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# Electrical properties of TaN–Cu nanocomposite thin films

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**Abstract**

TaN–Cu nanocomposite thin films used as materials for TFR (thin film resistor) were prepared by reactive co-sputtering of Ta and Cu in the plasma of $N_2$ and Ar. After deposition, the films were annealed using rapid thermal processing (RTP) at 400 °C for 2, 4, 8 min, respectively to induce the nucleation and grain growth of Cu. The results reveal that temperature coefficient of resistivity (TCR) values will increase with the increase of Cu content for both the as-deposited and annealed films. The increase of nitrogen will result in higher resistivity and more negative TCR. At a constant nitrogen flow rate, the resistivity and TCR may increase or decrease with the increase of annealing time depending on the Cu content. In general, to reach near-zero TCR value, more copper is needed to compensate the negative effect caused by Ta–N. Thus, electrical properties of thin films can be characterized as functions of $N_2$ flow rate, Cu concentration and annealing time.


*Keywords:* B. Nanocomposites; Resistivity; Thermal coefficient of resistivity; TaN–Cu; Thin film resistor

## 1. Introduction

Sputtered tantalum nitride films used as thin film resistors (TFR) have a wide variety of applications in modern electronic devices. These films have a wide range of electrical resistivity ($\rho$) and temperature coefficient of resistivity (TCR) that can vary with nitrogen content and/or the post-deposition [1]. So far, many efforts have been put in to determine the structural characteristics and understand the electrical behavior of the films [2].

On the other hand, nanocomposite thin films have recently become a very popular area of research due to their promising optical, electrical, magnetic and mechanical properties compared with the coarse-grained materials [3,4]. Furthermore, the metal clusters with a crystalline structure and characteristic sizes of the order of a few nanometers embedded in a ceramic matrix show many special properties which could be used for numerous potential applications [5]. This is mainly due to clusters' large surface to volume ratio. If the cluster size is smaller than the electron mean free path, electron scattering is then mainly caused by the grain boundaries, and hence, both the electrical resistivity and TCR are expected to change dramatically [6].

Experiments [2] show that an annealed tantalum nitride film normally has a negative TCR value while copper would normally possess a positive TCR. It seems rather natural that TaN–Cu composite could demonstrate a near-zero TCR and be highly stable as long as copper and nitrogen concentrations are well controlled. In this paper, TaN–Cu nanocomposite thin films were prepared using a reactive co-sputtering method. During deposition, the nitrogen flow rate and copper content were varied. After deposition and annealing, the structural and electrical properties, especially resistivity and TCR, were then characterized as functions of nitrogen flow rate, copper content and annealing time.

## 2. Experimental procedures

### 2.1. Deposition

TaN–Cu thin films were prepared using reactive co--sputtering with Ta and Cu targets. Each target had a diameter of 100 mm and was tilted by 30°. The distance of target-to-target and target-to-substrate is 200 and 150 mm, respectively. For deposition, the sputtering system was first pumped down to $7 \times 10^{-4}$ Pa and then Ar gas (60 sccm) was introduced to fill the chamber up to 0.93 Pa. During deposition, the power of Ta was kept at 250 W while the power

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of Cu was set at 40 W. By changing the location of the substrates, various Cu concentrations could be obtained. To introduce nitrogen into the prepared films, $N_2$ gas was also added at various amounts. The substrates were Si (1 0 0) with 50 nm $SiO_2$ grown on the surface. The thickness of these films was about 500–700 nm. Some deposited films were annealed for 2, 4, 8 min, respectively at 400 °C using rapid thermal processing (RTP) system (JIPLEC, JETFIRST). The annealing conditions would allow Cu clusters to form.

### 2.2. Characterization

Compositions of the films were determined using X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Ultra). Crystal structures of the films were analyzed by X-ray diffraction (XRD) measurement (Philips, PW 1830). Transmission electron microscopy (TEM) (JEM-2010) was used to identify different phases. Resistivity and TCR of the films were measured by a four-point probe attached with a hot stage. The whole probe stand was enclosed in a cabinet with Ar atmosphere. TCR values were calculated from the following equation [5]:

$$\mathrm{TCR}(\mathrm{ppm}/^{\circ}\mathrm{C}) = \frac{1}{\rho_{25}}\left(\frac{\rho_{150}-\rho_{25}}{150-25}\right)\times 10^{-6} \qquad (1)$$

where $\rho_{150}$ and $\rho_{25}$ are the resistivity of the measured film at 150 and 25 °C, respectively.

## 3. Results and discussion

In the preparation of TaN–Cu nanocomposite thin films, copper was sputtered simultaneously with tantalum in Ar and $N_2$ atmosphere, with nitrogen flow rate ranging from 0 to 8 sccm. With the varied $N_2$ flow rate, β-Ta, $Ta_2N$, TaN and Cu phases can be identified in the films, and resulting in different electrical properties. After deposition, RTP was used to anneal the films at 400 °C for 2, 4, 8 min, respectively. Then both the as-deposited and annealed samples were characterized. Fig. 1 shows the XRD pattern of a Cu-riched and a TaN-riched sample ($N_2$: 8 sccm), before and after annealing for 2, 4, 8 min. Compared with pure TaN and Cu, the peaks are shorter and broader, which suggests finer crystal grains and the existence of a near-amorphous phase [6,7]. With the increase of annealing time, Cu (1 1 1) and Cu (2 0 0) (Fig. 1a) become much sharper, especially the Cu (1 1 1) peak, which indicates better crystallinity and larger grain size of Cu grains. However, no significant change in the shape and intensity of TaN peaks is found. In TaN-riched film (Fig. 1b), Cu (1 1 1) and Cu (2 0 0) peaks become sharper just like the case in Fig. 1a and not much change with TaN peaks even for long annealing time. Thus, it can be concluded from Fig. 1 that annealing at 400 °C has a more obvious effect on the Cu grain growth than that of the TaN phase.

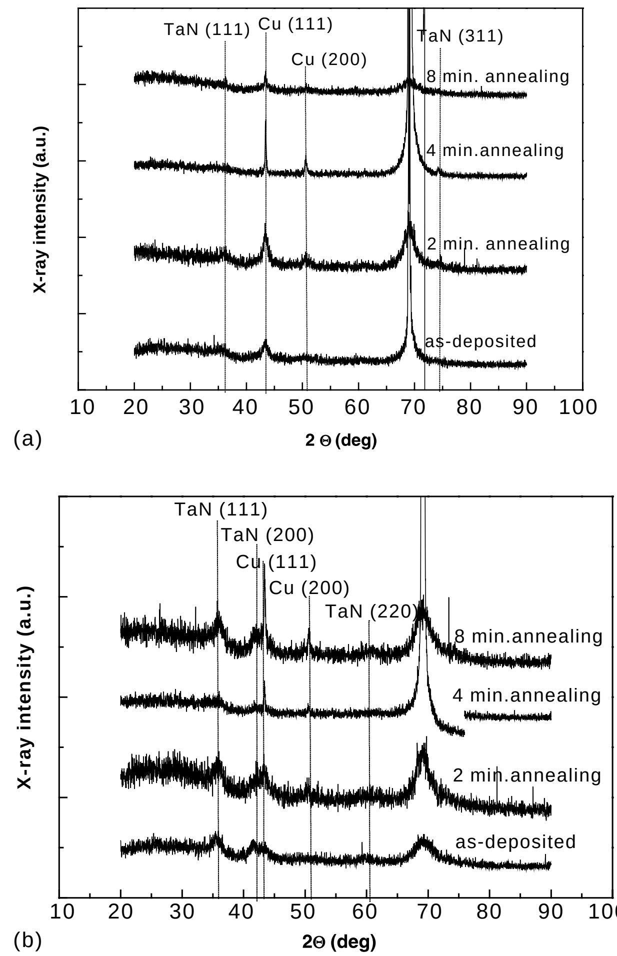


Fig. 1. XRD patterns of (a) Cu-riched (Cu = 75 at.%) and (b) TaN-riched (Cu = 30 at.%).

Fig. 2 shows three TEM images with diffraction patterns for a TaN-riched samples before and after annealing for 2 and 8 min. It is evident that copper clusters of 5 nm in diameter are formed after annealing for 2 min and become bigger for a longer annealing time, which matches well with the appearance of Cu peaks in XRD results. Also observed from the diffraction pattern is that these films may contain certain degree of amorphous phase as evidenced by diffused diffraction rings. This is also well consistent with the XRD results that show broadened diffraction peaks, indicating the possible existence of near-amorphous structure. Zeng et al. [8] also reported the possibility of forming amorphous structure in Ta–Cu alloy films.

Fig. 3 shows the resistivity change as functions of Cu content and annealing time. Prior to annealing, the resistivity seems to follow Nordheim's rule for randomly mixed elements. A maximum is found at 40–50 at.% Cu. The resistivity is further increased after annealing for 2 and 4 min and reaches the maximum when annealed for 4 min. This is mainly due to the continuous formation of randomly distributed Cu nano-particles embedded in TaN matrix. The occurrence of nano-sized Cu particles may enhance the

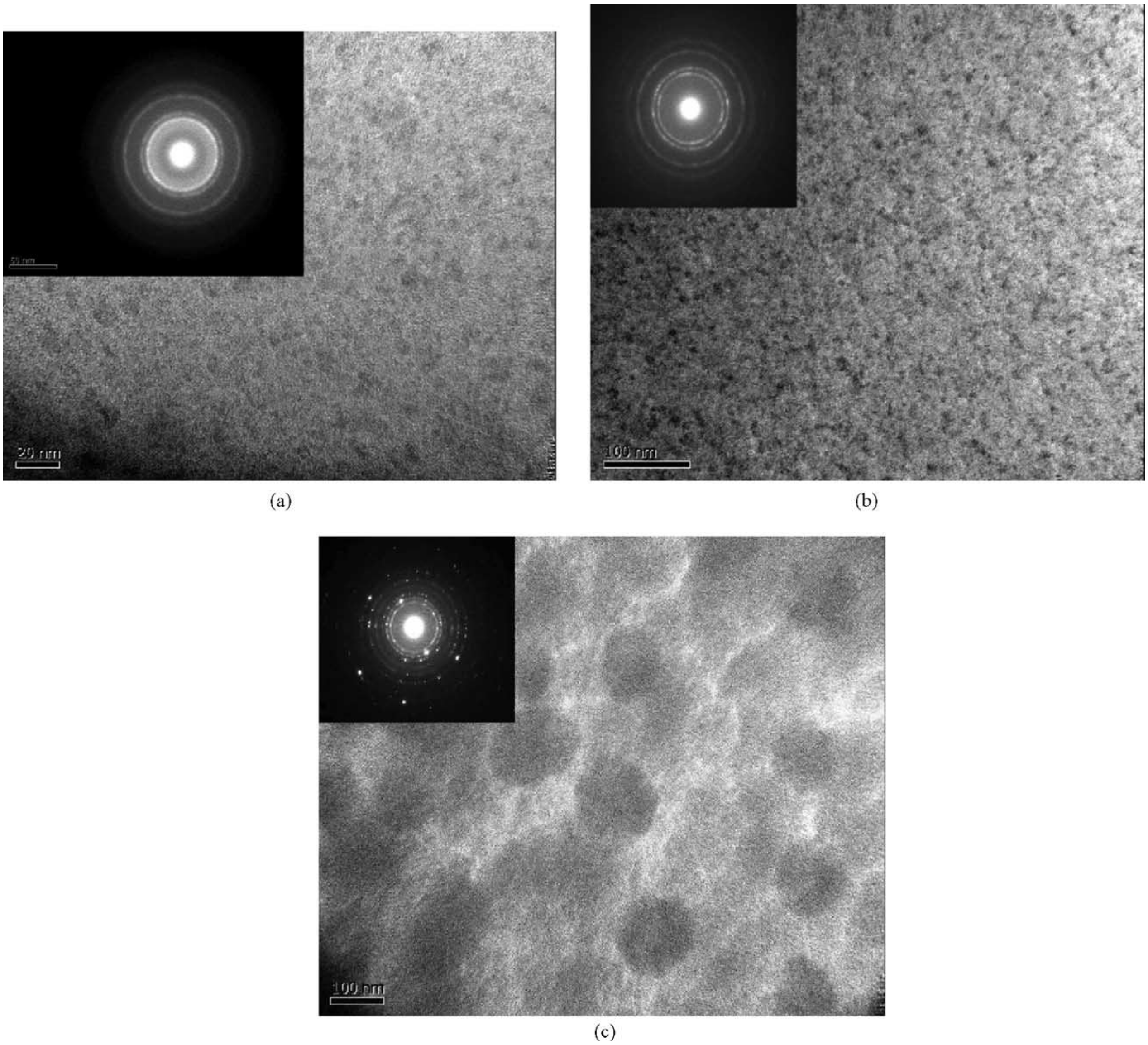


Fig. 2. Bright field TEM micrographs and selected area diffraction patterns of a TaN–Cu film: (a) as-deposited (b) 2 min annealing, (c) 8 min annealing.

probability of electron scattering, thus resulting in higher resistivity. With particle size smaller than few nanometers, grain boundary scattering could be the dominating factor that causes the increase of resistivity [4]. After annealing for 8 min, the resistivity decreases compared with that of the film annealed for 2 and 4 min. The better crystallinity quality and bigger grain size of Cu could explain this. For Cu-riched TaN–Cu films, the resistivity is nearly not affected by annealing. This result could be due to the switching of the continuous phase (matrix). For the Cu-riched films, TaN nanoparticles are embedded in the copper matrix, which is a reverse situation to that of the TaN-riched films. The temperature (400 °C) used for annealing may not be high enough to cause the grain growth of TaN particles, which results in the stable resistivity for Cu-riched films.

Fig. 4 shows the change of TCR as functions of annealing time and Cu content. Prior to annealing, the as-deposited TaN-riched films have far more negative TCR than TaN (−800 ppm/°C). This could be due to the existence of amorphous phase. Amorphous phase is known to contribute negatively to the total TCR because of its weak localization effect [8,9]. With the increase of Cu content, tiny Cu particles begin to form, making TCR shift towards the positive side. Eventually, a near-zero TCR point is found at Cu-riched side (Cu ≈ 75 at.%). Fig. 4 also shows that annealing for 2 and 4 min will cause TCR to be more negative and reaches to the minimum when annealed for 4 min. However, when annealing for 8 min, TCR will become less negative compared with that of the films annealed for 2 and 4 min. With the increase of annealing time, the zero-TCR point will shift to the left side with less Cu, which means the stronger offset effect by grown Cu grains. In Cu-riched side, however, TCR will become more positive when annealed for longer time, showing more and more metal-like behavior.

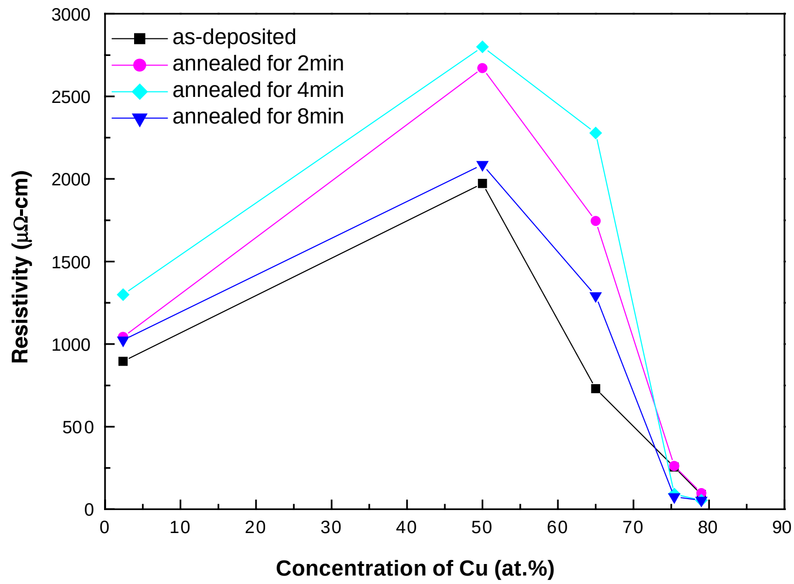


Fig. 3. Resistivity of the TaN–Cu films versus Cu concentrations before and after annealing.

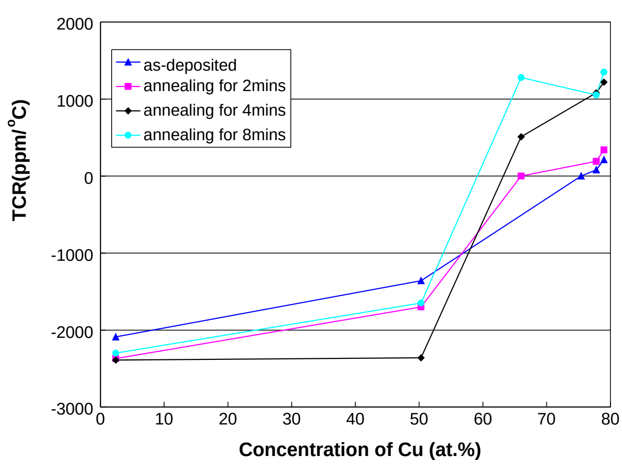


Fig. 4. TCR values of the TaN–Cu films versus Cu concentrations before and after annealing.

Fig. 5 shows the TCR values for the TaN–Cu films annealed for 2 min with the variation of nitrogen flow rates ranging from 0 to 8 sccm. It can be seen that these TCR values are affected by both Cu content and nitrogen flow. More Cu and less nitrogen in the film will result in less negative TCR. With the increase of nitrogen flow, the zero-TCR point is shifting toward Cu-riched side, which means that more Cu is needed to compensate the negative effect of nitrogen.

Fig. 6 shows the resistance change as a function of annealing temperature (25–150 °C) of three TaN–Cu films: TaN-riched, zero-TCR, and Cu-riched. The slope at every point of the plot is the TCR at the corresponding temperature. It can be seen clearly that for TaN-riched film, TCR is negative and remains almost constant within the range of testing temperature, showing a stable semiconductor-like behavior. For Cu-riched film, TCR is much more positive and unchanged with the change of temperature, exhibiting

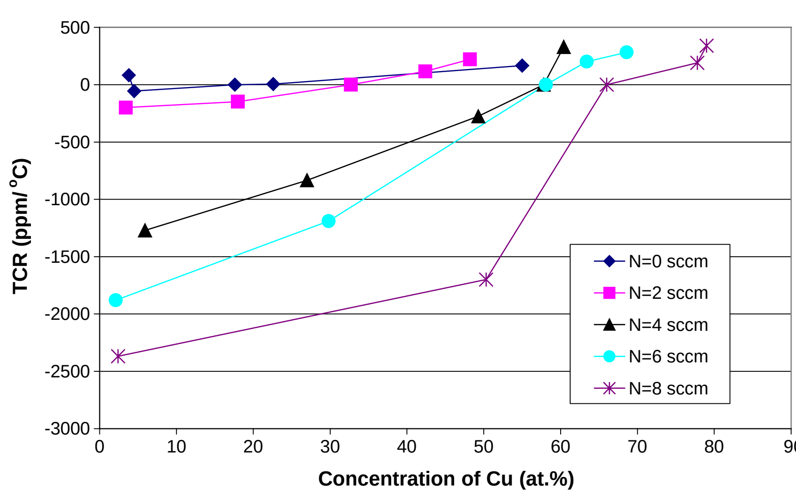


Fig. 5. TCR values of the TaN–Cu films versus Cu concentrations before and after annealing, with the variation of nitrogen flow rate.

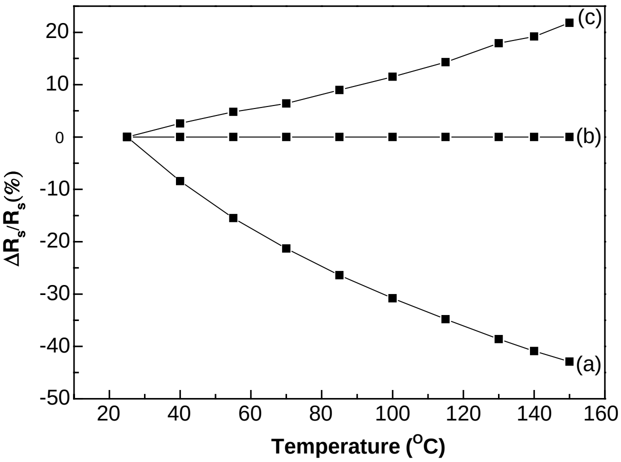


Fig. 6. Resistance change with the variation of temperature for (a) TaN-riched, (b) zero-TCR and (c) Cu-riched films.

normal metal properties. This figure also shows an example of temperature-insensitive resistivity obtained from a zero-TCR film.

## 4. Conclusion

TaN–Cu nanocomposite thin films were prepared using a reactive co-sputtering method. During deposition, nitrogen flow rate and copper content were varied. After deposition, rapid thermal annealing was applied to the films at 400 °C for 2, 4, 8 min, respectively. The structural and electrical properties (resistivity and TCR) were then found to be directly related to annealing time, Cu content, and nitrogen flow. The results reveal that more Cu will result in the increase in TCR. The resistivity will first increase then decrease after reaching a maximum value. More nitrogen will cause the increase in resistivity and decrease in TCR. Generally, in order to reach near-zero TCR, more copper and a suitable annealing is needed to compensate the increase of nitrogen concentration.

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