Sputter deposition of nanostructured antibacterial silver on polypropylene non-wovens

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Nanostructured silver films were deposited at room temperature on polypropylene non-wovens by radio frequency magnetron sputter coating to obtain the antibacterial properties, and the relationship between sputter parameters and antibacterial properties were investigated in this paper. The antibacterial activity of the materials was assessed using shake flask test. The effects of silver film deposition on surface morphology were characterised using SEM and AFM. Surface elemental compositions were also analysed using EDX analysis. The results of antibacterial tests revealed that deposition time was the key parameter affecting the antibacterial properties of the materials, while sputtering power and argon pressure seemed to have a slight effect on antibacterial performance. It is believed that the total amount of silver ions released from the silver coating was increased as the deposition time increased. The AFM images and quantitative analysis by EDX respectively revealed that increase in deposition time led to the increased coverage of silver film and the increased silver weight percentage per unit surface, which provided evidences for the increased release rate of the silver ions from coating.

Keywords: Magnetron sputter coating, Nanostructured silver films, Antibacterial, SEM, AFM, EDX

Introduction

Silver has been increasingly used in medical devices ranging from wound dressings to urinary catheters[1] because of its remarkable advantages such as broad spectrum antibacterial activity, non-toxicity to human cells and long lasting biocide effect.[2]

Various techniques have been successfully used in preparing silver films, including chemical silver plating and vacuum vapour deposition. Chemical silver planting is a simple and conventional approach.[3,4] However, this technique generally suffers from many demerits, which include low silver pick-up onto the substrates and the disadvantages to the environment. Another method of coating silver onto a substrate involves vacuum vapour deposition. This method also has some drawbacks because of the poor adhesion and technological repetitiveness.

In this study, radio frequency magnetron sputter coating was selected to deposit nanostructured silver films on the surfaces of polypropylene (PP) non-wovens. Shake flask test was used to investigate the antibacterial properties of all coated samples. Both scanning electron microscope (SEM) and atomic force microscope (AFM) were employed to observe the surface morphology of nanostructured silver films. Energy dispersive X-ray (EDX) analysis was used to analyse the surface elemental compositions. In addition, the effects of the sputtering parameters such as deposition time, gas pressure and sputtering power on antibacterial properties of the samples were also investigated in this paper.

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Experimental

Materials preparation

The substrate used was spun bonded PP non-wovens with an area mass of 50 g m^{-2}. The samples were first immersed into acetone solution for 30 min to remove the finishes of the textile production, and then were rinsed twice in deionised water. The samples were dried at the temperature of 40–45°C before cutting into $6{\cdot}5\times5{\cdot}5$ cm for sputtering.

Film deposition

The deposition of the silver films was realised using magnetron sputter coating system with a radio frequency sputter source supplied by Shenyang Juzhi Co. Ltd. The high purity silver target (diameter: 50 mm; purity: 99·99%) was placed below the substrate at a distance of 170 mm. Before the deposition process, the sputter chamber was evacuated to a base pressure of 5×10^{-4} Pa. Argon was used as the sputtering gas. In the experiment, parameters including sputtering power, deposition time and argon pressure were changed to investigate their effect on the antibacterial properties. During the sputtering, the substrate holder was rotated at a speed of 93 rev min^{-1} to facilitate the uniform distribution of silver particles on the substrate, and the

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coating thickness was measured using a film thickness monitor (FTM-V) fixed in the sputtering chamber.

Antibacterial activity assessment

The antibacterial effect was investigated using the shake flash test in accordance with 'Hygienic standard for disposable sanitary products' (GB15979-2002).[5] The test bacteria were Staphylococcus aureus and Escherichia coli. In addition to the coated samples, an uncoated corresponding material was tested for comparison. After incubation at $37 \pm 1^{\circ}$C for 36 h, bacteria were counted.

The antibacterial properties of the substrates coated with the silver film were evaluated by calculating the reduction percentage of bacteria using the following formula

$$X_s = \frac{A - B}{A}$$

where X_s is the reduction percentage of bacteria (%), A is the number of bacteria colonies on the agar plate recovered from bacterial solution at zero contact time and B is the number of bacteria colonies on the agar plate recovered from the specimen after shaking for 1 h. If the number of the bacteria after shaking is larger than the number at zero contact time, $X_s = 0$.

Characterisation of SEM and AFM

A SEM (JEOL JSM-5610LV) was used to examine the microstructure of samples. The scanning was operated at 5·0 kV.

The AFM used in this work was a CSPM4000 AFM made by Benyuan Co. Ltd. Scanning was carried out in the contact mode. The scanning size was 2500×2500 nm, and the scanning frequency was set at 1·1 Hz.

Analysis using EDX

Elemental analysis of the silver clusters deposited on the PP non-wovens was carried out using EDX analysis provided by Oxford Co. Ltd.

Results and discussion

Antibacterial performance

Film thickness effect

Table 1 shows the antibacterial test results of non-wovens deposited with silver films for different deposition times, but at the same gas pressure of 2 Pa and the same sputtering power of 40 W.

All silver coated PP non-wovens were very effective against both test bacteria, Staphylococcus aureus and Escherichia coli, as shown in Table 1. The results also showed that the coated samples were more effective against Staphylococcus aureus than Escherichia coli, and the antibacterial performance was significantly improved as the film thickness was increased. In Refs. 2 and 6, it has been reported that the antibacterial effect of silver mainly depended on the total amount of silver released from the coating. It is believed that increasing the coating thickness obviously leads to the release of a larger amount of silver ions, which contributes to the antibacterial performance. Because silver is very expensive and when the silver coating thickness exceeds 28 nm, it may be toxic to certain human cells.[2] To assure the excellent antibacterial properties and to save the cost, the optimal coating thickness was found to be ~3 nm.

Table 1 Effect of film thickness on antibacterial properties

Film thickness, nm	Deposition time, s	Reduction of bacteria, %	
		S. aureus	E. coli
Uncoated	0	0	0
0·5	71	100	51·44
1	137	100	78·05
2	253	100	98·53
3	424	100	100

Sputtering power effect

Table 2 indicates the antibacterial test results of non-wovens with deposited silver films under variable sputtering powers, but with a constant film thickness of 1 nm and argon pressure of 2 Pa.

Results in Table 2 demonstrate that the antibacterial properties show no obvious change as the sputtering power is increased.

Argon pressure effect

Table 3 gives the antibacterial test results of non-wovens deposited with silver films under different argon pressures but with the same film thickness of 1 nm and sputtering power of 40 W.

As the argon pressure is reduced, there was a slight improvement in the antibacterial properties.

These results reveal that the film thickness was the key factor affecting the antibacterial properties of the coated materials. The effect of coating thickness was further analysed using SEM, AFM and EDX.

Observations using SEM

The SEM image in Fig. 1*a* shows a smooth surface with some dust like particles on the surface of the uncoated PP surface. The SEM images in Fig. 1*b–e* show the fibres coated with 0·5–3 nm silver films respectively. It can be seen that all the coated fibres have silver particles with varying sizes on their surfaces. The surface details can be further examined by AFM.

Observations using AFM

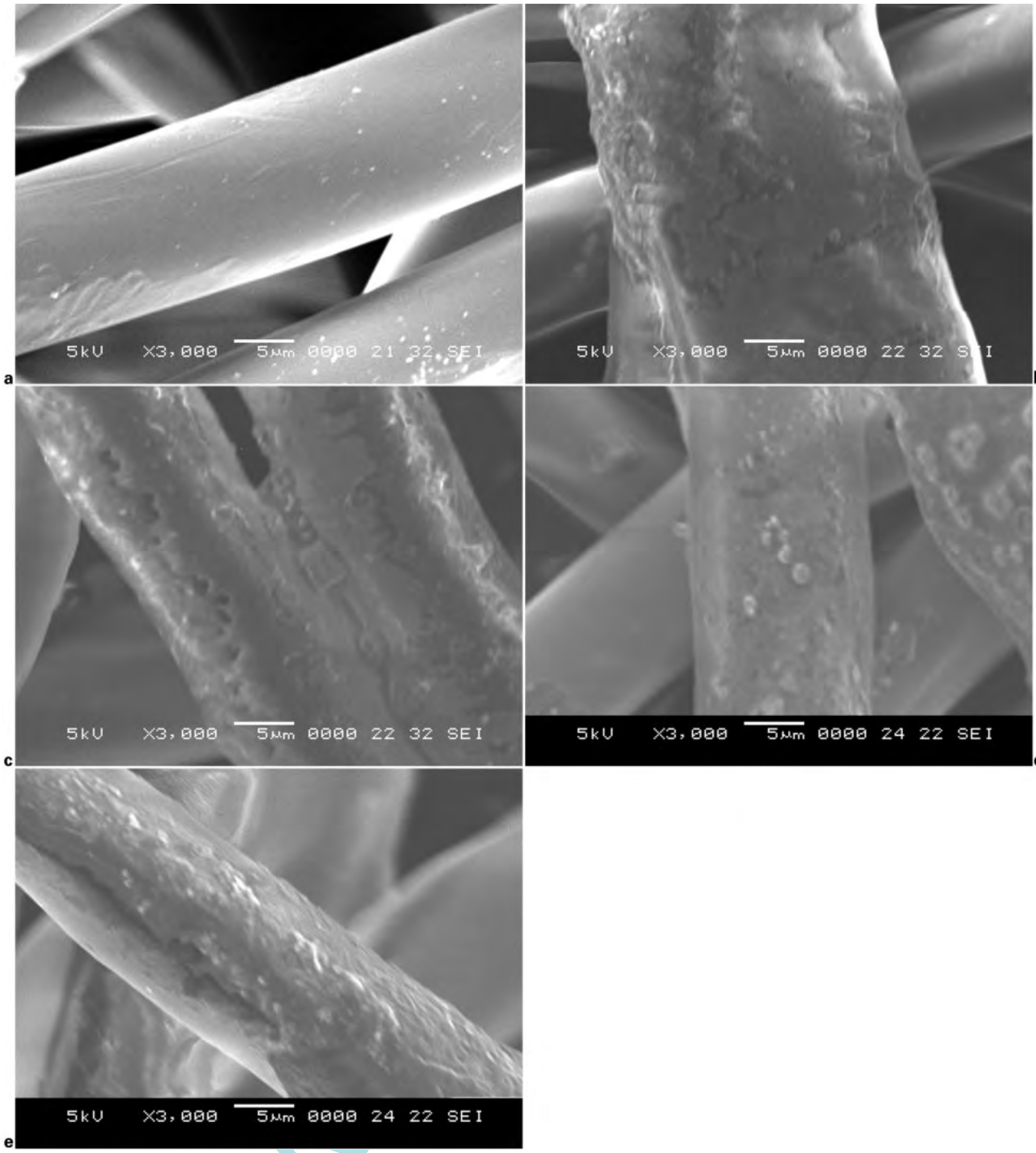
The AFM image of the uncoated PP surface is presented in Fig. 2*a*. The AFM images of PP surfaces deposited with silver films of different thicknesses range from 0·5

Table 2 Effect of sputtering power on antibacterial properties

Sputtering power, W	Deposition time, s	Reduction of bacteria, %	
		S. aureus	E. coli
40	137	100	78·05
80	42	100	79·39
120	26	100	77·93

Table 3 Effect of argon pressure on antibacterial properties

Argon pressure, Pa	Deposition time, s	Reduction of bacteria, %	
		S. aureus	E. coli
2	137	100	78·05
5	824	100	77·96
8	2838	100	77·03



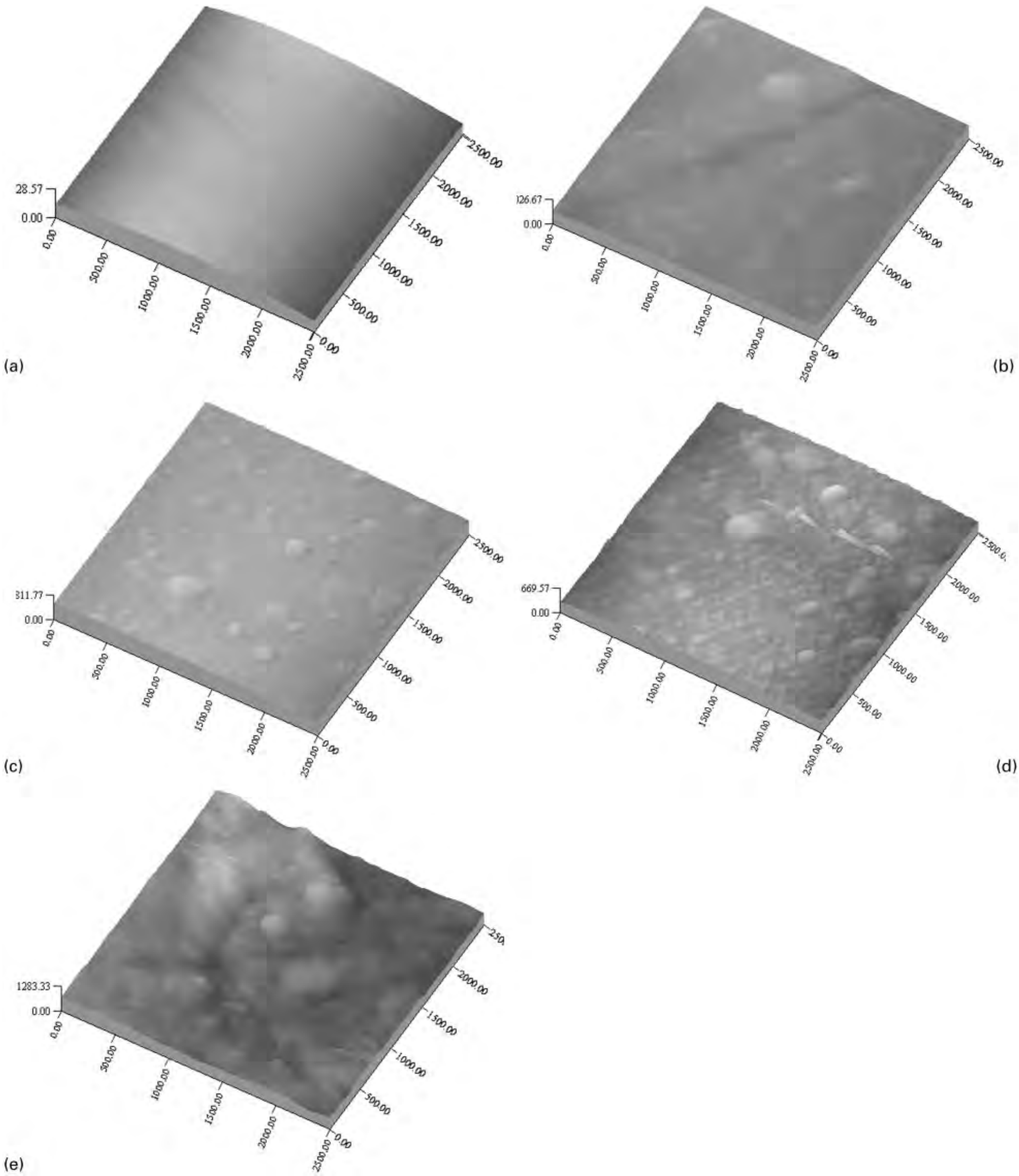
a uncoated; *b* 0·5 nm coating; *c* 1 nm coating; *d* 2 nm coating; *e* 3 nm coating

1 Images (SEM) of samples coated with silver films of different thicknesses

to 3 nm, and with the same pressure of 2 Pa and the same sputtering power of 40 W, are given in Fig. 2*b*–*e*.

The uncoated PP surface shows a smooth surface with clear periodic stripes on its surface, as shown in Fig. 2*a*. The periodic stripes were oriented in the fibre axis direction, which was probably induced by the drawing of the fibres. Figure 2*b* indicates that when the film thickness was ∼0·5 nm, some small silver particles scattered on the PP surfaces, and the original structure of PP was still clearly recognised. With a PP coated silver film of 1 nm, a mass of small silver particle aggregates with the average grain diameter of 38·4 nm were present on the PP surface, as illustrated in Fig. 2*c*. The image also indicates that the silver thin film covered up the fibre surface, thus the original structure of PP surface was not visible. Figure 2*d* reveals that when the film thickness was extended to 2 nm, the layer was composed of silver clusters with the average grain diameter of 49 nm, and the interspaces between particles were slightly decreased. Figure 2*e* displays the surface structure of the PP fibre coated with a silver film of 3 nm, and it can be seen that the surface of PP fibres were covered with dense silver particles with an average grain diameter of 71·4 nm.

The AFM images reveal that the increased deposition time led to more aggregates of silver particles and a more compact film structure. It is believed that as the deposition time became prolonged, the silver particles on PP surface became denser, and the collision probability between sputtered particles and the deposited



a uncoated; *b* 0·5 nm coating; *c* 1 nm coating; *d* 2 nm coating; *e* 3 nm coating

2 Images (AFM) of samples coated with silver films of different thicknesses

silver particles significantly increased, thus contributing to a larger grain size.

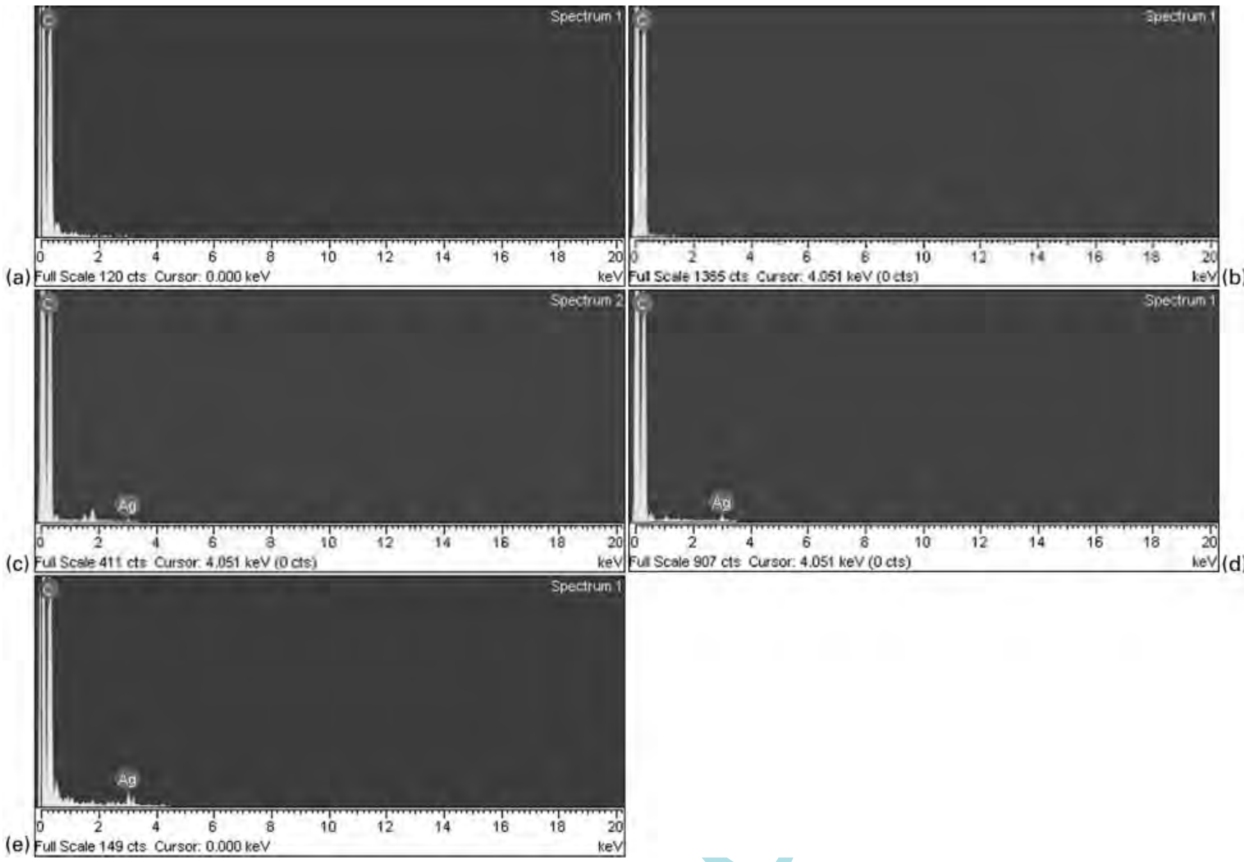
By comprehensive analysis of the AFM images and bacterial test results, it can be concluded that as the deposition time is prolonged, the coverage of silver film increased, leading to an increased release rate of silver ions, which contributed to the improvement in antibacterial properties.

Analysis using EDX

Figure 3 shows EDX results for nanostructured silver film with different thicknesses. It can be seen from the results that the uncoated sample shows a single carbon peak, while after sputter coating, the element silver was detected. Quantitative analysis of EDX data in Table 4 shows that as the film thickness is increased, the silver weight percentage per unit surface of samples gradually increased, which provides evidence for the improved antibacterial properties.

Conclusions

In this work, the correlation between the sputtering parameters and antibacterial properties was



3 Energy dispersive X-ray spectra of nanostructured silver film obtained under sputtering power of 40 W, pressure of 2 Pa and with film thicknesses of *a* uncoated, *b* 0·5 nm, *c* 1 nm, *d* 2 nm and *e* 3 nm

Table 4 Quantitative analysis by EDX

Coating thickness, nm	Weight (C), %	Atomic (C), %	Weight (Ag), %	Atomic (Ag), %
Uncoated	100·00	100·00	0·00	0·00
0·5	95·24	99·44	4·76	0·56
1	78·19	96·82	21·81	3·18
2	63·30	93·85	36·70	6·15
3	40·11	85·74	59·89	14·26

investigated. The authors' results show that the deposition time affected the antibacterial properties and grain size significantly, while the sputtering power and argon pressure did not show an obvious effect on antibacterial properties.

The increased deposition time led to increased coverage of silver film and increased silver weight percentage per unit surface, leading to an increase in the release rate of silver ions from the coating, which resulted in improved antibacterial properties.

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