J. Coat. Technol. Res., **5** (3) 393–397, 2008
DOI 10.1007/s11998-008-9087-7

BRIEF COMMUNICATION

Physical properties of Al-doped ZnO films deposited on nonwoven substrates by radio frequence magnetron sputtering

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Abstract In this study, the polyethylene terephthalate (PET) spunbonded nonwoven materials were used as substrates for creating electro-optical functional nanostructures on the fiber surfaces. A magnetron sputter coating was used to deposit Al-doped ZnO (AZO) films onto the nonwovens. The influences of the deposition time on the structural, optical, and electrical properties of AZO films were investigated. Atomic force microscopy (AFM) was employed to examine the topography of the fibers. The AFM observation revealed a significant difference in the morphology of the fibers before and after the AZO sputter coating. The examination by UV–visible spectrophotometer analysis showed that the nonwovens deposited with transparent nanostructure AZO films had better UV absorption, and an average transmittance was approximately 50% in the visible light wavelength region. The surface conductivity of the materials was analyzed using a four-probe meter, and it was found that electrical resistance was significantly decreased as the sputtering time increased.

Keywords Nonwoven, Magnetron sputtering, Al-doped ZnO (AZO), AFM, UV–visible spectrophotometer, Four-probe meter

Introduction

The nonwoven industry has recently become one of the fastest growing industries in the world. Nonwoven materials have been increasingly used in various industries ranging from agriculture, manufacturing, defense, and many other areas due to their characteristics of abundant surface area, fibrous networks, the various sizes of pores, and the properties of flexibility and permeability, etc. The surface inertness of the polymer fibers in nonwovens, however, limits the potential use of these materials in many industries.[1,2] Researchers and engineers have tried various techniques, such as physical vapor deposition (PVD), chemical vapor deposition, pulsed laser deposition, and magnetron sputtering deposition[3–5] to modify and improve the surface properties of nonwovens and expand their applications. Magnetron sputtering deposition has been proven to be one of the most promising techniques to functionalize textile materials due to the advantages of low process temperature, complex chemical combination and multilayer functional structures, and the higher bonding strength between coating and substrate.[5]

Al-doped ZnO (AZO) thin films deposited on rigid glass substrates have been extensively studied in recent years because they combine attractive properties with high visible transparency and electrical conductivity.[6] As is well known, glass is very heavy and brittle and can be easily deformed, especially for certain applications such as smart cards and electronic maps, where flexibility and light weight materials are required.[7] Transparent conducting films deposited on flexible polymer substrates, therefore, could overcome these problems, and it is important to investigate the characteristics of oxide thin films deposited on polymer substrates such as nonwovens.

In this report, AZO thin films were deposited by radio frequence (RF) magnetron on polyethylene terephthalate (PET) spunbonded nonwoven materials. The surface morphology of the fibers was observed using atomic force microscopy (AFM) under contact mode. The optical transmittance measurements of the samples were carried out with an UV–visible spectrophotometer. The electrical properties of the samples were examined with a four-probe meter.

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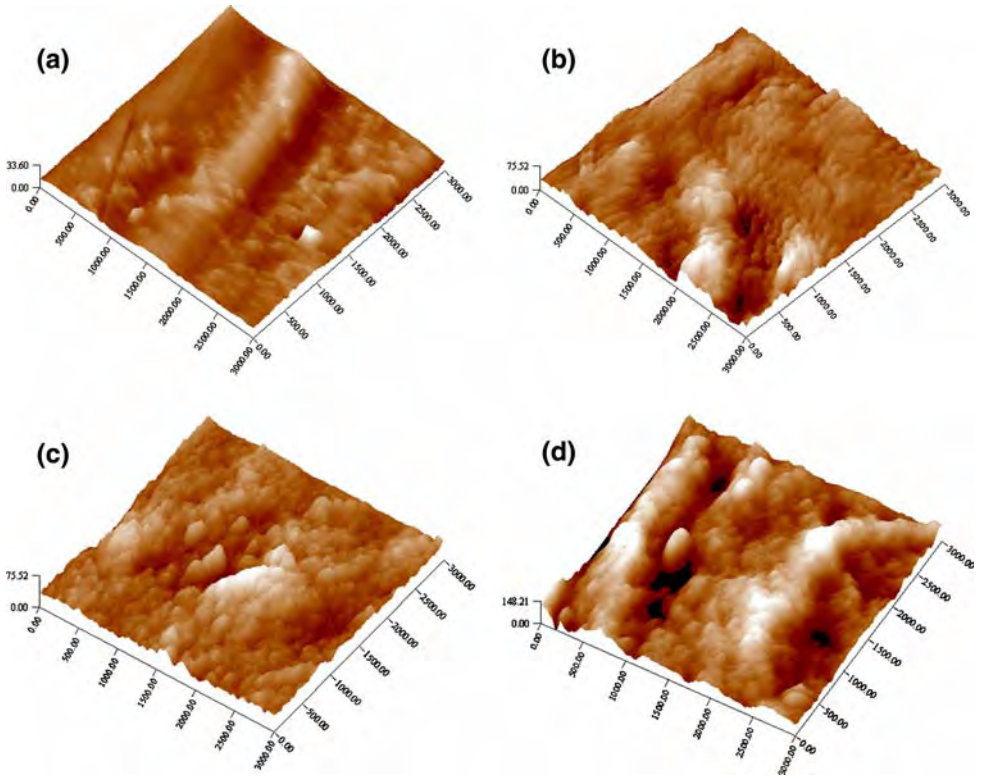

Fig. 1: AFM image of the fiber surface of original nonwoven and sputtered nonwoven (3.0 × 3.0 μm^2): (a) Original sample; (b) Sample 1; (c) Sample 2; (d) Sample 3

Experimental

Materials

Commercial PET spunbonded nonwovens with a mass per area of 60 g/m^2 were used as the substrates in this study. The nonwoven samples were ultrasonically cleaned in ethanol and distilled water before the sputter coatings were applied. The samples were dried in an oven at 40°C for 24 h after washing. The dried samples were cut into a size of 2.5 × 7.5 cm^2 for sputtering coating.

Sputter coating

The sputter coating of the functional layer was performed on a magnetron sputter coating system supplied by Shenyang Juzhi Co, Ltd., P.R. China. The target used was an AZO (97 wt% ZnO + 3 wt% Al_2O_3) target (diameter: 50 mm, thickness: 4 mm), which was mounted on the cathode. The PET spunbonded nonwoven samples were fixed on the substrate holder with a distance of 60 mm between target and substrate. The base pressure of the process chamber was pumped down to 5×10^{-4} Pa before introducing the high purity argon gas as a bombardment gas. The film thickness was measured online during the process. The sputtering was performed at room temperature.

Table 1: Sputtering parameters

Sample	Ar flow (sccm)	Pressure (Pa)	Power (w)	Time (min)	Thickness (nm)
1	20	0.5	150	30	50
2	20	0.5	150	60	80
3	20	0.5	150	90	100

The details of the sputtering conditions are listed in Table 1.

Surface characterization

AFM

The surface nanostructures were examined by a CSPM 4000 atomic force microscope (AFM) provided by Benyuan Co., Ltd. Scanning mode used in this study was contact mode AFM[8,9] using a silicon cantilever. All images were scanned under ambient conditions.

XRD

An X-ray diffraction (XRD) analysis was performed by using a Rigaku D/MAX-2550PCX diffractometer

with Cu $K\alpha$ radiation (40 kV, 300 mA) to identify the crystalline phase of AZO thin films.

Optical transmittance

The optical properties of the samples were measured using a LAMBDA 900 UV–visible spectrophotometer supplied by PerKinElmer—USA. The scan range was set between 250 and 600 nm.

Electrical resistance

The electrical properties of the samples were measured using a SX1934 four-probe meter made by Suzhou Baishen Technology Co. Ltd. The four-probe meter measured the surface resistivity of the samples.

Results and discussion

Surface morphology

An AFM image was obtained by 3.0×3.0 μm^2 scan of the fiber surface of original PET nonwoven and sputtered AZO nonwoven as shown in Fig. 1. Figure 1a shows that the surface of the original PET fiber appears to be smooth, as indicated by the typical feature of the PET fiber. Figures 1b–1d illustrate that the AZO sputter coating significantly modifies the surface characteristics of the PET fibers.

The effect of the sputtering time on the surface morphology of the coated PET fibers was revealed by AFM analysis with the condition of a constant sputtering pressure (0.5 Pa) and sputtering power (150 W). The AFM images were listed in Figs. 1b–1d, and the effect of the sputtering time can be clearly seen in the images. The film thickness was about 50 nm, and the average size of the AZO nanoclusters analyzed by AFM was about 47.1 nm after coating for 30 min. The film thickness was increased to about 80 nm, and the average grain sizes were increased to 53.1 nm after 60 min of coating. The compactness and homogeneity of the nanofilms deposited on nonwovens was improved by covering the fiber surface continuously as the film thickness increased. The average size of the sputtered AZO nanoclusters on the PET fibers was also increased to 53.1 nm as the film thickness was further increased to about 100 nm. The nanoclusters appeared to be round and more uniform shapes, and the roughness of the fiber surface was also increased as the sputter coating time was expanded to 90 min. This phenomenon can be attributed to the nucleation and island formation[6,7] on the fiber surface as AZO grains were growing. It is obvious that the increase of deposition time caused the increase of film thickness, which resulted in the formation of large AZO aggregates on the fiber surface. It clearly indicated an increase of the sizes of AZO nanoclusters with the increase of sputtering time. It can, therefore, be concluded that the sputtering time was a main factor affecting the morphology of AZO nanostructures built on the fiber surface of nonwovens under certain conditions.

Optical proprieties

The UV–visible spectra revealed the effect of sputtering time on the optical properties of the AZO coated nonwovens as presented in Fig. 2. It is evident that the curves of transmittance show a similar pattern in the range between 250 and 600 nm. The transmittance is very low, from 250 to 300 nm, indicating the shielding effect of all samples. The transmittance is gradually increased as the wavelength increases. The transmittance decreases when the sputtering time is increased from 30 to 90 min. This is attributed to the increase in the thickness of AZO nanostructure films while the sputtering time is increased. The increase in the coating thickness leads to a decrease in light scattering losses.[7] Figure 2 also shows that the average transmittance of the AZO coated samples is over 50% in the range of 450–600 nm wavelength, displaying the good characteristic of AZO coatings transparency. It is also observed that the coating thickness has an obvious effect on the transmittance of the samples in the wavelength range from 300 to 400 nm, indicating the positive ability of the AZO coatings to absorb ultraviolet light (UV). The UV absorption is attributed to the characteristics of direct transition-type semiconductors—the optical bandgap of the AZO film.[10]

Electrical proprieties

The experimental results indicated that the structures of AZO nanofilms depended largely on the parameters of sputter coatings as shown in Fig. 3. It was observed that the room temperature resistance of the sputtered

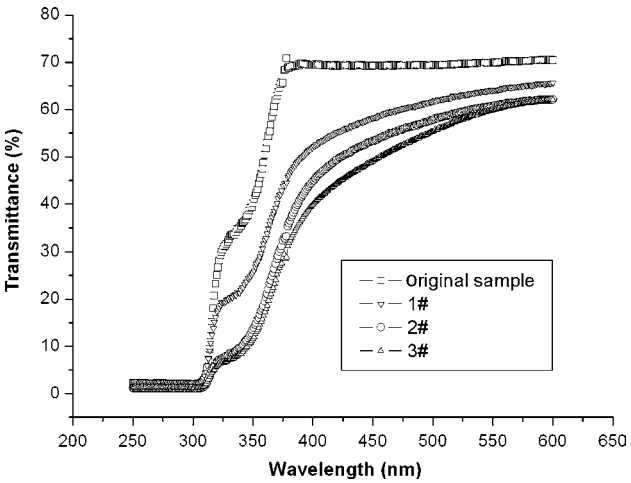

Fig. 2: Optical transmittance of original nonwoven and sputtered AZO nonwoven

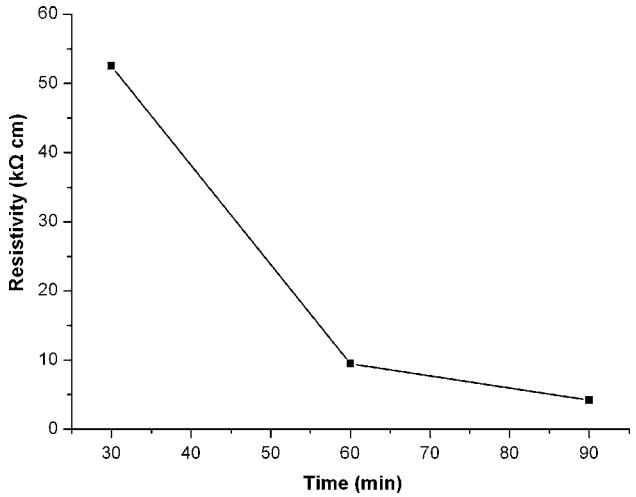

Fig. 3: Resistivity of sputtered AZO nonwoven

AZO nonwoven was gradually decreased as the sputtering time was increased. The specific electrical resistance was also decreased to 5.2×10^3 Ω cm from 50×10^3 Ω cm as the deposition time was increased from 30 to 90 min. The main reason for this was that the increase of film thickness arose from the increase of deposition time. Consequently, the compactness and homogeneity of the nanofilms deposited on nonwovens was improved by covering the fiber surface continuously as the thickness of AZO nanofilms increased. Moreover, the XRD patterns in Fig. 4 show that the preferred orientation (002) was clearly observed for all the AZO nanofilms deposited on PET nonwovens. In addition, no Zn, Al, and Al_2O_3 characteristic peaks were detected. The diffraction peak at about 34° corresponded to the diffraction from the (002) plane of the ZnO. The intensity of the (002) peak increased with the increased film thickness. It was also observed that the increase in film thickness led to improvement in the crystallization of the films,[6,7] as indicated in Figs. 4a–4c. The increase in grain sizes caused a weakening of the scattering among crystal grains, an improvement in the lifespan and mobility[10] of carriers at the same time, and the improved conductivity of the nanofilms. On the other hand, the dopant atoms (Al) were consequentially incorporated at Zn sites in the ZnO lattice for AZO films. The number of free electrons in the films increased as the film thickness increased, under the assumption that every dissolved Al atom provided one free electron. Thus, it was concluded that the film thickness was the main factor affecting the conductivity of AZO nanostructures built on nonwovens under certain conditions.

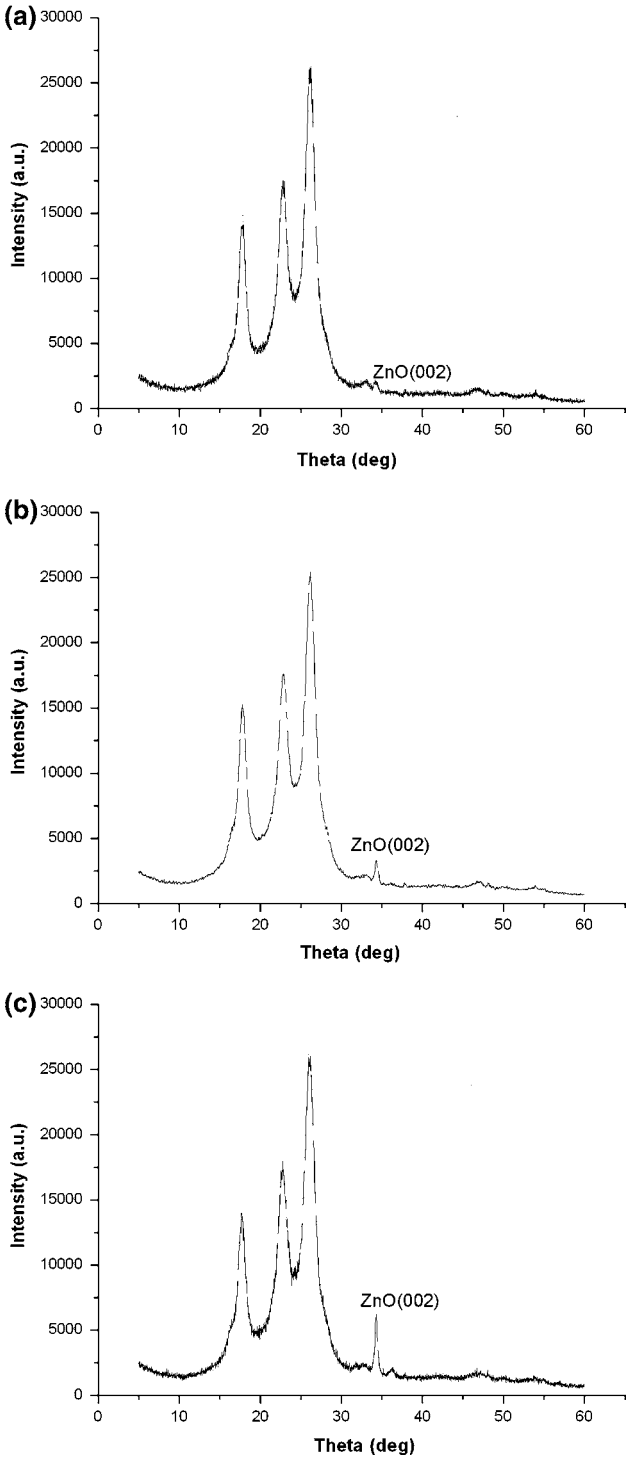

Fig. 4: X-ray diffraction patterns for sputtered AZO nonwoven: (a) Sample 1; (b) Sample 2; (c) Sample 3

Conclusion

Al-doped ZnO films were prepared by RF magnetron sputtering on PET nonwoven materials. AFM was employed to examine the topography of the fibers. The AFM results indicated a significant difference in the morphology of the fibers before and after the AZO sputter coating. The nonwovens deposited with transparent nanostructure AZO films showed high optical transmittance of approximately 50% in the visible

light wavelength range. Besides this, the nonwovens deposited with transparent nanostructure AZO films also provided better UV absorption. The room temperature resistance of sputtered AZO nonwovens gradually decreased with an increase in the sputtering time.

Acknowledgments The financial support by the Key Project of Chinese Ministry of Education (No. 106089), the Program for New Century Excellent Talents in University (NCET-06-0485), and the Open Project Program of Key Laboratory of Eco-textiles (Southern Yangtze University), Ministry of Education, P.R. China, (No. KLET0608) is gratefully acknowledged.

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