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# Fabrication of cobalt-organic composite thin film via plasma-enhanced chemical vapor deposition for antibacterial applications

Young-Man Jeong<sup>a</sup>, Jae-Keun Lee<sup>a</sup>, Sam-Chul Ha<sup>b</sup>, Soo H. Kim<sup>c,\*</sup>

<sup>a</sup> Department of Mechanical Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

<sup>b</sup> Digital Appliance Research Laboratory, LG Electronics, 327-23 Gasan-dong, Geumcheon-gu, Seoul 153-802, Republic of Korea

<sup>c</sup> Department of Nanosystem and Nanoprocess Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

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## ABSTRACT

In this paper, cobalt (Co)-organic composite thin films were fabricated from an organometallic precursor by plasma-enhanced chemical vapor deposition (PECVD) under various conditions. The amount of Co in the thin film was controlled by adjusting the operating parameters of the PECVD, including the vaporizer temperature, plasma deposition time, and organometallic precursor flow rate. The antibacterial performance of the Co-organic composite thin films with various amounts of Co was tested by a 'film attachment' method using *Staphylococcus aureus* and *Escherichia coli*. It was observed that the antibacterial performance was enhanced by increasing the amount of Co in the Co-organic composite thin film, and the critical amount of Co for preventing the growth of bacteria was found to be  $\sim 1.6$  ppm/cm<sup>2</sup>.

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## 1. Introduction

Recently, multifunctional products with antibacterial properties have been developed because of the increased general desire for hygiene [1]. In most cases, the antibacterial properties of these products result from organic or inorganic antibacterial coatings on their surface. The applications of organic antibacterial agents (e.g. triclosan, vinyzene) are generally limited, due to their low chemical durability and thermal stability. However, inorganic antibacterial agents (e.g. silver, copper) have the advantages of strong heat resistance and chemical durability [2].

In general, metal ions including Ca<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>, are essential nutrients for supporting microorganisms, and they are required as trace elements at nanoscale molar concentrations. These metal ions play the role of a biochemical catalyst in the living body. They can also stabilize protein structures and cell walls and balance the osmotic pressure [3–5]. However, when the concentrations of these metal ions reach the micro- or milli-molar level, they become toxic to the microorganisms, due to the absorption and destruction processes that follow in the cell [3,4]. These toxic effects generally result from the binding and adhering of the metal ions to the sulfhydryl groups in the bacterial proteins, which lead to the inactivation of the proteins [6,7]. This phenomenon is the so-

called "oligodynamic action", and it eventually restrains the reproduction of the bacterial cell [8].

There are a variety of techniques for preparing materials with metal ions associated to antibacterial properties such as the sol-gel method [9], cold plasma deposition [10], ion implantation [11,12], and sputtering [13,14]. Among these methods, the sol-gel method [9] is commonly employed because of its simplicity and easy control of the chemical elements. However, it is difficult to adjust the thickness of the thin films when using the sol-gel process. Furthermore, it requires a secondary heating process for removing the by-products. Even though the related technique, cold plasma deposition [10], is also a relatively simple process in which the organometallic compounds can be easily converted into metal-organic composite thin films, little work has been done so far on this process because volatile and stable organometallic compounds are both expensive and few and far between [15]. To reduce the cost of the precursor, we selected dicobalt hexacarbonyl t-butylacetylene (Co<sub>2</sub>(CO)<sub>6</sub>(TBA)) as a cobalt precursor, as it is known to have sufficient volatility and stability in a plasma process and shows strong antibacterial performance [16–20].

In this paper, we demonstrate the fabrication of Co-organic composite thin films using a PECVD process. The Co-organic composite thin film was then examined by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-mass spectrometry (ICP). We also investigated the antibacterial performance of the Co-organic composite thin films as a function of the amount of Co.

\* Corresponding author. Tel.: +82 55 350 5287; fax: +82 55 350 5653.  
E-mail address: [sookim@pusan.ac.kr](mailto:sookim@pusan.ac.kr) (S.H. Kim).

## 2. Experimental apparatus and methods

### 2.1. Experimental apparatus

Fig. 1 shows a schematic of the PECVD system employed in this study. The experimental system was composed of a power unit, a discharging unit, an exhaust unit, a vacuum detection unit, and a gas supply unit. The substrate fixture and plasma-discharging electrode were installed in the plasma chamber. The distance between the grounded substrate and the electrode was about 100 mm. The plasma-generating electrode was connected to a direct current (DC) power supply operated at 1.0 kV, and the substrate used for depositing the Co-organic composite thin film was connected to a ground. The vacuum unit was composed of both rotary and booster pumps, which provided a vacuum of 40 Pa. The flow rate of the He carrier gas was kept at 200 sccm by a mass flow controller (MFC, MKS Co.). The flow rate of the dicobalt hexacarbonyl t-butylacetylene precursor solution (Mecharonics Co., Ltd, 373.12 g/mol, boiling point 52 °C/110.6 Pa) was controlled by a liquid mass flow controller (Bronkhost Co.).

### 2.2. Plasma generating processes

Aluminum substrates (100 mm×100 mm×0.1 mm) were used for the plasma-assisted Co-organic composite thin films. Various amounts of the Co-precursor, viz. 3 vol.%, 6 vol.%, and 10 vol.% in Tetrahydrofuran were prepared at a fixed vaporizing temperature of ~100 °C. It is noted that the vaporizing temperature is an important parameter to effectively deposit the desired amount of Co in Co-organic thin films, as will be discussed later in detail.

The Co-organic composite thin film deposition process can be summarized as follows: (i) the aluminum substrate was washed with methanol to clean on the surface. The cleaned aluminum substrate was placed parallel to the electrode, (ii) the pressure of the reaction chamber was adjusted to 40 Pa, (iii) the Co precursor solution was carried by He gas at a flow rate of 200 sccm, (iv) the plasma was then generated by applying a voltage of 1.0 kV between the electrode and aluminum substrate, (v) the deposition time of the Co precursor was varied between 5 and 60 s and its flow rate was varied between 0.6 and 1.2 sccm, (vi) the DC power supply was turned off and the He carrier gas supply was stopped, and then (vii) after venting the reaction chamber, the Co-organic composite thin film formed on the aluminum substrate was taken out for further chemical analysis.

### 2.3. Structural analysis of Co-organic composite thin film

The surface and particle configuration of the Co-organic composite thin film were characterized by SEM (JSM-6300, Jeol) and their chemical compositions were analyzed by XPS (ESCA-5400, PHI). The samples were prepared by coating them with a ~3 nm thick Pt layer to prevent electron charging during the SEM characterization performed using an operating voltage of 3 kV. The XPS characterization was performed with the as-prepared samples. The XPS spectra were recorded on an ESCA-5400 system (Perkin Elmer) using Mg  $K_{\alpha}$  (1253.6 eV) radiation. The base pressure of the analysis chamber was  $\sim 1 \times 10^{-8}$  Pa.

The amount of Co in the Co-organic composite thin film formed on the aluminum substrate was analyzed using ICP (Otima4100DV, Perkin Elmer). The preparation of the samples for the ICP analysis was performed as follows: (i) The Co-organic composite thin film on the aluminum substrate with a weight of 0.027 g per square centimeter (i.e. 0.1 mm in thickness) was ground in a Freezer/Mill (6850, Spex). For dissolution, 0.1 g of the milled sample was digested with 4 ml 60%  $HNO_3$  using a multiple-stage microwave system (i.e. total duration: 60 min, power: 250–450 W). Then, the digest was diluted with 46 ml of double-distilled  $H_2O$ . The amount of Co measured by ICP was converted into ppm per unit area of the Co-organic composite thin film on the aluminum substrate.

### 2.4. Antibacterial property analysis of Co-organic composite thin film

The antibacterial properties of the Co-organic composite thin films on the aluminum substrate were tested by a film attachment method [21]. Briefly, 50×50 mm<sup>2</sup> samples of the Co-organic composite thin film were prepared. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC 25922) in nutrient agar were inoculated at 37 °C for 24 h. The samples were first washed with 70% ethanol to kill all of the bacteria on the surface. After drying them completely, 0.4 ml of the test inoculum [ $\sim 2 \times 10^6$  colony forming units/ml (i.e. cfu/ml)] was instilled onto each test sample in a Petri dish and the samples were covered by a 40×40 mm<sup>2</sup> polyethylene film (Stomacher 400). The samples were incubated for 24 h under conditions of relative humidity not less than 90% and a temperature of 35 °C. Afterwards, the bacteria were washed out of the test sample and covering film with 10 ml of phosphate buffer solution containing 0.85% sodium chloride solution and nonionic surfactant (Tween 80) with a pH of 7.2. To count the

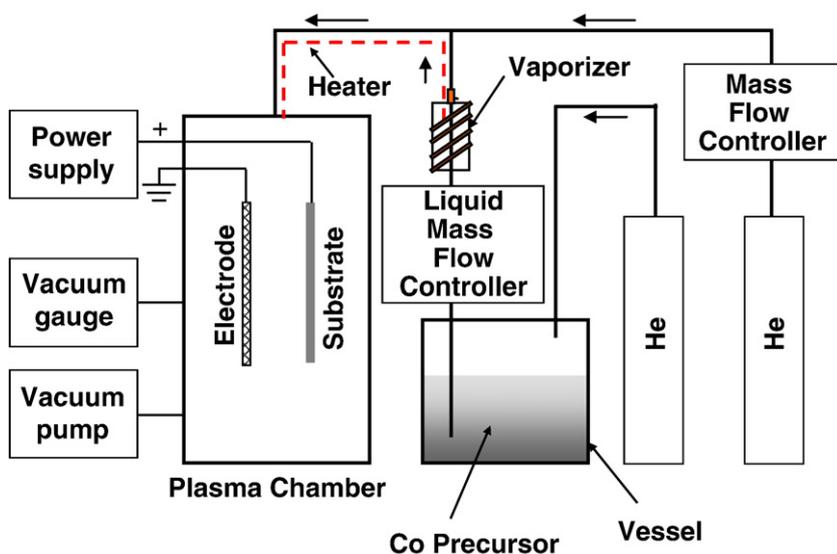
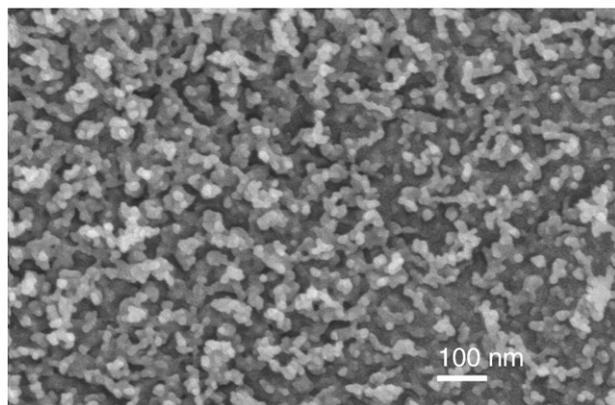


Fig. 1. Schematic diagram of the plasma deposition apparatus.



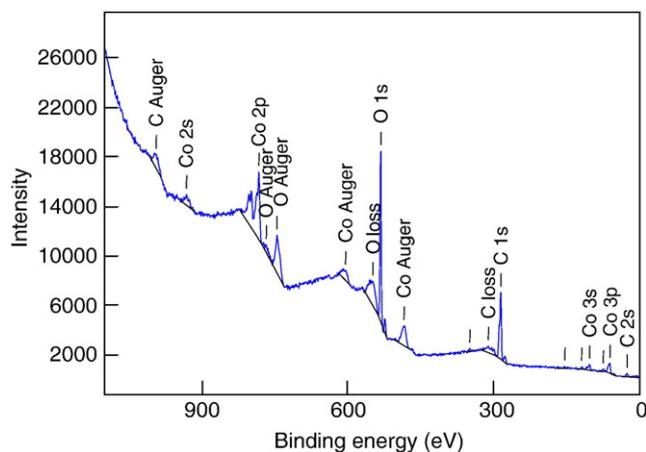
**Fig. 2.** SEM image of the Co-organic composite thin film with primary particles 10–30 nm in size at a 10 vol.% Co precursor flow rate of 1.2 sccm, a plasma deposition time of 60 s, and vaporizer temperature of 100 °C.

viable bacteria cells, 0.2 ml of washing solution were added to different Petri dishes containing nutrient agar, which were then incubated at 35 °C for 48 h. After incubation, the number of colonies in the serially diluted Petri dishes was counted visually by the colony count method.

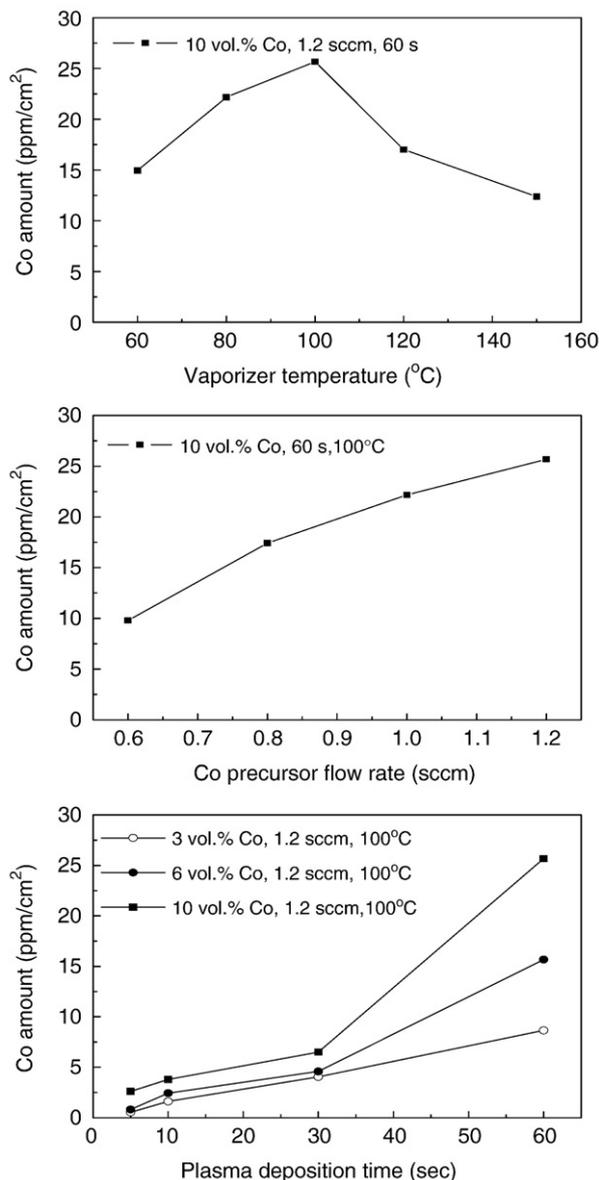
### 3. Results and discussion

SEM and XPS analyses were carried out to observe the surface structure and chemical composition of the Co-organic composite thin film deposited at a Co precursor flow rate of 1.2 sccm and plasma deposition time for 60 s. The sizes of the nanoparticle clusters are known to play an important role in the surface structure of a thin film [22–24]. Fig. 2 shows SEM image of a Co-organic composite thin film, which appears to consist of primary particles with 10–30 nm in diameter. As shown in Fig. 3, the strong signatures of Co, carbon, and oxygen appeared, as expected, indicating that the thin film was composed of Co-organic composite nanoparticles formed in the gas phase during the plasma deposition.

It is important to know the evaporation temperature of the Co precursor. Therefore, the amount of Co was measured as a function of temperature in order to determine the optimum temperature for increasing the amount of Co deposited using a fixed amount of the Co precursor (i.e. a Co precursor flow rate of ~1.2 sccm) with 200 sccm He



**Fig. 3.** XPS spectrum of Co-organic composite thin film formed under the experimental conditions of 10 vol.% Co precursor flow rate of 1.2 sccm, plasma deposition time of 60 s, and vaporizer temperature of 100 °C.



**Fig. 4.** ICP analysis of the Co content in an arbitrary area of the Co-organic thin film as a function of the vaporizer temperature, the precursor solution flow rate and the plasma deposition time.

gas for a plasma deposition for 60 s. Fig. 4a shows that the highest amount of Co was deposited when the temperature of the vaporizer and the precursor supply line was 100 °C. This is presumably because the Co precursor remains as a liquid in the vaporizer at temperatures less than 100 °C. However, at higher temperatures (>100 °C), a considerable proportion of the Co precursor vapor was presumably deposited inside the precursor supply line, as a result of thermophoretic and diffusion loss, which would decrease the Co deposition rate. Using the optimum vaporizer temperature of 100 °C, the amount of Co precursor was varied in order to observe the changes in the amount of Co deposited in the final Co-organic composite thin film. The Co precursor flow rate was varied from 0.6 sccm to 1.2 sccm. Fig. 4b shows that the amount of Co deposited in the thin film increased with increasing Co precursor flow rate. As another operating parameter, the plasma deposition time and Co-precursor concentration were also varied to observe their effects on the amount of Co deposited at a fixed vaporizer temperature of 100 °C and a fixed Co precursor flow rate of 1.2 sccm. The amount of Co deposited and the Co

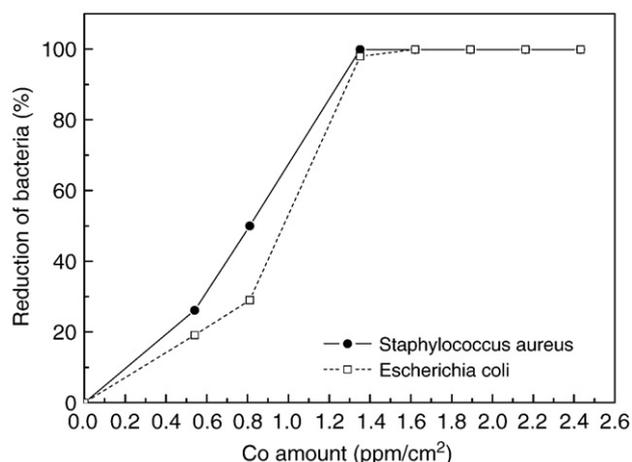


Fig. 5. Antibacterial performance as a function of the Co content using *Staphylococcus aureus* and *Escherichia coli* by the film-attachment method.

precursor concentration were analyzed by ICP as a function of the plasma deposition time, as shown in Fig. 4c. The amount of Co increased with increasing plasma deposition time and Co precursor concentration. It should be noted that the amount of Co deposited was considerably higher at a plasma deposition time of 60 s than at a plasma deposition time of less than 30 s. This was attributed to the increase in the aluminum substrate temperature at the longer plasma deposition time, which significantly increased the Co deposition rate by the enhanced thermal decomposition of the incoming Co precursor.

The amount of Co deposited was examined by varying the operating parameters. According to the results,  $\sim 100$  °C was the optimum vaporizer temperature of the Co precursor. The amount of Co contained in the Co-organic thin film was increased by increasing the plasma deposition time, Co precursor concentration and flow rate. The amounts of Co in the Co-organic composite thin films formed under the various operating conditions ranged from 0.5 to 26 ppm/cm<sup>2</sup>. The antibacterial performance of the Co-organic composite thin films was tested using these controlled amounts of Co. The antibacterial test used in this study was based on the film-attachment method. *S. aureus* (ATCC 6538) and *E. coli* (ATCC 25922) were added to the Co-organic composite thin film and incubated for 24 h. Fig. 5 shows the results of the antibacterial test. The antibacterial performance increased with increasing amount of Co in the Co-organic composite thin film. When the amount of Co exceeded  $\sim 1.6$  ppm/cm<sup>2</sup>, the initial number of living bacteria was significantly reduced, indicating that a critical Co content is required to prevent the growth of the bacteria.

#### 4. Conclusion

In this work, we investigated the characteristics of PECVD-generated Co-organic composite thin films by varying the operating parameters, including the Co precursor flow rate and concentration, evaporator temperature, and plasma deposition time. The amount of Co obtained in the Co-organic composite thin film increased with increasing the Co precursor flow rate and plasma deposition time. By adjusting the various operating conditions, a Co content of up to  $\sim 26$  ppm/cm<sup>2</sup> was obtained in the Co-organic composite thin film. The antibacterial performance of these Co-organic composite thin films was tested as a function of the amount of Co added. A threshold amount of Co (i.e.  $\sim 1.6$  ppm/cm<sup>2</sup>) was found to be essential to kill more than 99.0% of the initial bacteria of *Staphylococcus aureus* and *Escherichia coli*.

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