(REFEREED RESEARCH)

STRUCTURES AND PROPERTIES OF NONWOVENS DEPOSITED WITH ZnO BY DC REACTIVE SPUTTER COATING

DOĞRU AKIM REAKTİF PÜSKÜRTME KAPLAMASINDA ZNO İLE YATIRILAN DOKUSUZ YÜZEYLERİN YAPISI VE ÖZELLİKLERİ

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ABSTRACT

The ZnO (zinc oxide) functional thin films were deposited on PET (polyester) spun-bonded non-woven by DC (direct current) reactive magnetron sputtering through the reaction of Zn with O2. XRD (X-ray diffraction) revealed the existence of ZnO and the polycrystalline with hexagonal crystal structure of the deposited ZnO film. The deposited ZnO showed a strongly preferred orientation of c-axis perpendicular to the substrate surface. The sputter coating of ZnO significantly altered the surface microstructures of the PET fibers examined by Atomic Force Microscope (AFM). The bonding between the sputtered ZnO and PET fibers was observed by Scanning Electron Microscope (SEM). The results of the UV/Visible spectrum indicated the transparent and ultraviolet (UV) absorption properties of the sputtered ZnO films. The anti-static tests revealed that the sputter coating of ZnO significantly improved the anti-static function of the samples and the anti-static function also obviously enhanced as the deposition thickness increased.

Key Words: Coatings, Fibers, Interfaces, Reactive processing, Surfaces.

ÖZET

Çinkooksit (ZnO) fonksiyonel ince filmler, Zn ve O2'nin reaksiyonuyla doğru akım (DC) reaktif magnetron püskürtme yöntemi ile PET (Poliester) spunbonded nonwoven üzerinde ince filmler oluşturulmuştur. XRD (X ışını difraksiyonu), ZnO ile oluşan ZnO filmin polikristalin ve hekzagonal kristal yapısını göstermiştir. ZnO film, son derece tercih edilen c-ekseninin materyal yüzeyine dik oryantasyonunu göstermiştir. ZnO'nun püskürtme kaplaması PET liflerinin yüzey mikro yapılarını önemli ölçüde değiştirmiş ve bu değişim Atomik Kuvvet Mikroskobu (AFM) ile incelenmiştir. Püskürtülen ZnO ile PET lifleri arasındaki bağlanma Taramalı Elektron Mikroskobu (SEM) ile gözlenmiştir. UV/Görünür spektrumu ZnO filminin transparan ve UV (ultraviyole) absorpsiyon özelliklerini göstermiştir. Antistatik testler, ZnO nun püskürtme kaplamasının, numunelerin antistatik fonksiyonunu geliştirdiğini, aynı zamanda kaplama kalınlığı arttıkça belirgin bir şekilde arttığı ortaya konmuştur.

Anahtar Kelimeler: Kaplamalar, Lifler, Ara yüzler, Reaktif işlem, Yüzeyler.

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1. INTRODUCTION

Zinc oxide (ZnO), crystallizing in a hexagonal wurtzite structure as illustrated in Figure 1, is a novel II–VI group direct-wide-band-gap (3.37eV at 100K) semiconductor with high chemical sensitivity to volatile and other radical gases. It has high luminous transmittance and piezoelectric properties, high chemical stability and suitability to doping, good electro-optical characteristics, excellent substrate adherence and hardness, non-toxicity and low cost (1-2). These properties have made ZnO a multifunctional material that has been applied in many areas such as light emitting diodes, thin film solar cells, thin film transistors, photovoltaic devices, and transparent electrodes, etc (3-4). In addition, the grain growth of ZnO films shows preferential orientation along the c-axis, so that it is widely used in optical wave-guide, surface acoustic wave (SAW), and acoustic-optic devices (4).

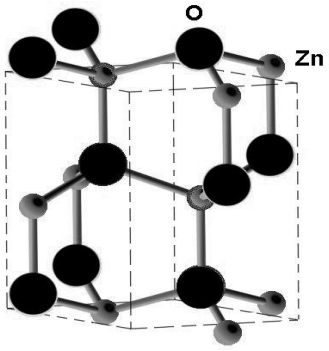


Figure 1. Hexagonal wurtzite structure of ZnO

Recently depositing thin films on flexible substrates has attracted more attention and has been used in lot of fields, such as flexible displays, sensor arrays, curved circuits, curved detector arrays, sensor skins, and other large-area electronics (5).

The ZnO thin films have been produced by numerous techniques such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), magnetron sputtering, pulsed laser deposition (PLD), atomic layer deposition, spray pyrolysis, filtered cathode vacuum arc, sol-gel process and so on (4, 6). Among these, one of the most commonly used techniques is sputter coating with simple apparatus, high deposition rate, low substrate temperature, the possibility of obtaining good orientation and uniform films, good surface flatness, transparency and dense layer (7).

In this paper, the ZnO functional thin films were deposited on PET (polyester) spun-bonded nonwovens by DC (direct current) magnetron sputtering, as the reaction of Zn and O_2 happened in the vacuum chamber. The structures and properties of the nonwoven sputter coated with ZnO were analyzed and discussed.

2. MATERIALS AND METHODS

2.1 Materials preparation

Spun-bonded PET non-woven samples with an area mass of 100 g/m^2 were used as the substrates. The samples were cut into a size of 65mm×65mm. First samples were immersed into acetone solution for 30 minutes to remove the organic solvent and dusts on the materials. Then they were rinsed with de-ionized water twice. The samples were dried at the temperature of 60□ for 10 minutes. The prepared samples were put in drying vessel for experiments later.

2.2 Thin film deposition

The ZnO thin films were deposited by a magnetron sputtering system JZCK-420B. And the system has two kinds of power supply, including direct current (DC) power and radio frequency (RF) power. High purity (99.99%) Zn target with the diameter of 2 inches was used as the target.

In the experiments, the base pressure of the chamber was 1.3×10^{-3} Pa. The distance between substrate and target was 170mm. And high purity (99.999%) oxygen and argon were respectively used as reaction gas and bombardment gas. In order to avoid the possible deformation of substrate under high temperature, water-cooling was used to control the temperature during the sputtering process. And the substrate holder was rotating at a speed of 100 rpm so that ZnO particles could deposit on the substrates uniformly. Meanwhile, a from-down-to-up sputtering method was adopted to avoid the impurity falling onto the substrates. The deposition thickness was measured by using a quartz film thickness monitor (FTM-V) fixed in the sputtering chamber.

2.3 X-ray diffraction analysis

In this experiment, the nonwoven sample sputtered with 100nm ZnO was tested. The X-ray diffraction spectra were obtained by the Focus D8 X-ray diffractometer produced by Bruker, Germany.

2.4 Surface microstructures

A Benyuan CSPM4000 Atomic Force Microscope (AFM) was employed to image the morphology of the fiber surfaces. Scanning was carried out in contact mode, with a silicon cantilever CSC11. All images were obtained at ambient conditions. The scanning size was 3000nm×3000nm.

2.5 Interface observation

The interface between the ZnO film and the PET fibers was examined by a Hitachi S-4800 Ultra-High Resolution FE-SEM produced in Japan. The SEM images were obtained at a magnification of 5,000.

2.6 Optical properties

The optical properties of the samples, including the original one and those with different deposition thicknesses (50nm, 70nm, 150nm and 200nm), were analyzed by UV-1901 UV/VIS spectrophotometer from Beijing PGENERAL instrument company. The transmittance of the samples was measured in the wave length range from 250nm to 600nm.

2.7 Anti-static properties

The samples before and after sputter coatings were further examined by anti-static test using YG(B)342D texture response static tester. The machine uses a high voltage electrical field to discharge the fabrics in a given time, so that the fabrics respond the static and then the quantity of electricity. Then the semi-decay time of the static voltage's attenuation and the residual volume of the static can be tested, which explains the anti-static properties of the fabric tested.

The main parameters in the experiments (referring to the standard, FZ/T01042-1996 'the Testing of Static Properties and Static Voltage's Semi-decay of Textile Materials' and BG/T12703-91 'Static Electricity's Testing of Textiles' were set as follows. The distance between sample and discharge electrode was 20mm and the distance between sample and probe was 15mm. The speed of the turntable was 1500rpm and the high voltage added was10 KV. The discharge time of the high voltage was 30s and the size of the sample was 60mm×80mm. During the test, the temperature was 25 and the relative humidity was 40%. Each sample was tested for three times and the average values were used.

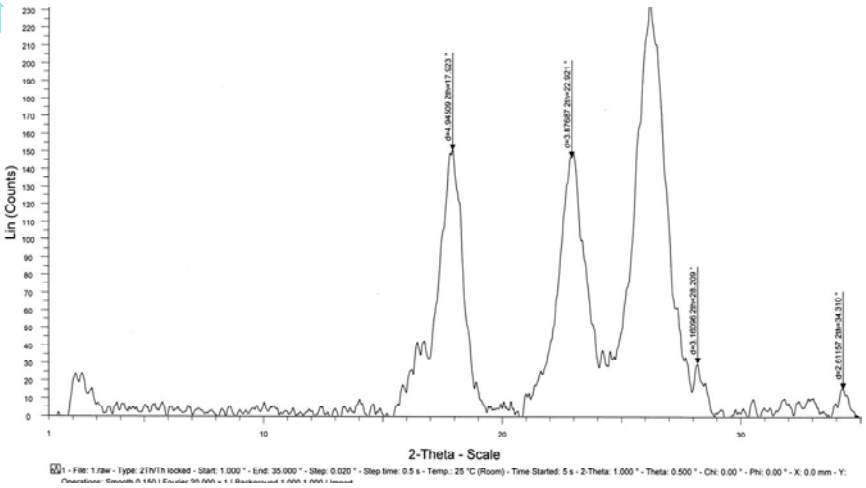


Figure 2. XRD spectrum of the PET substrate sputtered with nanostructured ZnO

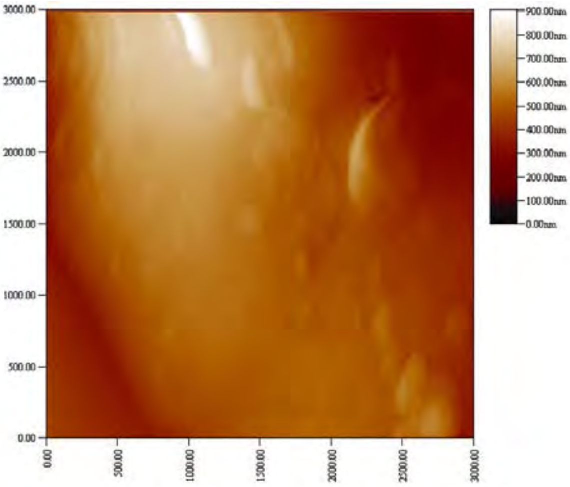
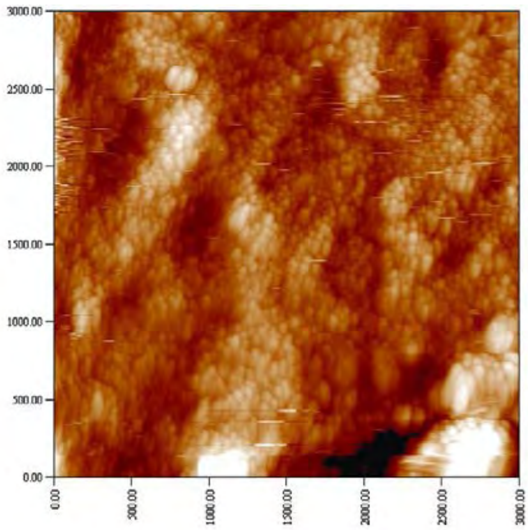
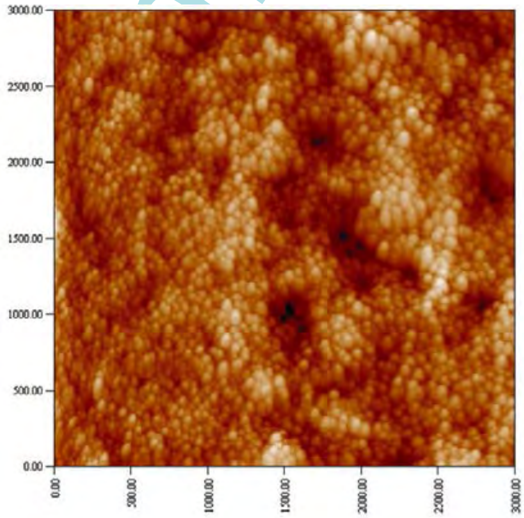


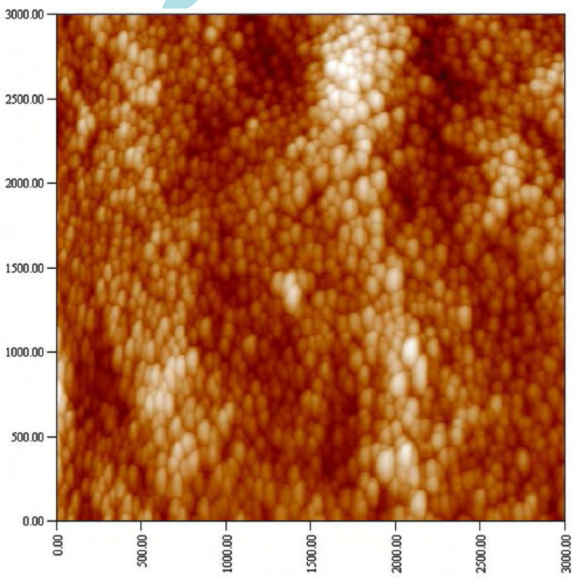
Figure 3. AFM topography image of the original sample



(a)



(b)



(c)

Figure 4. AFM topography images of the samples with different deposition thicknesses: (a) 70nm; (b) 100nm; (c) 150nm

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The peaks of 2θ at 17.923° and 22.921° in Figure 2 are the characteristic peaks of PET substrate. It is observed that there is peak at 34.310°, which is assigned to the characteristic peak of ZnO. The XRD spectrum clearly shows the much higher PET characteristic peaks compared to the ZnO peak as displayed in Figure 2. The ZnO peak in the XRD spectrum reveals the crystal and c-axis orientation structure of the film deposited on the nonwoven substrate.

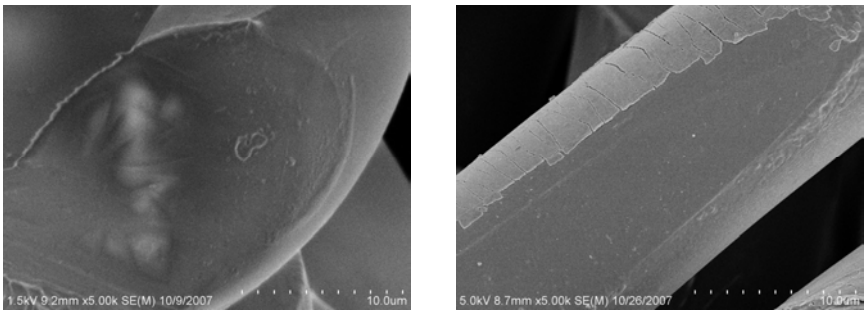
3.2 Surface microstructures

The AFM images in Figures 3 and 4 show the surface morphologies of the original sample and the sample deposited with ZnO. The images show a clear contrast in surface morphology between the PET fibers and ZnO coated ones. The surface of the original sample appears quite smooth with the sporadic grains existed, which should be impurities like dust adhering on the fibers. The surfaces of the ZnO deposited samples, however, are covered with the clearly recognized nanoclusters.

All the images in Figure 4 reveal that the ZnO nanoclusters deposited on the surface of the fibers are spread evenly. It is also observed that the sizes of the ZnO clusters increase as the coating thickness increases. The average diameter of the ZnO clusters is 26.5nm for the deposition thickness of 70nm, as shown in Figure 4a. It is increased to 30.0nm as the deposition thickness is increased to 100nm, as presented in Figure 4b. The average diameter of the ZnO clusters is further increased to about 36.6nm when the deposition thickness reaches 150nm, as illustrated in Figure 4c.

3.3 Interface observation

The SEM images in Figure 5 show the cross sections of the PET fibers before and after the ZnO coating. The cross section of the PET fiber without ZnO coating clearly shows the consistent structure, as illustrated in Figure 5a. The image in Figure 5b clearly demonstrates the coating on the fiber surface. It is also observed that the coating is tightly integrated with the polymer substrate. There are some cracks formed in the coating layer on the fiber surface as shown in Figure 5b. These cracks are believed to be formed during the preparation of the sample sliced by blade for SEM imaging.



(a) (b)

Figure 5. SEM images of the samples' cross sections: (a) original sample; (b) ZnO deposited sample

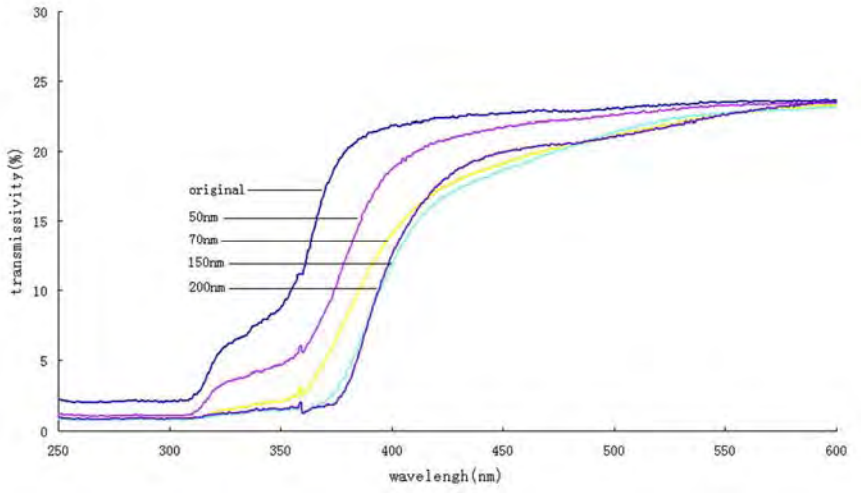


Figure 6. Effect of deposition thickness on the transmittance of the samples

Table 1. Results of the anti-static tests

Samples \ Results	Peak Voltage(V)	Static Voltage(V)	Semi-decay time(s)
Original Sample	2600	2637	99.9
100 nm film	4080	4090	9.55
150 nm film	3740	3780	2.72

3.4 Optical properties

The UV/Vis spectra reveal the effect of sputtering time on the optical properties of the ZnO coated nonwovens as presented in Figure 6. It is evident that the curves of transmittance show similar pattern in the range between 250nm and 600nm. The transmittance is much lower than 5% for the wavelength from 250nm to 300nm, indicating the shielding effect of all samples tested. The transmittance is gradually increased as the wavelength increases from 300nm to 400nm. The ZnO coated samples show very similar transmittances to that of the uncoated sample in the wavelength from 400nm to 600nm, indicating the transparent behavior of the ZnO films deposited on the PET fibers. The transmittance decreases in the wavelength range from 300nm to 400nm when the sputtering thickness is increased from 70nm to 150nm, revealing the UV absorption effect of the ZnO coating. The curves in Figure 6 clearly demonstrate the effect of the coating thickness on the UV absorption of ZnO coatings. It is also observed that the 200nm coating shows very similar effect to that of 150nm coating.

3.5 Anti-static function properties

The results of anti-static test are listed in Table 1. Semi-decay time, which measures the time needed for the

reduction of the static voltage on the fabric to half of the initial value, is used to represent the anti-static property of a fabric. Therefore the shorter semi-decay time is, the better the capability to neutralize the surface charge of the sample is, indicating better anti-static property.

Compared with original sample, the semi-decay time of the ZnO deposited samples is considerably shortened, which means that the anti-static property is greatly improved. Table 1 also clearly reveals that the semi-decay time decreases obviously as the deposition thickness increases. The anti-static property is enhanced by the increase in coating thickness. The anti-static property of the coating is attributed to the hexagonal dense-heaped polar wurtzite structure of the ZnO clusters deposited on the nonwoven. It has characteristic defect and the ionization of filling-gap zinc ion at common temperature. When the high voltage is exerted to the sample, ZnO can on one hand prevent producing the static charge, and on another hand disperse the static charge quickly, to achieve excellent anti-static effect.

4. CONCLUSIONS

The structures and properties of the PET nonwoven deposited with nanostructured ZnO films were investigated in this paper. The ZnO nanostructures were revealed by XRD and AFM. The coating layer was integrated with the PET fibers examined by SEM. The PET nonwoven deposited with ZnO film showed improved UV absorption property. The UV absorption of the ZnO coated nonwoven was also affected by the coating thickness. It was found that the ZnO deposition significantly improved the anti-static property of the PET nonwoven and the anti-static property was also enhanced with increasing deposition thickness.

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