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# Antibacterial properties of TaN–(Ag,Cu) nanocomposite thin films

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A B S T R A C T

TaN–(Ag,Cu) nanocomposite films were deposited by reactive co-sputtering on Si(001). The films were then annealed using RTA (Rapid Thermal Annealing) at 200–400 °C to induce the nucleation and growth of metal particles in TaN matrix and on film surface. After the surface morphologies were analyzed, the samples were tested for their antibacterial behaviors against Gram-negative (Escherichia *coli*) and Gram-positive (Staphylococcus *aureus*) bacteria. It is found that the antibacterial efficiency against either *E. coli* or *S. aureus* can be much improved for TaN–(Ag,Cu), comparing with TaN–Ag or TaN–Cu films. The annealing temperature for TaN–(Ag,Cu) can be as low as 250 °C. Being annealed at this temperature, the film still shows good antibacterial behaviors against either bacterium. The synergistic effect due to the co-existence of Ag and Cu is obvious, while the films still shows good tribological behaviors.


## 1. Introduction

It is widely known that materials containing copper or silver show antibacterial property [1,2]. However, in many applications of hard films, antibacterial property and good tribological behavior are both required. Surgical tools, catheters, hospital equipment, kitchenware are some of the typical examples. On the other hand, metal-embedded nanocomposite thin films have recently received a great deal of interest in many fields, such as catalysis, sensor engineering, optics, and tribology [3–6], owing to their unique physicochemical properties.

Sputter-deposited TaN thin films have been reported to exhibit excellent mechanical properties [7,8], such as good wear- and oxidation-resistance, high hot hardness, as well as good impact toughness. Copper or silver, when used as a dopant, is proved immiscible with TaN, which makes the synthesis of TaN–Cu or TaN–Ag nanocomposite thin films possible [9]. Recently, TaN–Cu and TaN–Ag nanocomposite films were deposited by reactive co-sputtering followed by rapid thermal annealing at 400 °C for various length of time to induce the emergence of Cu or Ag particles in films' inner matrix and on the surface [10,11]. These studies confirmed that the improvement of mechanical property of the TaN-soft metal nanocomposite films was dependent on metal contents and annealing time. More importantly, some related studies showed that these composite coatings had an excellent anti-bacteria behavior, due to the exposed Cu or Ag particles [12]. However, from further studies, it was found that the anti-bacteria behaviors might vary depending on the type of metals [13]. For example, Cu might be more effective against Gram-positive bacteria, such as Staphylococcus. *aureus*, while Ag was more effective against Gram-negative bacteria, such as Escherichia. *coli*. Therefore, in order for TaN-soft metal nanocomposite films to extend their applicable areas against bacteria, it could be much interesting to co-deposit Cu and Ag with hard nitride, which may provide a surface film with good tribological behavior and certain synergistic effect against various bacteria. Another area that may need some improvement is the determination of annealing temperature. According to some previous studies, the most suitable annealing temperature for TaN–Ag and TaN–Cu was between 350 °C and 400 °C. To make this type of thin film more practical, it is necessary to lower down the annealing temperature.

In this study, TaN–(Ag,Cu) nanocomposite thin films were prepared by a hybrid process combining reactive three-targets co-sputtering and rapid thermal annealing. After the processing, soft metal particles would form in TaN matrix and on film surface. The effects of annealing temperature on these films' surface morphologies and anti-bacteria behaviors against *E. coli* and *S. aureus* were then studied. The results were compared with those obtained from TaN–Ag's and TaN–Cu's.

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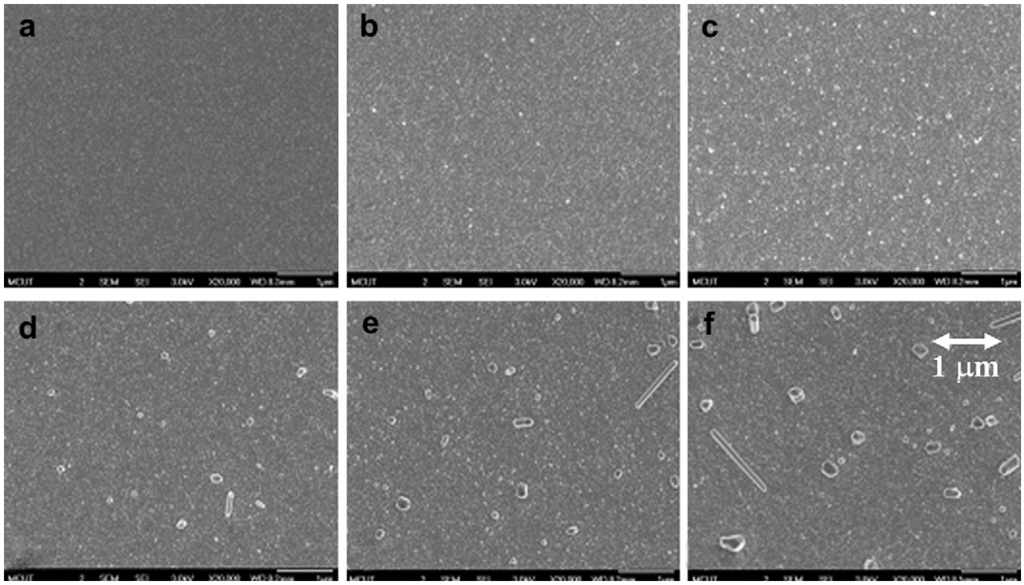


**Fig. 1.** Surface SEM micrographs of TaN–(Ag,Cu) thin films, before and after annealing: (a) un-annealed, (b) annealed at 200 °C, (c) annealed at 250 °C, (d) annealed at 300 °C, (e) annealed at 350 °C, (f) annealed at 400 °C.

## 2. Experimental methods

TaN–Ag, TaN–Cu, and TaN–(Ag,Cu) thin films were prepared on Si(001) substrates using reactive co-sputtering with Ta, Ag, and Cu targets. Each target had a diameter of 50 mm and was tilted by 30°. The distance of target-to-target and target-to-substrate was 150 mm and 100 mm respectively. For deposition, the sputtering system was first pumped down to $7 \times 10^{-4}$ Pa. Then, Ar gas (35 sccm) was introduced to fill the chamber up to 0.65 Pa. During deposition, the power of Ta was kept at 170 W while the powers of Ag and Cu was set at 40 W(RF) and 22 W(DC) respectively in order to prepare films with 11.0 at.% soft metal (with 5.5 at.% of Ag and 5.5 at.% Cu in TaN–(Ag,Cu) films). $N_2$ gas was added at 4.5 sccm to produce stoichiometric TaN. During deposition, the substrate was biased with 40 W (RF), and the temperature was measured to be less than 100 °C. The thickness of these films was about 0.7 μm. Deposition rate was estimated to be 12.5 nm/min. The deposited films were then annealed at 200 °C–400 °C for four minutes by a rapid thermal annealing (RTA) system (SJ, ARTS-150) with ramping rate at 100 °C/s. The flow rate of Ar was fixed at 2000 sccm during RTA, under which the chamber pressure is higher than 1 atm. This can avoid any possible reaction between the samples

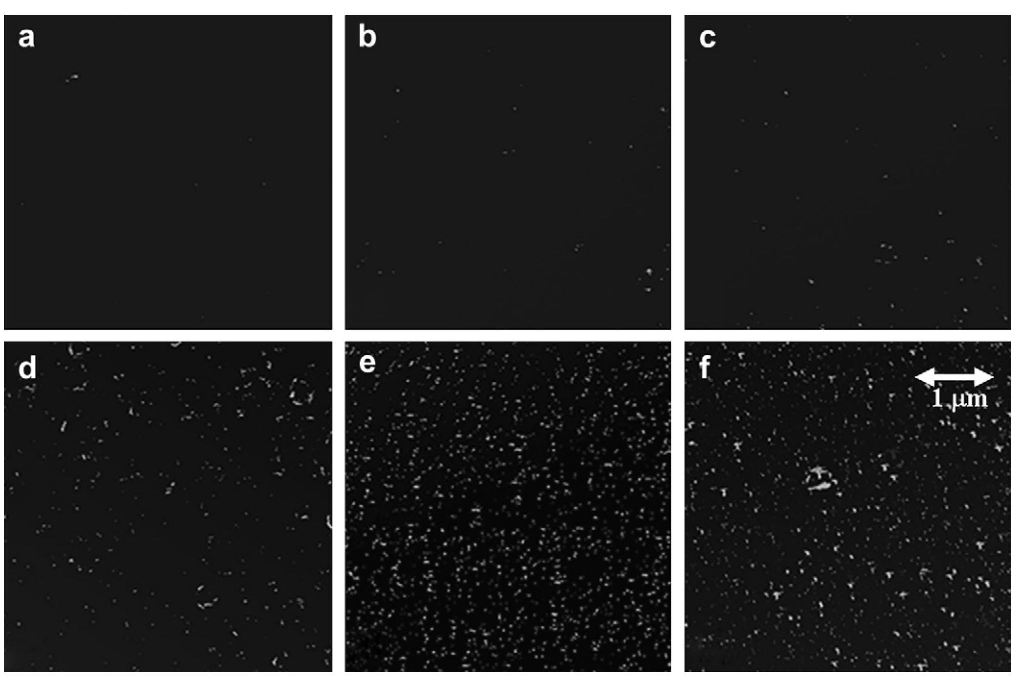


**Fig. 2.** C-AFM micrographs of TaN–(Ag,Cu) thin films, before and after annealing: (a) un-annealed, (b) annealed at 200 °C, (c) annealed at 250 °C, (d) annealed at 300 °C, (e) annealed at 350 °C, (f) annealed at 400 °C. The scanning area is 5 μm × 5 μm.