Antibacterial behavior of TaN–Ag nanocomposite thin films with and without annealing

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C-AFM

A B S T R A C T

TaN–Ag nanocomposite films were deposited by reactive cosputtering on Si. The films were then annealed using RTA (rapid thermal annealing) at 350 °C for 2, 4 and 8 min respectively to induce the nucleation and growth of Ag particles in TaN matrix and on film surface. FESEM (field emission scanning electron microscopy) were applied to characterize Ag nanoparticles emerged on the surface of TaN–Ag thin films. The effect of annealing on the antibacterial properties of these films was studied. The results first confirm that annealing by RTA can cause Ag nanoparticles with various sizes to emerge on the TaN surface. Consequently, the antibacterial behavior will vary, depending on the amount and size of the surfaced Ag particles.

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1. Introduction

It is widely known that materials containing silver may have the most promising antibacterial behavior against some bacteria [1–3]. When Ag atoms transform into ions and enter the environment, the multiplication of bacteria may be stopped, probably due to their engagement with bacteria’s DNA structure [4]. More importantly, these positively charged ions may interact with cell wall membrane (slightly negative), leading to the breakage of the cell wall [4]. The term “antibacterial effect” in this study is then defined as the effectiveness of the TaN–Ag films to stop the multiplication of the bacteria and to kill the bacteria.

However, in many applications, antibacterial property is not the only requirement. Many medical- or biorelated devices or instruments require both antiwear and antibacterial properties. Surgical tools, catheters, hospital equipment, kitchenware are some of the typical examples. Recently, it was reported that the mechanical properties of Ag-doped TaN films could be improved after rapid thermal annealing (RTA) [5]. This is due to the formation of nanosized Ag particles in the nitride matrix. This type of coating is categorized as an nc–MeN/soft-metal (nc: nanocrystalline; MeN: metal nitride) nanocomposite thin film. The nitride phases can be TiN, ZrN, or other hard nitrides while the soft metals can be Cu, Ag, or Ni. Although other metals can also be incorporated into the nitride phase, one of the requirements to form the nc–MeN/soft-metal nanocomposite thin films is the immiscibility between MeN and metal phases.

In the previous study [5], it was also shown that Ag particles could form on the surface of TaN, which implies that these TaN–Ag nanocomposite films could have strong antibacterial effect. In addition, Ta metal and alloys are known to have excellent biocompatibility, which makes TaN an excellent protective coatings in biorelated applications [6]. Ag, as a doping element, is proved not miscible with TaN, which makes the synthesis of TaN–Ag nanocomposite thin films possible [7].

In this study, TaN–Ag nanocomposite thin films were prepared by a hybrid process combining reactive cosputtering and rapid thermal annealing. After the processing, Ag nanoparticles would agglomerate inside the TaN matrix and on the film surface. The objective of this work is to study the effects of annealing time and Ag contents on the films’ antibacterial behaviors. These films could provide good mechanical protection over certain substrates, and show controlled antibacterial behaviors as well. Besides providing mechanical protection, one of the advantages of using these films over simple Ag films is that the release rate of Ag ions can be controlled by controlling particle

Table 1

Deposition conditions and annealing times for the samples used in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power of Ag target (W)</th>
<th>RTA time (min)</th>
<th>Ag concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaN</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>TaN–1.6%Ag–AN–0</td>
<td>13</td>
<td>0</td>
<td>1.6</td>
</tr>
<tr>
<td>TaN–1.6%Ag–AN–4</td>
<td>13</td>
<td>4</td>
<td>1.6</td>
</tr>
<tr>
<td>TaN–1.6%Ag–AN–8</td>
<td>13</td>
<td>4</td>
<td>1.6</td>
</tr>
<tr>
<td>TaN–3.8%Ag–AN–0</td>
<td>16</td>
<td>0</td>
<td>3.8</td>
</tr>
<tr>
<td>TaN–3.8%Ag–AN–4</td>
<td>16</td>
<td>4</td>
<td>3.8</td>
</tr>
<tr>
<td>TaN–3.8%Ag–AN–8</td>
<td>16</td>
<td>4</td>
<td>3.8</td>
</tr>
<tr>
<td>TaN–10.1%Ag–AN–0</td>
<td>20</td>
<td>0</td>
<td>10.1</td>
</tr>
<tr>
<td>TaN–10.1%Ag–AN–4</td>
<td>20</td>
<td>4</td>
<td>10.1</td>
</tr>
<tr>
<td>TaN–10.1%Ag–AN–8</td>
<td>20</td>
<td>4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

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size. Also, the Ag particles can be reborn after being consumed, by another annealing process.

2. Experimental methods

TaN–Ag thin films were prepared using reactive cosputtering with Ta and Ag 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 power of Ag was varied from 13 to 20 W in order to prepare films with different Ag concentrations, as indicated in Table 1. N$_2$ gas was added at 4.5 sccm to produce stoichiometric TaN. The substrates were Si (100) wafers. During deposition the substrate temperature was measured to be less than 100 °C. The thickness of these films was about 700 nm. Some deposited films were annealed for 2, 4 and 8 min respectively at 350 °C using a rapid thermal annealing (RTA) system (SJ, ARTS-150) with ramping rate set at 100 °C/s. The annealing temperature was determined using digital scanning calorimetry (DSC). By judging the

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Fig. 1. SEM micrographs of TaN–10.1%Ag: (a) before annealing (plane view), (b) before annealing (cross-sectional view), (c) after annealing for 4 min (plane view), and (b) after annealing for 4 min. (cross-sectional view).

Fig. 2. XRD patterns for as-deposited TaN and TaN–Ag (10.1 at.% of Ag) thin films before and after annealing for 2, 4 and 8 min: (a) as-deposited TaN, (b) as-deposited TaN–Ag, (c) TaN–Ag after annealing for 2 min, (d) TaN–Ag after annealing for 4 min, (e) TaN–Ag after annealing for 8 min.

Fig. 3. Hardness values of the films, as functions of annealing time and Ag contents.
heat flow in DSC, one can make sure that Ag atoms can agglomerate in the matrix and on the surface of the TaN–Ag films [5].

The phases of the deposited films, before and after annealing, were examined by X-ray diffraction (XRD) technique. The X-ray diffractometer (Philips PW 1830) used monochromatic high intensity Cu Kα radiation (\(\lambda = 1.51418 \text{ Å}\)). The scanning angle was from 25°-2 \(\theta\) to 65°-2 \(\theta\), with a step size of 0.02° and a measuring time of 1.25 s per step. Through this examination, the forming of Ag phase after annealing could be confirmed. For the investigation of surfaced of Ag particles, the coating was examined using field emission scanning electron microscopy (JEOL 6700F). The films' hardness was measured using a nanoindentation instrument (UMIS 2000) with a Berkovich indenter.

Fig. 1 shows the SEM micrographs for one of the TaN–Ag nanocomposite films. It is confirmed that Ag particles can form on the films' surface. The size of the emerged Ag particles ranges from 10 nm to more than 200 nm. Interestingly, many Ag particles are having the shape of nanorod, as seen in Fig. 1(c). Also found from the SEM study is that Ag particle size would increase with the increase of Ag content and annealing time.

3. Results and discussions

3.1. Surface emergence of Ag particles

For the antibacterial testing, the coated and uncoated samples were cut and placed on a tray and then incubated with a calibrated bacterial suspension of E. coli (Escherichia coli, ATCC53010). The samples were then incubated at 37 °C for various times up to 24 h. After incubation, the antibacterial property could be evaluated according to the value of antibacterial efficiency (E) which was calculated according the following equation:

\[ E(\%) = \left( \frac{|A-B|}{A} \right) \times 100\% \]  

where \(A\) = number of viable bacteria with uncoated (standard) sample in the tray; \(B\) = number of viable bacteria with coated sample in the tray.

The value of \(E\) obtained from each sample was then compared as functions of annealing time and Ag concentration.

3.2. Structural analysis

Fig. 2 shows the XRD patterns for the films containing 10.1 at.% Ag, before and after annealing at 350 °C. This figure also shows the effect of antibacterial testing, the coated and uncoated samples were cut and placed on a tray and then incubated with a calibrated bacterial suspension of E. coli (Escherichia coli, ATCC53010). The samples were then incubated at 37 °C for various times up to 24 h. After incubation, the antibacterial property could be evaluated according to the value of antibacterial efficiency (E) which was calculated according the following equation:

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The value of \(E\) obtained from each sample was then compared as functions of annealing time and Ag concentration.
Table 2
Samples that may (Yes) or may not (No) reach 80% antibacterial efficiency in 24 h

<table>
<thead>
<tr>
<th>Annealing Time(min)</th>
<th>Ag contents (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0%</td>
</tr>
<tr>
<td>2 min</td>
<td>1.6%</td>
</tr>
<tr>
<td>4 min</td>
<td>3.8%</td>
</tr>
<tr>
<td>8 min</td>
<td>10.1%</td>
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</tbody>
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<thead>
<tr>
<th>Annealing Annealing Annealing Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
</tr>
<tr>
<td>2 min</td>
</tr>
<tr>
<td>4 min</td>
</tr>
<tr>
<td>8 min</td>
</tr>
</tbody>
</table>

0% No No No No
1.6% No No Yes Yes
3.8% No No Yes Yes
10.1% Yes Yes Yes Yes

of annealing on the microstructure of these samples. Without annealing, there is no Ag phase can be found, which implies that the as-deposited Ag atoms are trapped in the TaN structure. Prior to annealing, the structure evolution is similar to that predicted by Barna and Adamik model [8]. With the increase of Ag contents, a dense fine-grained TaN–Ag film without a columnar structure tends to form. When this structure appears, the hardness would decrease significantly due to the disruption of fine columnar structure [8].

The Ag peaks appears after annealing, which confirms the effect of rapid thermal annealing on the formation of TaN–Ag nanocomposite thin films. With annealing time changed from 2 min to 8 min, Ag (111) and (200) peaks become higher and sharper, especially Ag (111) peak, indicating the growth of Ag particles. However, the patterns of TaN are not affected by the annealing, which means the annealing temperature is not high enough to cause any structure change of TaN. This XRD result is consistent with that of the TaN–Cu nanocomposite thin films reported in Ref. [9].

3.3. Hardness variation

Fig. 3 shows the values of hardness for TaN–Ag films, as functions of Ag contents and annealing time. Apparently, annealing for 8 min can give the samples high hardness, especially for the samples with 1.6 at.% Ag. This is also consistent with TaN–Cu films [9].

3.4. Antibacterial behaviors

The antibacterial efficiency as a function of Ag concentration for those samples annealed for 4 min is presented in Fig. 4. Fig. 5 shows the pictures of the incubators after antibacterial testing. The initial population of the E. coli bacteria is 10^6 CFU (colony forming unit), and the cultivation temperature is 37 °C. It is seen that TaN–10.1%Ag-AN-4 and TaN–3.8%Ag-AN-4 have the most significant short-term antibacterial effect. It is not surprised that TaN–10.1%Ag-AN-4 has a quick antibacterial effect since a large amount of Ag particles can form on the surface. The behavior of TaN–3.8%Ag-AN-4 is the one that needs to be explained. One reasonable explanation is that this sample has much smaller (<10 nm) Ag particles formed on the surface than TaN–10.1%Ag-AN-4, although the total amount of the exposed Ag may be less. These small Ag particles may dissolve in the solution faster due to its size effect [10]. Consequently, the concentration of Ag ions in the solution may reach a critical limit sooner, and, therefore, kill bacteria in a short time. TaN–1.6%Ag-AN-4 may also have the same size effect but the particle density could be too little. This result implies that samples with small Ag particles (<10 nm) may be applied on short-term (<3 h) medical devices to prevent unwanted infections [11]. Finally, Table 2 summarizes the results of antibacterial testing for the samples that may (Yes) or may not (No) reach 80% antibacterial efficiency in 24 h (long term). It is observed that the antibacterial efficiency of these annealed TaN–Ag films is related to Ag contents.

4. Conclusions

TaN–Ag nanocomposite thin films were prepared using a hybrid method that combines reactive cosputtering method and RTA. FESEM was applied to examine the emergence of Ag nanoparticles on the surfaces of TaN–Ag thin films. For the samples with large amount of Ag particles (ex: TaN–10.1%Ag) formed on the surface, the antibacterial effect is obvious. Apparently, it is due to that total exposed Ag amount is high enough. However, for samples having small-size Ag particles (ex: TaN–3.8%Ag) formed on the surface, the antibacterial efficiency could also be significant in short time due to a possible nanosized effect. According to this result, it can be summarized that both Ag particle size and total exposed Ag amount are critical in making short-term antibacterial effect (<3 hrs). For long term (>24 h), the antibacterial efficiency of these annealed TaN–Ag films is related to Ag contents.

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References