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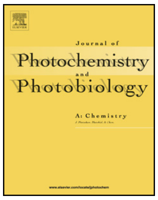

Metal oxide composite thin films made by magnetron sputtering for bactericidal application

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ABSTRACT

To broaden the application of antibacterial catalysts, ZnO/Ag_2O composite thin films with different Ag_2O contents have been successfully synthesized on non-woven fabric at room temperature by radio frequency (RF) sputtering with a single ceramic target formed by hot pressing ZnO/Ag_2O nanocomposite powder in Ar atmosphere at 180 °C for 30 min. The composite thin films were also sputtered on glass substrates for characterizations. The best sputtering condition was found with the Ar/O_2 gas flow ratio at 7:1 to obtain pure Ag_2O thin film. The deposition of Ag_2O nanoparticles on commercially available ZnO particles was also confirmed by HR-TEM prior to hot pressing for synthesizing ceramic targets. In this work, an appropriate amount of Ag_2O incorporated in the composite film was endeavored by forming *p*–*n* junction to lower the cost without decreasing bactericidal ability of composite film. The amount of 45 wt% Ag_2O in composite thin film to provide bactericidal effect was found to be as good as pure Ag_2O. The feasibility in bactericide is due to the light sensitization of low bandgap Ag_2O and the formation of nano *p*–*n* heterojunction between p-type Ag_2O and n-type ZnO for efficient photo carrier separation. The dependence of antibacterial effect of ZnO/Ag_2O thin films on the Ag_2O content is demonstrated and elucidated in this work.

1. Introduction

Recently, infectious diseases related to the antibiotic-resistant bacteria have increased. It had been reported that the number of multidrug-resistant *Staphylococcus aureus* (MRSA) infections had significantly increased. In Europe, 17 of 22 countries reported 85–100% of *Escherichia coli* isolates were extended-spectrum beta-lactamase (ESBL) positive which was resistant to antibiotic [1]. Klebsiella pneumoniae with the same EBSL percentage was also reported. The ESBL cases for Clostridium difficile, *Staphylococcus aureus*, Enterobacteriaceae, *Neisseria gonorrhoeae*, and *Streptococcus pneumonia* were also reported by many other countries such as United State, New Zealand, Australia, India, and China [1]. Antibiotic resistance may develop via multiple mechanisms by the alteration of antibiotic target site or metabolic pathway to avoid disruptive effect of antibiotic and to reduce the drug accumulation from cell [2]. As an example, the antibiotic resistance may be caused by the bacteria due to the beta-lactamase enzymes which can neutralize the beta-lactam of antibiotics such as penicillin. Therefore, the development of antibiotic is required to keep up with the constantly changing antibiotic resistance of bacteria [2]. The pathogen resistance against medication has been emerged as a serious problem, therefore it is essential to develop new non-toxic, durable, cost-effective, and efficient antibacterial agents.

Furthermore, nosocomial infection due to the growth of multidrug resistant bacteria has been a worldwide problem in hospital nowadays [3,4]. This situation becomes worse when the

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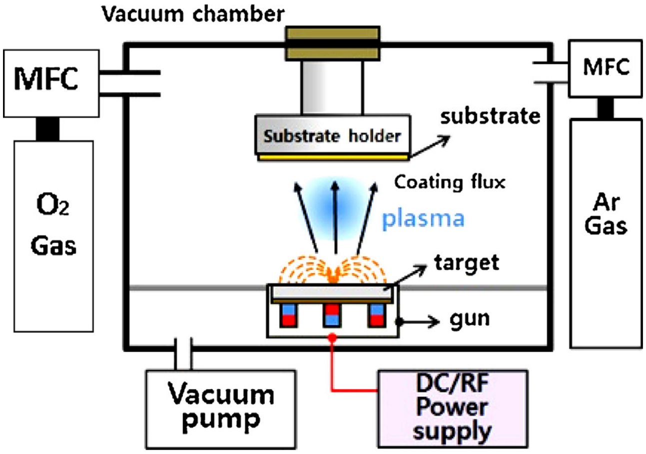

Fig. 1. Experimental setup for RF sputtering with the Ar and O_2 gas mass flow controllers (MFC).

medical staff move from one patient to another without regularly practicing correct hygiene procedures. To remove the infectious pathogens existing in indoor air environment, many conventional methods such as UV radiation [5], chlorination [6], ozone [7], and other advance filtrations are readily to be used. However, they are expensive, carcinogenic, and not environmentally benign. One of the compelling alternatives and promising approaches for removing pathogens and volatile organic compounds is applying photocatalysis-containing semiconductor materials [8–10].

Due to the fast spread of nosocomial infections, inorganic materials have been emerged as alternative antimicrobial agents [11]. The bactericidal properties of inorganic materials such as metallic nanoparticles [11,12], semiconductor and metal oxide powders [8–10,13] have been used in different forms, such as powders and coating on cellulose fibers [11]. Semiconductor coating for antibacterial application also has been successfully done in our previous work [14] and other works [15,16]. In many other works, nanostructure-based materials have shown their antimicrobial properties for immense applications in water treatment, synthetic textiles, food processing and packaging, biomedical and surgical devices [17–19].

The semiconductor nanoparticles which are often used for antibacterial applications are ZnO, TiO_2, Ag, and Ag_2O nanoparticles [20–27]. ZnO nanoparticles has been shown to naturally reduce the activity of mostly Gram positive bacteria strain without the use of antibiotics [28]. The bactericidal effect of ZnO was related to the reactive oxygen species (ROS) [29,30] produced in the photocatalytic process and the release of antibacterial metal ions which finally caused the disruption of cell membranes [31,32]. However, small particle size of photocatalyst was preferable to enhance the activity of antibacterial behavior of nanoparticles due to the increasing surface area to volume ratio [33]. ZnO is n-type UV-driven material with the bandgap value ranging from 3.1–3.3 eV [34]. In our previous work, [35] the visible light photoactivity of ZnO can be improved by the formation of *p*–*n* heterojunction with low bandgap materials such as Ag_2O which serve as visible light sensitizer. Ag_2O as one of the best p-type visible light active materials has the bandgap values varying from 1.2–1.6 eV, depending on the preparation procedure [36–38]. Ag_2O has been identified as a great material for antibacterial applications, organic dye degradation, and other industrial applications such as electrode materials, colorant, olefin epoxidation, cleaning agent, catalyst for alkane activation, and preservation [39,40]. However, the high cost of silver as a raw material caused a drawback for large scale application. Therefore, introducing Ag_2O with a reduced amount to form visible light-driven ZnO/Ag_2O composite is considerably required to make it economically viable. Most of the works on ZnO/Ag_2O composite particles were done for organic pollutant degradation [40,41], however to the best of our knowledge, the ZnO/Ag_2O composite thin film has not been studied for antibacterial application.

To have better understanding on bactericide effects of ZnO and Ag_2O semiconductors, preliminary works have been done to initially test the capabilities of ZnO, Ag_2O, ZnO/Ag_2O composite powders in killing *Escherichia coli*. The methods and results (Figs. S1 and S2) were shown in the Supplementary information. It was found that the as-prepared Ag_2O powder has a great bacterial killing ability with and without visible light illumination, ZnO powder had bactericide effect under visible light illumination however only a little bactericide effect was found in dark condition. The composite powder of ZnO/Ag_2O also has a comparable ability in killing bacteria to Ag_2O powder with and without light illumination. Based on this preliminary results, the idea to reduce the amount of Ag_2O by forming ZnO/Ag_2O composite thin film can be accomplished to make it economically viable for real application. The performance of *p*–*n* heterojunction between p-type Ag_2O and n-type ZnO has been confirmed and examined toward organic dye degradation in our previous work [35].

In this work, ZnO/Ag_2O composite thin films were deposited on non-woven fabric substrate by using radio frequency (RF) magnetron reactive sputtering for bactericidal purpose. The

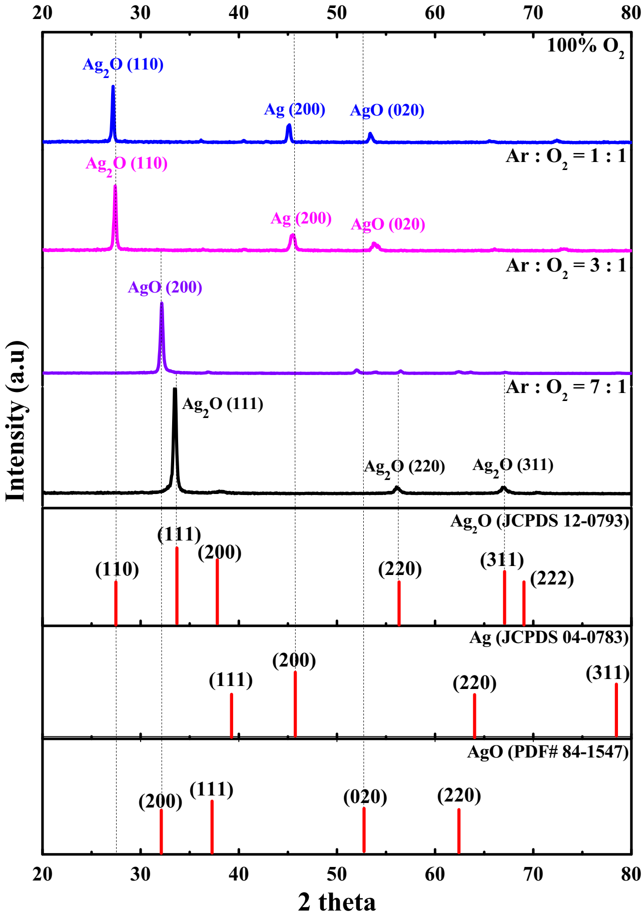

Fig. 2. XRD patterns of Ag_2O thin films deposited on glass substrate at different Ar/O_2 rations.