of the ITO sputter-coated PP fiber: (a) 20 nm; (b) 50 nm; (c) 100 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The shielding effect of ultraviolet (UV) from 250 to 450 nm by the ITO- and AZO-coated samples is obviously affected by the coating thickness, as indicated in Figure 5. The transmittance drops gradually from 57% to 22% in the wavelength range between 250 and 450 nm, as the ITO coating thickness is 20 nm. The transmittance changes from 55% to 16% in the range between 250 and 450 nm, as the ITO coating increased to 50 nm, indicating better UV shielding effect than the 20 nm coating. The transmittance is further lowered as the ITO coating thickness reaches 100 nm. UV shielding effect of the ITO coating is attributed to its chemical structure of the material.[11]

The transmittance of AZO-coated nonwoven is also affected by the coating thickness, as presented in Figure 5. The average transmittance of the AZO-coated samples is also over 50% in the wavelength range between 450 and 600 nm, displaying the transparency of the AZO coatings. The transmittance

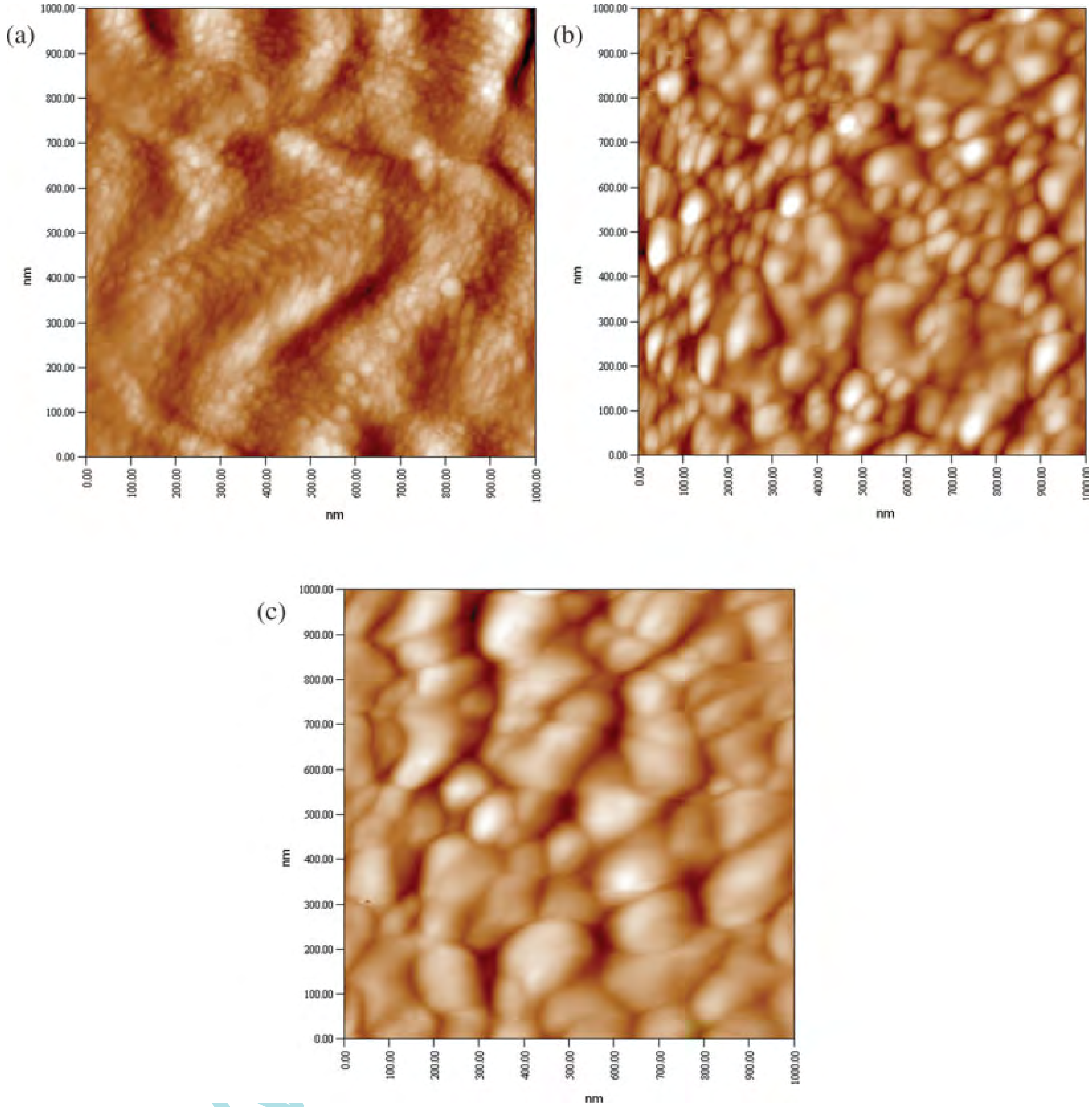

Figure 3 Surface morphology of the AZO sputter-coated PP fiber: (a) 20 nm; (b) 50 nm; (c) 100 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

changes gradually from 55% to 15% in visible light range between 250 and 450 nm, as the AZO coating thickness is 20 nm. The transmittance varies 50% and 5% in visible light range, as the ITO coating increased to 100 nm, indicating improved UV shielding effect than the 20 nm coating. The UV shielding is attributed to the characteristics of direct transition-type semiconductors, the optical bandgap of the AZO film.[12]

It looks like that the AZO coating shows a little better UV shielding effect than the ITO coating at the same thickness, as revealed in Figure 5. The increase in the grain sizes of AZO coating may contribute to the light scattering effect among crystal grains, leading to the improved better UV shielding effect of the coated nonwoven.

Electrical conductivity

The resistivity results of the nonwoven materials are listed in Table I. It reveals that the original PP nonwoven has a very high surface resistance, which is out of the range of testing equipment. The functional

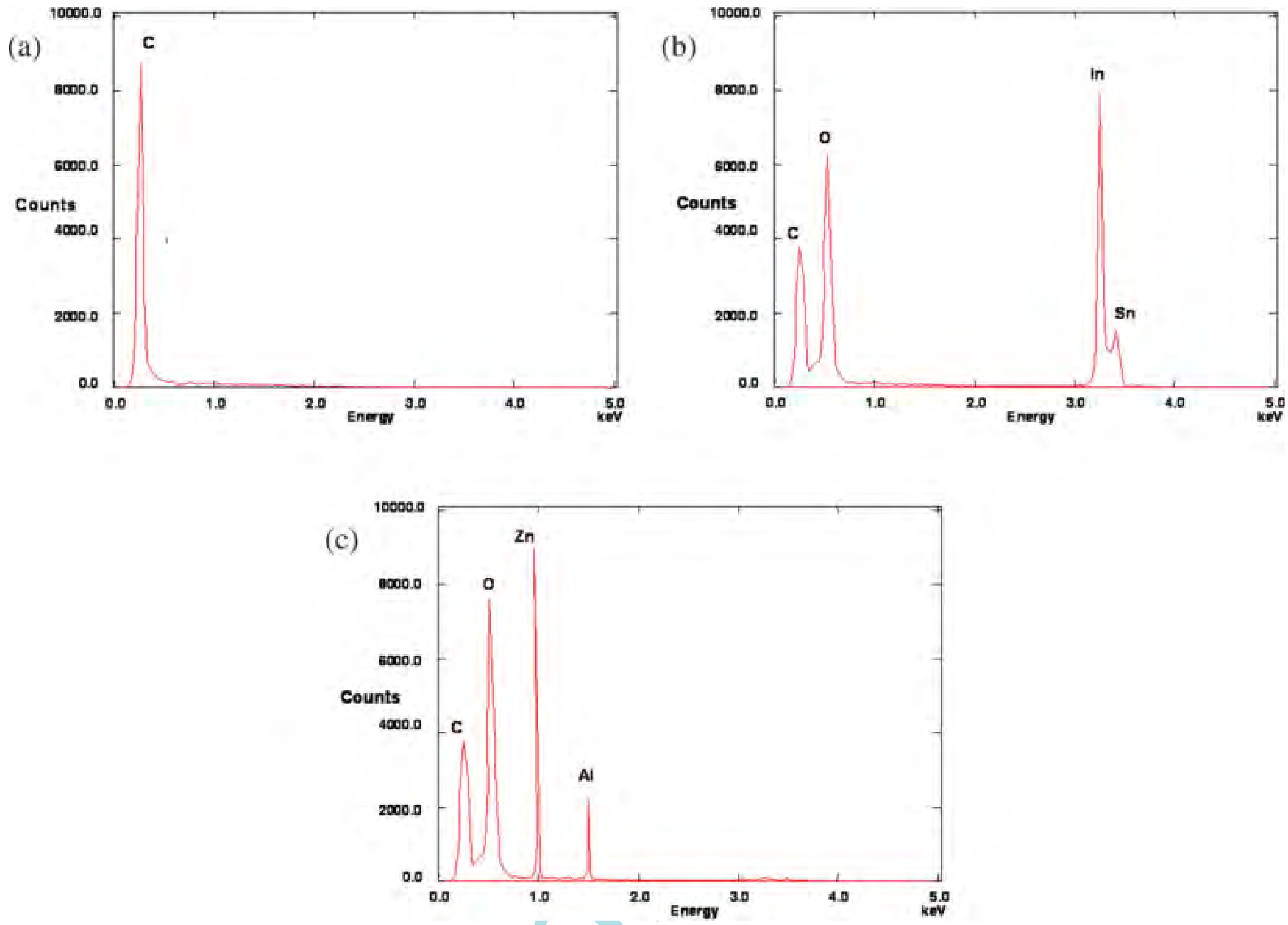

Figure 4 EDX spectra of the nonwoven material before and after sputter coating: (a) original nonwoven; (b) ITO coating; (c) AZO coating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

coatings by ITO and AZO significantly lower the surface resistance as shown in Table I. The surface resistivity of the nonwoven material is 31.06 kΩ cm, as the ITO coating thickness is 20 nm. The test results clearly indicate that the resistivity of the nonwoven material is decreased as the coating thickness is increased. The surface resistivity drops to about 4.76 kΩ cm, as the ITO coating has a thickness of 50 nm. The resistivity is further reduced to about 0.93 kΩ cm, as the coating is increased to 100 nm. As revealed in the AFM observations, the increase of the coating thickness leads to the formation of compact and improved coverage of the functional clusters on the nonwoven material, resulting in better conductivity.

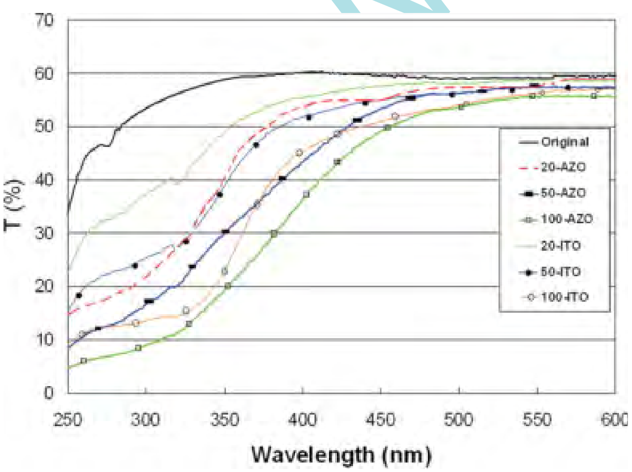

Figure 5 Optical properties of the nonwoven material before and after sputter coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Results of Resistivity Measurements

Sample	Resistivity (kΩ cm)
PP nonwoven	Out of range
ITO- 20 nm coating	31.06
ITO-50 nm coating	4.76
ITO-100 nm coating	0.93
AZO-20 nm coating	356.45
AZO-50 nm coating	167.00
AZO-100 nm coating	17.52

The surface resistivity of the nonwoven material sputtered with 20 nm AZO is about 356.45 kΩ cm. It is found that the surface resistivity drops to 167.00 and 17.52 kΩ cm, as the thickness of ITO coating is increased to 50 and 100 nm, respectively. Table I also clearly shows the better surface conductivity of the nonwoven material coated with ITO than those coated with AZO in the same coating thickness. This is attributed to the smaller sizes of the deposited ITO clusters and the compacter surface structure of ITO coating.

CONCLUSION

The structures and properties of the functional nonwovens sputter coated with ITO and AZO were investigated and compared in this work. The AFM observations revealed that the functional coatings of ITO and AZO formed nanosized clusters scattered or covered on the fiber surface subject to the deposition thickness. Sputtering thickness affected the grain sizes of the ITO and AZO clusters. As the sputtering thickness was increased, the grain sizes of the sputtered clusters were increased and the coating layer became compacter. It was found that the sputtered ITO had compacter structures on the fiber surface than the sputtered AZO under the same sputtering conditions. The functional coating with ITO and AZO significantly altered the electrical and optical properties of the nonwoven materials. It was also found that the nonwoven materials coated with ITO had lower electrical resistance than those of AZO coating for the same coating thickness. The transmittance of the materials by UV/vis analysis indicated that the nonwoven substrates deposited with nanostructural AZO showed better UV shielding effect than the ones coated with ITO. The work revealed that the textiles deposited with ITO and AZO had difference properties; therefore, the functional textiles can be made according to the needs required to better meet the use of the materials.

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