Electrical and mechanical properties of Ta-N-Cu nanocomposite thin films

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**ELECTRICAL AND MECHANICAL
PROPERTIES OF TA-N-CU
NANOCOMPOSITE THIN FILMS**

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SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2007

Electrical and Mechanical Properties of Ta-N-Cu Nanocomposite Thin Films

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Abstract

Sputtered tantalum nitride (TaN) thin films can be used as thin film resistors (TFRs), since these thin films have been proved to have a wide range of electrical resistivity (ρ) which is around $400\sim 3\times 10^4 \mu\Omega cm$, and a relatively low and stable temperature coefficient of resistivity (TCR). However, the TCR of TaN thin film is normally negative ($-150 \text{ ppm}/^\circ\text{C}\sim -50 \text{ ppm}/^\circ\text{C}$) which will create a serious thermal stability problem for the performance of TaN TFRs.

On the other hand, nanocomposite thin film shows many special and superior properties that can be used in numerous potential applications, since it is a multi-phase thin film. Nanocomposite thin films can be defined as the thin films that are composed of at least two different phases with one or more presenting in nano-scale. In this study, Cu phase acting as the second phase was incorporated into TaN matrix in order to tune the negative TCR of TaN. Experimental results show that annealed TaN thin films have a negative TCR ($-850 \text{ ppm}/^\circ\text{C}$) while Cu films would normally give a positive TCR ($+4300 \text{ ppm}/^\circ\text{C}$). It seems rather natural that TaN-Cu nanocomposite could demonstrate a near-zero TCR and the experiment result show that when proper Cu concentrations reach to 66 at.%~75 at.%, a zero-TCR could be obtained.

In this project, Ta-N-Cu thin films with various nitrogen (10 at. %~45 at.%) and Cu content (2.1 at. %~80 at.%) were prepared using a reactive co-sputtering method. After deposition, the films were annealed using rapid thermal processing (RTP) at

400°C for 2, 4, 8 minutes respectively in order to induce the nucleation and grain growth of Cu particles. The annealing temperature at 400°C was determined by DSC result for TaN-Cu thin films. The DSC result shows that Cu began to crystallize from 300°C and above until 400°C, thus 400°C was chosen to anneal the films. The electrical properties (ρ and TCR) and the microstructures were then characterized. It was found that resistivity and TCR would change as functions of Cu concentration, N_2 flow rate, and annealing time. The resistivity ranges from 125 $\mu\Omega\cdot\text{cm}$ to 2750 $\mu\Omega\cdot\text{cm}$ and TCR has a range from -2400 ppm/°C to 1500 ppm/°C with the change of annealing time from 2 minutes to 8 minutes, N_2 from 0 sccm to 8 sccm, and Cu content from 2.1 at. % to 80 at. %. It is exciting to find that between the negative and positive TCR, a zero-TCR can always be obtained in Cu-rich films with a Cu content from 66 at. % to 75 at. %. As a conclusion, in order to achieve a zero-TCR, a suitable balance among annealing time, Cu concentration, and N_2 flow rate must be reached. These zero-TCR films would be suitable for TFR application.

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List of Symbols

ρ	Resistivity
TCR	Temperature coefficient of resistivity
Y	Young's modulus
H	Hardness
A	Contact area
E	Elastic modulus
P	Test indentation load
T_m	Melting point
T_s	Substrate temperature
V_s	Substrate bias
λ	X-ray wavelength
ν	Poisson's ratio
θ	Brag angle
γ	Gauge factor
R_s	Sheet resistance
L	Film length
W	Film width
D	Film thickness
K	Constant for R_s calculation
$d.r.$	Deposition rate
A	Neutral charged atom
$h \nu$	Photo energy

Scm

Standard cubic centimeters per Minute

Chapter 1 Introduction

1.1 Background

Resistors are essential components in any electrical circuit requiring current regulation or voltage division [1]. Since World War II, a rapid development in microelectronics has brought a revolution to the electronic circuits and the electronics system, making them much smaller, quicker, cheaper and more integrated. In order to achieve this, miniaturization of essential passive components, like resistors is unavoidable. Since then, intensive researches have been conducted to obtain smaller physical sizes, better performance and higher reliability.

Initially, thick film resistor was developed and fabricated by thick film printing method. However, the low reliability and poor performance like poor temperature coefficient of resistivity (TCR) has limited its application. On the other hand, thin film resistor (TFR) was invented and has been dominating extensively in practical use due to its smaller physical size and better performance. The earliest forms of TFR were developed in Germany in 1950's based on 'cracked-carbon' that was deposited onto ceramic cores during a high-temperature chemical vapor deposition (CVD) process. The performance of these carbon-film resistors was greatly improved [2].

For TFR, the basic requirement and most important character are a stable and near-zero TCR [3], otherwise it will create a serious thermal stability problem for the performance of TFR. So TCR is the main electrical property by which different types of resistors, positive TCR (PTCR) or negative TCR (NTCR) TFRs, are most often characterized or differentiated.

So far, the most widely used TFRs are NiCr, RuO₂, and TaN TFR. Among them, NiCr TFRs, nichrome, are the earliest developed and most widely used metallic TFRs. However, it was later discovered that nichrome had a nonlinear TCR and is subject to electromigration under high humidity. For these reasons, other material, ruthenium oxide (RuO₂) and tantalum nitride (TaN) have been developed at Bell Labs.

RuO₂ TFR is a further improvement over NiCr thin film resistors with its high thermal stability and acidic or environmental hardness. However, it was found that a PTCR would be obtained when films were deposited at relatively high temperature and films deposited at relatively low temperature would give a NTCR. So, this material is very sensitive and it is very hard to precisely control the TCR of RuO₂. In this case, another material, TaN is more superior and desirable in this respect.

TaN TFR is more attractive than NiCr and RuO₂ TFRs, since it owns a linear TCR, physiochemical inertness, suitable hardness, corrosion and wear resistance. Nitrogen doped tantalum resistive thin films (Ta-N) have been known to be the best resistive thin films. TaN thin films can be deposited by magnetron reactive sputtering, and a post-deposition annealing will be usually applied to stabilize the as-deposited thin films. However, even by controlling the deposition parameters and application of thermal annealing after deposition, TaN still has an intentional negative TCR, which can be controlled to be within the range of $-150 \sim \pm 5$ ppm/°C. This negative TCR will cause thermal stability problems for TFRs, especially those used for high precision networks.

On the other hand, nanocomposite thin films are attracting increasing interest due to their superior optical, mechanical, and electrical properties [4]. A novel type of

nanocomposite thin films, cermet, with nano-sized metal particles embedded in the ceramics matrix is gaining much more attention since the nano-sized metal particles will have a strong influence on the properties of the films [5]. It has been proved that this film would undergo a transition from semiconductor to metal with the continuous increase of the metal content [6]. Thus, it is expected to find a zero-TCR point during this transition, which is the exact spark of our project. Based on this finding, we try to incorporate Cu, a metal with positive TCR, into TaN, a semiconductor with negative TCR to achieve a zero-TCR in this study.

1.2 Objective

1. Characterization of the microstructures by means of XRD, TEM and XPS analysis and electrical properties by four-point probe for Ta-N thin films as functions of N_2 flow rate (0~12 sccm) and annealing at 400°C for 2, 4, and 8 minutes.
2. Characterization of the microstructures and electrical properties of Ta-N-Cu thin films with emphasis on the effects of Cu content (2.16 at. %~80 at.%), annealing time (2, 4, and 8 minutes at 400°C), and N_2 flow rate (0~8 sccm) on the change of resistivity and TCR. By XRD, TEM and XPS analysis, the microstructures and the chemical state of Ta, N, and Cu can be investigated.
3. Study of the piezoresistive (gauge factor) and mechanical properties (hardness and Young's modulus) of Ta-N-Cu thin films for the basic knowledge of these thin films as functions of Cu content (2.16 at. %~80 at.%), N_2 flow rate (0~8 sccm) and annealing time (2, 4, and 8 minutes at 400°C).

2.5 Scope

1. Deposition of Ta-N and Ta-N-Cu thin films by d. c. magnetron reactive co-sputtering technique. Subsequently, rapid thermal annealing (RTA) at 400°C for 2, 4, and 8 minutes was applied to stabilize the TaN and cause the nucleation and grain growth of Cu particles.
2. After that, the as-deposited and annealed thin films were characterized using XRD (X-ray diffraction), TEM (transmission electron microscopy), and XPS (X-ray photoelectron spectroscopy) for the analysis of crystal phases, microstructures and chemical states of elements respectively.
3. High temperature four-point probe with hot stage attached was applied to measure the resistivity and TCR. TCR and resistivity of Ta-N-Cu will then be studied as a function of Cu content (2.16 at.%~80 at.%), N₂ flow rates (0~8 sccm) and annealing time (2, 4, and 8 minutes at 400°C). Consequently, an optimized Ta-N-Cu nanocomposite thin film with zero-TCR was found when Cu is between 66 at. % and 75 at. %.
4. Strain gauge factor was also measured by a hand-made three-point bending equipment. Finally, hardness and Young's modulus were tested by using nanoindentation technique as functions of Cu content (2.16 at. %~80 at.%), N₂ flow rate (0~8 sccm) and annealing time (2, 4, and 8 minutes at 400°C).

Chapter 2 Literature Review

2.1 Description of thin film

Thin film is defined as the $1\sim 10^4$ of atomic layer or molecular layer deposited along the normal direction of the substrate, which is normally ceramics, glass or silicon. It can also be classified as a resistive or conductive coating layer that is deposited onto bulk materials (substrates) to achieve surface properties unattainable or not easily attainable in the substrates alone [7]. Table 2-1 shows thin film applications in six broad categories.

Table 2-1 Thin-Film Applications [8]

Thin-film property category	Typical applications
Optical	Reflective/antireflective coatings Interference filters Decoration (color, luster) Memory discs (CDs) Waveguides
Electrical	Insulation Conduction Semiconductor devices Piezoelectric drivers
Magnetic	Memory discs
Chemical	Barriers to diffusion or alloying Protection against oxidation or corrosion Gas/Liquid sensors
Mechanical	Tribological (wear-resistant) coatings Hardness Adhesion Micromechanics
Thermal	Barrier layers Heat sinks

2.2 Preparation of thin film

Thin film deposition techniques can be broadly classified as either physical or chemical. Under physical methods we have vacuum evaporation and sputtering, where the deposition takes place after the material to be deposited has been transferred to a gaseous state either by evaporation or an impact process [9]. In this project, the technique used to prepare Ta-N-Cu thin films is magnetron-sputtering PVD.

2.2.1 Magnetron sputter source

The class of sputter sources called magnetrons has a magnetic field at about 50 to 500 gauss parallel to the target surface, which in combination with the electric field causes the secondary electrons to drift in a closed circuit, or ‘magnetron tunnel’, in front of the target surface. This electron confinement significantly increases the efficiency. Usually, magnetron sputtering is used to enhance the efficient use of secondary electrons, resulting in higher gas ionization rate. Figure 2-1 shows a cross-sectional view of a typical planar magnetron. One disadvantage of the planar magnetron is poor utilization of the target material, which is typically 20-30 % of the starting target material. However, this problem can be overcome by providing relative motion of the target with respect to the magnets.

Figure 2-1 Cross sectional view of a planar magnetron sputter source

Magnetrons work well with either r.f. or d.c. power. The magnetic field doesn't affect the ion motion; however, due to electrostatic attraction, the ions move with the electrons, keeping the plasma neutral. In a conventional magnetron, most of the discharge is confined close to the cathode surface and, therefore, bombardment of the growing film by electrons and ions is minimized. Substrate bombardment can be significantly increased by 'unbalancing' the magnetics. In an unbalanced magnetron, the flux from the north pole is unequal to that entering the south pole, as indicated in Figure 2-2. This configuration gives larger ion currents and electron currents to the substrate. Electrons are channeled along field lines extending from the discharge region to the substrate, and the ions are electrostatically dragged by the electrons and, thereby, bombard on the substrate. In practice, it is difficult to construct a perfect, 'balanced' magnetron because magnetic field lines are difficult to focus. Thus, magnetron sources are always accompanied by substrate bombardment by ions and electrons from the plasma discharge.

Figure 2-2 Schematic representation of an unbalanced magnetron

2.2.2 Reactive sputtering

Dielectric coatings, such as oxides and nitrides, can be deposited either by sputtering an insulating target of the desired material, or by reactively sputtering a metal target in a mixture of an inert and a suitable reactive gas. This project makes use of the reactive sputtering method.

The traditional method of reactive sputtering involves introducing sufficient reactive gas into the chamber to keep the target completely covered with dielectric. This 'covered-mode' operation is limited by the low sputter yield of the dielectric layer. On the other hand, high-rate reactive sputtering can be achieved in the 'metallic-mode', where the sputter eroded area of the cathode remains bare, while sufficient reactive gas is present at the substrate to form the dielectric compound. Figure 2-3 illustrates the two modes of reactive sputtering.

Figure 2-3 Two modes of reactive sputtering: (1) covered-mode and (2) metallic-mode

2.2.3 Co-sputtering

Co-sputtering is a process with simultaneously sputtering from more than one target material to form alloyed composite on the substrate. **Figure 2-4** is the schematic of a co-sputtering system. Co-sputtering is a preferred sputtering method to fabricate alloyed composite materials having a controlled composition by precisely and independently controlling the power applied to each magnetron target. Co-sputtering is more desirable in achieving the same composition of thin films as the alloy target.

Figure 2-4 A schematic of co-sputtering system

2.3 Microstructure of thin film

2.3.1 Structure of single-phase thin film

By control of film microstructure, film properties can be promoted. Microstructure is determined primarily by the surface and near-surface environments during film growth, more specifically, the adatom mobility. The main parameters for the control of adatom mobility are the substrate temperature and particle bombardment.

The microstructure of a single-phase film can be described by the so-called structural zone model developed by Movchan and Demchishin and modified by Thornton for sputtered films [10]. Figure 2-5 shows the zone diagram of film morphology and structure as a function of normalized temperature (T/T_m) and Ar pressure (ion bombardment).

Figure 2-5 Zone diagram of film morphology and structure as a function of normalized temperature (T/T_m) and sputtering pressure or energy per deposited atom for sputtered films [11]

As shown in Figure 2-5, the microstructure of sputtered films is usually classified in terms of four zones. Zone 1 structure, consisting of tapered columns and significant voids between columns, is prevalent when the ratio T/T_m is less than 0.3. Zone 2 is usually found when $0.3 < T/T_m < 0.5$. Zone 2 structures are characterized by columnar, platelet, or whisker grains separated by dense intercrystalline boundaries. Zone 3 occurs at high relative temperatures, $T/T_m > 0.5$. Zone 3 is associated with equiaxed grains and epitaxial growth on the substrate.

The fourth zone, zone T ('transition'), is the result of bombardment-induced surface mobility. It is a plasma related microstructure zone. Zone T films, produced by bombardment, tend to have smooth surfaces, high densities, high hardness and intrinsic stress and other properties close to the bulk values. Thus, these films are usually the desired types of coatings for applications [12]. Films that would have been expected to be zone 1 structures on the basis of T/T_m can be grown to zone T structure by bombarding the growing film with energetic particles during film growth. The main bombarding species in case of magnetron sources are ions and energetic neutrals.

2.3.2 Structure of alloy thin film

The model presented above doesn't work when impurities or additives are incorporated in the film [13, 14]. Impurities or additives stop the grain growth and stimulate a re-nucleation of the grain that results in the granular structure. In order to describe the microstructure of thin film with alloying element, Barna and Adamik [15] developed a two-phase film microstructure model as shown in Figure 2-6.

Figure 2-6 Schematic diagram of the effect of impurities or additives on the microstructure [15]

With the alloying element increasing from low content to medium content and finally to high content, the grain size becomes finer and changes from a porous column structure to a very dense and granular structure in all of the four zones, especially in zone 1. Accordingly, the change in microstructure will cause the corresponding change in the properties of the materials due to the mixing effect.

For instance, SEM pictures for ZrN-Cu two-phase thin films with a low Cu content of 1.2 at. % and a higher Cu content of 20 at. %. SEM results show that the incorporation of Cu into the ZrN films would make the ZrN (111) preferred orientation with columnar structure transit into a denser and finely grained structure with randomly distributed orientation, as shown in Figure 2-7 [16].

Figure 2-7 SEM fracture morphology of ZrN-Cu nanocomposite thin films for (a) with 1.2 at. % of Cu and (b) with 20 at. % of Cu [16]

2.4 Electrical Properties of Thin Film

Thin film properties refer to the film's interactions with its environment. These interactions determine the film's performance in its application. It is well known that thin film properties are governed by microstructure and thin film microstructure is very different from the coarse-grained bulk material. In this section, the general electrical properties of thin films will be reviewed.

There are two main considerations when it comes to the electrical properties of thin films. They are the electrical resistivity and TCR. Thin films possess unique characteristics in conductivity that is different from bulk, and the most important factors are the size effect that arises due to the small dimensions.

2.4.1 Resistivity

Electrical resistivity of thin films is mainly caused by the electron scattering from the thin film surface and grain boundaries. Electron scattering from film surface happens when an electron fails to execute the full mean-free path and is interrupted through collision with the film surface. The electrons then undergo either elastic or inelastic scattering. In elastic scattering the resistivity is almost the same as in the bulk, and there is no film thickness effect on resistivity. If the collision is inelastic, the electron trajectory after collision is independent of the impinging direction, and the subsequent scattering angle is random. Thus resistivity rises due to fewer electrons flowing through the reference plane registering current flow. The calculation of resistivity value will be introduced in chapter 3 when four-point probe is mentioned.

The same principle applies to grain boundary scattering. Grain boundaries, across which crystal orientations change, are expected to be effective electron scatterers and behave like film interfaces in this regard. As the crystallite size becomes smaller than the electron mean-free path, a contribution to the film resistivity from GB scattering arises.

In almost all cases, thin metal and semi conductive films are more resistive, while insulating films are more conductive than their respective bulk counterparts.

2.4.2 TCR

Temperature Coefficient of Resistivity is another so important parameter related with transport properties in thin films, especially when thin films are used as TFRs. The most basic and important requirement for TFRs is to obtain a stable near-zero

TCR [17]. A near-zero TCR is also absolutely advantageous and necessary in integrated circuit operation.

TCR explains exactly the thermally electrical stability of thin films, which refers to small, normalized changes around a reference temperature. TCR (α_0) is defined as the fractional change in the resistivity per unit temperature increase at the reference temperature T_0 , that is,

$$\alpha_0 = \frac{1}{\rho_0} \left[\frac{\delta \rho}{\delta T} \right]_{T=T_0} \quad (2-1)$$

where ρ_0 is the resistivity at the reference temperature T_0 , usually 273 K (0°C) or 293 K (20°C), and $\delta \rho = \rho - \rho_0$ is the change in the resistivity due to a small increase in temperature, $\delta T = T - T_0$.

When the resistivity follows the Matthiessen's rule $\rho = AT + B$, then according to equation 2-1, α_0 is constant over a temperature range T_0 to T , and equation 2-1 leads to the well-known equation,

$$\rho = \rho_0 [1 + \alpha_0 (T - T_0)] \quad (2-2)$$

This equation is actually only valid when α_0 is constant over the temperature range of interest, which requires the Matthiessen's rule to hold. Normally, there are two kinds of TCR, one is the linear positive TCR for pure metals and the other is the linear negative TCR for semiconductors, as shown in Figure 2-8.

Figure 2-8 two types of TCR found in (a) most metallic thin films and (b) most semiconductive thin films

As illustrated above, for most metallic thin films, the resistance arises from the electrons scattering from lattice thermal vibrations and impurities, defects, interstitial atoms, film surface and grain boundaries. The former one increases as temperature increases, while the latter one shows very little temperature dependence. When temperature increases, the overall resistivity increases, which results in the positive TCR. On the other hand, for semi-conductive films, TCR value is usually negative since the main conduction mechanism is thermally activated.

2.4.3 TCR tuning

For achievement of a zero-TCR, many efforts have been made to tune the positive or negative TCR to be zero. The most conventional method is by thermal annealing [17], however, the tuning range for resistive films is very small. Another method is to prepare multi-layered TFRs, such as $\text{RuO}_2/\text{Ta}_2\text{N}$ double layer TFR [18, 19]. In our

project, a new concept of “nanocomposite” thin films will be introduced in order to achieve a zero TCR. In this case, nanocomposite thin films with Cu metal particles embedded in TaN matrix were prepared and it was expected to offset negative TCR of TaN matrix by metallic Cu phase with positive TCR.

2.4 Mechanical properties

Due to the big difference in the microstructure between bulk material and thin film, mechanical properties including hardness, toughness, adhesion, stress, and so on are quite different from that of the bulk material [20]. Grain size and film texture are among the important microstructural characteristics that govern the mechanical response of thin films. It was observed that as the grain size decreases, the hardness of the films increases [21].

Hardness can be defined as the resistance of materials to plastic deformation while young's modulus is a measurement of the stiffness of a material. Hardness of thin films can be determined by ‘nanoindenter’, a miniaturized version of Vickers hardness test for bulk materials, in which the point of a pyramidal diamond stylus is pressed onto the surface with a specified force. The size of the resulting dimple is inversely related to hardness. The film should be thicker than about 10 times the depth of the dimple so as to avoid substrate influence. Hardness can be calculated using the following formula:

$$H = \frac{P}{A} \quad (2-3)$$

where P is the test indentation load, A is the contact area. The load can be read directly, while the contact area can be determined with different methods. During the indentation, a load-displacement curve is obtained. Based on different load-

displacement curve analysis, there are several hardness test methods, and the most widely used method is that of Oliver and Pharr, with its load-displacement curve shown in Figure 2-9.

Figure 2-9 Load-displacement curve for Oliver and Pharr method

The stiffness of a material is characterized by its elastic modulus or Young's modulus, Y (Pa), defined as,

$$\epsilon_x = \frac{\sigma_x}{Y} \quad (2-4)$$

Y varies with microstructure, so its value in a thin film is not necessarily the same as in the bulk material.

2.5 Piezoresistive properties

Piezoresistance effect means a change in electrical resistance of a specimen, when it is subjected to a physical strain. The use of a strain gauge employs this phenomenon. The strain gauge factor γ is defined as

$$\gamma = \frac{1}{R_0} \frac{\Delta R}{\Delta \varepsilon} \quad (2-5)$$

where $\Delta R = R - R_0$, R is the resistance of the specimen when stressed by a strain $\Delta \varepsilon$, R_0 is the unstrained resistance. For a continuous metal or an alloy specimen, γ value for a thin film form will be lower than γ_b for the bulk form [22]. However, it was reported by other researchers that when the film is thin enough to be at the coalescence region (i.e. $t < \lambda$, λ is the mean free path of the free electrons), γ will increase sharply [23].

Metallic thin-film strain gauges, commonly used in pressure sensors and accelerometers, exhibit low gauge factors (2-4), while semiconductor strain gauges own high gauge factors [24]. The piezoresistive properties of TaNO have been studied by Ayerdi that this film has a GF of 2.5~3.5 [24]. Nevertheless, so far, no previous study has been done on the piezoresistive properties of TaN-Cu nanocomposite thin films.

2.6 Study of Ta-N thin film

2.6.1 Ta-N thin film system

Ta-N thin films can be deposited on various substrates by using many methods, like reactive electron beam evaporation [25], metal organic chemical vapor deposition (MOCVD) [26, 27], plasma-enhanced atomic layer deposition (ALD), ion-beam assisted deposition (IBAD) [28, 29, 30] and reactive sputtering physical vapor deposition (PVD) [31~34]. The most desirable and widely used method is the reactive sputtering PVD [35, 36], since the sputtered Ta-N thin films generally have high chemical and mechanical stability and good conductivity for use in both mechanical industry and integrated circuits system.

Ta-N thin film system is very complex [37]. Generally, with the increase of N_2 flow rate or N_2 partial pressure in the plasma, pure α -Ta or β -Ta phase, Ta(N), Ta_2N , TaN, and Ta_3N_5 may be observed in the films succeedingly. However, it is not always the case that these phases will be observed continuously, especially Ta_2N phase [38]. In some literatures, Ta_2N was reported to be obtained under special deposition conditions [39, 40]. Figure 2-10 shows the XRD patterns of reactively sputtered Ta-N thin films studied by T. Riekkinen, in which Ta_2N phase appeared at 10% of nitrogen partial pressure. Kuo also presents the formation of Ta_2N phase in his research as observed by XRD and TEM [39].

Figure 2-10 XRD patterns of as-deposited films reactively sputtered in: A) 5%; B) 10%; and C) 15% nitrogen partial flow [40]

However, most literatures report the phase transition from pure Ta to TaN phase directly without appearance of Ta₂N. Figure 2-11 shows an example explaining the phase change of Ta-N from β -Ta to f.c.c. TaN directly without Ta₂N observed.

Figure 2-11 XRD patterns of 100 nm Ta-N thin films sputtered in Ar/N₂ gas mixture [41]

What talked above is the phase transition of Ta-N thin films with the change of N_2 flow rate or partial pressure. However, it must be pointed out that the phase formation is also greatly dependent on the types of substrates and the deposition parameters, such as the substrate temperature and so on. Some researchers have tested the application of Ti buffer layer on the surface of the Si wafer [42], and some use oxidized Si (100), MgO (100) as substrates [43], with the widest use of Si (100). It was verified that different phases of Ta-N would be induced by applying different substrates.

2.6.2 Preferred crystal orientation

Ta-N thin films are easy to have a preferred crystal orientation which is strongly influenced and even controlled by deposition method and parameters. For PVD prepared TaN film, the (111) plane is the most commonly observed preferred orientation [44]. For Ta-N films, H. B. Nie has found a highly preferred orientation of (111) in the film deposited on Si (100) substrates when N_2 partial pressure was above 20% [45]. Aita observed a highly preferred (111) orientation for the films deposited on Si (111) obtained by sputtering [46]. The same situation has appeared for the films under high-energy ion irradiation at low intensities obtained by W. Ensinger [25].

Figure 2-12 HRTEM cross-section image of the TaN film grown on Si (100) wafer shows clear (111) stacks parallel to the substrate surface [45]

Figure 2-12 shows a TEM image of a (111) preferred Ta-N thin film, in which the stacks of (111) preferred TaN layer parallel to the Si substrate, though not perfect, can be observed easily.

2.6.3 Effects of thermal annealing

Tantalum nitride thin films possess very fine crystal grains and a high density of defects when prepared by reactive sputtering [47]. It has been pointed out that a better crystallinity and fewer defects can be obtained if the substrate is intentionally heated during the deposition [48]. If the substrate is not intentionally heated, a post-deposited annealing must be applied to anneal the films as a necessary step for the processing of the films [49]. When Ta-N thin films are used as TFRs, thermal annealing will be critically important [3, 47], since a stable resistivity and TCR can only be achieved after thermal annealing.

Figure 2-13 GA-XRD patterns for TaN_x layers grown on MgO (001) at temperatures (a) T_s=600°C, (b) 700°C, and (c) 800°C [43]

Figure 2-13 shows the XRD patterns of Ta-N thin films deposited on MgO (001) at different substrate temperatures. With the increase of intentional heating temperature from 600°C to 800°C, higher peak intensity was observed, which indicates better crystallinity.

Figure 2-14 TaN film resistance as a function of the post-deposition sintering temperature at different sintering durations [50]

Figure 2-14 shows the resistivity change as functions of annealing temperature and time. While heating at temperatures up to 300°C, the film resistance stabilized after about 1h of heating. Heating at higher temperatures, however, results in a continuous increase of the resistance with the sintering time. The similar trend that implies the more stability after annealing with the increase in the resistivity has also been found by other researchers [40, 41, 44].

2.6.4 Conduction mechanisms for Ta-N thin films

For pure Ta, the conduction mechanism follows the principle of conductors. For metals, each atom contributes one or more electrons, the conduction electrons, to the conduction band. These electrons are free to move under an electrical field to conduct the electric current [51].

However, allowing for the conduction mechanism of Ta-N thin films, a more complex case may occur in which a combination of semiconductor conduction and matrix tunneling may be active at the same time. For semiconductors, there is a larger gap between the conduction band and valence band. The population density is highly dependent upon temperature and impurities in semiconductors. Tunneling refers to the conduction across the energy barriers. The barriers are produced either by grain boundaries and the impurities precipitated or by forming a heterogeneous mixture of a conductive material within a matrix of a non-conductor, called “cermet”.

In Ta-N films, nitrogen atoms may combine with Ta to form the nitride and may also be trapped in the films, which can act as impurities. Thus, resistivity in these films is mainly caused by electron tunneling across the grain boundaries and scattering by impurities and grain boundaries [52]. The resistivity is much higher than

pure tantalum, normally within the range of $400\sim 3\times 10^4\ \mu\Omega cm$ depending on the process parameters. TCR value is within the range of $-800\text{ ppm}/^\circ\text{C}\sim -25\text{ ppm}/^\circ\text{C}$, exhibiting semiconductor-like behaviors.

2.7 Nanocrystalline materials

Nanocrystalline materials are single phase or multi-phase polycrystalline materials characterized by a microstructural length or grain size of up to 100 nm. Nanocrystalline materials exhibit various shapes and forms, and possess unique chemical, physical, electrical and mechanical properties. When the grain size is below a critical value of 10~20 nm, more than 50 vol. % of atoms is associated with grain boundaries or interfacial boundaries and this brings special properties to these materials, which are superior to those of conventional polycrystalline coarse-grained materials. The extensive investigations in recent years on structure-property correlations in nanocrystalline materials have begun to unravel the complexities of these materials and achieved many important results and theories [6]. Nowadays, new concepts of nanocomposites are being investigated with special emphasis on ceramics composites with nano-sized metal particles imbedded in the ceramics matrix [53, 54]. Our Ta-N-Cu nanocomposite thin films belong to this hot topic.

2.7.1 Synthesis

Increased activity on the synthesis of nanocrystalline materials in recent years dates back to the pioneering investigations of H. Gleiter in Germany in 1981. He synthesized ultrafine nanometre sized metallic particles using inert gas condensation

technique and consolidated them in-situ into small discs under ultrahigh vacuum conditions. A number of techniques were listed in Table 2-2.

Table 2-2 Methods to synthesize nanocrystalline materials

Starting phase	Techniques
Vapor	Inert gas condensation, Sputtering, plasma processing, vapor deposition
Liquid	Electrodeposition, rapid solidification
Solid	Mechanical alloying/milling, sliding wear, spark erosion

In principle, any method capable of producing very fine grain sized polycrystalline materials can be used to produce nanocrystalline materials. The methods that have been commonly employed to synthesize these materials include inert gas condensation [55], mechanical alloying [56], PVD [57, 58], sol-gel process [59, 60] and so on. Among all the techniques mentioned above, the gas condensation, mechanical alloying, PVD have been most commonly employed to produce nanocrystalline materials. Our Ta-N-Cu nanocomposite thin films were prepared by plasma sputtering (PVD) in this study.

2.7.2 Microstructures

In order to understand the interrelationship between structure and properties, nanocrystalline materials need to be characterized on nanometer scale. A lot of experimental techniques have been applied to investigate the microstructures, including transmission electron microscopy (TEM), scanning tunneling microscopy (STM), field ion microscopy (FIM), and the less direct electron, X-ray and neutron diffraction techniques, with the most widely use of TEM. The studies indicated that nanocrystalline metals consist of small crystallites of different crystallographic orientations separated by grain boundaries. Figure 2-15 shows a TEM image recorded from a nanocrystalline NiAl specimen synthesized by inert-gas condensation method. The clusters of nano-sized NiAl crystals can be observed clearly.

Figure 2-15 TEM morphology of the grains and diffraction pattern of n-NiAl

[56]

2.7.3 Electrical properties

Due to the very fine grain sizes, nanocrystalline materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained polycrystalline materials.

Referring to the electrical properties, due to the increased volume fraction of atoms lying at the grain boundaries, the electrical resistivity of nanocrystalline materials is expected to be higher than that in coarse-grained polycrystalline materials. Actual measurements of electrical resistivity on the nanocrystalline materials have been carried out only recently. Wang [61] and Liu [62] measured ρ of $126 \mu\Omega cm$ at $25^\circ C$ for nanocrystalline $(Fe_{99}Cu_1)_{78}Si_9B_{13}$ (30nm). Nanocrystalline Ni-P alloys were also measured by researchers [63, 64]. The resistivity of nanocrystalline metals Cu, Pd, Fe, and Ni was also studied [65], and values are all higher than those in coarse-grained materials of similar compositions. It is amazing that a negative TCR is frequently observed in amorphous alloys [66], and this phenomenon was also reported in nanocrystalline materials by some researchers [67].

From the study on the variation of ρ with temperature and grain size, the main conclusions can be drawn:

1. The resistivity is proportional to temperature for different grain sizes and in a wide temperature range.
2. At a constant temperature, ρ increases with decreasing grain size (Figure 2-16).

For example, the resistivity of Fe-Cu-Si-B nanocrystalline alloy increases from $44 \mu\Omega cm$ to $126 \mu\Omega cm$ when grain size decreases from 90 nm to 30 nm.

3. Temperature coefficient of resistivity (TCR) has been found to decrease with a decreasing grain size for metal particles.

Figure 2-16 Change of resistivity with temperature for nanocrystalline Fe-Cu-Si-B alloys as a function of grain size [62]

The relations between conductivity and temperature, composition, and compaction pressure have been recently studied for a series of nanocrystalline oxide samples- LaFeO_3 , LaCoO_3 , and $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ [68]. The results show that though the conductivity is lower, the slope of the conductivity temperature curve is higher for the nanocrystalline materials in comparison with the coarse grained materials.

2.8 Nano-sized metal particles

Nano-sized metal particles, usually with a crystalline structure and with characteristic sizes of less than 10 nm, show very special properties like quantum size effect, weak localization effect that make them attractive for many technological applications. Here, these behaviors closely associated with its characteristic size are discussed.

2.8.1 Quantum size effect

Quantum size effect is related to metal particles with characteristic sizes. Schaper pointed out that the metal particles embedded in the ceramics matrix would have a strong effect on the properties of the matrix [69]. When particle size is less than 10 nm, the metal particles will not show the metallic properties, but semiconductor-like properties. In this case, the electron energy band becomes discretized, and electrons in the valence band cannot jump to the conduction band [70]. If the electrons can obtain enough energy by thermal irritation or bombardment caused by other particles, the electrons can then jump out to the conduction band, which is called as the **quantum size effect**. However for bulk metal, valence band overlaps with conduction band, thus, electrons can move freely and contribute to the current conduction.

Figure 2-17 Resistivity change of n-Ag versus temperature as a function of grain size [55]

Figure 2-17 shows the resistivity change of n-Ag with temperature as a function of grain size. For n-Ag with larger grain size ($d=11$ and 18 nm), resistivity increases with increase of temperature, implying positive TCR and normal metal behavior. However, smaller grain size ($d=5.3$ nm and 6.8 nm), resistivity decreases with increase of temperature, suggesting negative TCR and semiconductor behavior. In this case, resistivity of n-Ag is mainly controlled by temperature.

Figure 2-18 TCR change of n-Ag versus grain size [55]

Figure 2-18 shows TCR change of n-Ag versus grain size. With decrease of grain size from 25 nm to 11 nm, TCR (at 100 K and 250 K) decreases slowly and keeps positive. From 11 nm to 5 nm, TCR decreases sharply and changes its value from positive to negative at 10 nm.

2.8.2 Weak localization theory

Figure 2-19 Illustration of weak localization of electrons [71]

Weak localization theory refers to the amorphous phase that causes the localization of conduction electrons in crystals. In this case, amorphous or extremely fine crystals (≤ 10 nm) can limit the movement of the electrons to a potential well (crystal). As a result, a fraction of conduction electrons is localized within this well, and the effective conduction electron density is limited to those which tunnel through all the boundaries, resulting in the decrease of effective density of conduction electrons and thus the higher resistivity and lower TCR, as illustrated in Figure 2-19. It has also been proved in other study that amorphous phase will contribute to the higher resistivity and lower TCR [71].

2.8.3 Density effects

Figure 2-20 Variation of resistivity ratio $\rho(T)/\rho_5$ of poly-Ag (a) and n-Ag (b, c, d) with different densities [55]

It has been reported by L. D. Zhang that resistivity would increase and TCR will reduce with decreasing density for n-Ag (grain size: 25~30 nm) [56]. Microscopically, the existence of some defects, such as porosity, vacancy, which lowers the density of films, will result in the increase in resistivity and decrease in TCR. The precipitation of a second phase will also cause the decrease of matrix density. It can be seen from Figure 2-20 that the slope of the curve, which represents TCR, decreases with decreasing density.

2.8.4 Core-level binding energy of nano-sized metal particles

As discussed above, nano-sized particles exhibit some special properties compared with bulk material. These physical properties are found to be particle size dependent [72]. When a solid forms at nanometer size, the gap between the conduction band and the valence band expands, and the binding energy of a core level which is a measure of the atomic trapping to the core electron in a particular energy level will shift to higher binding energies in the X-ray photoelectron spectrum (XPS) [73]. There have been many reports on the size dependence of the core-level shift of nanosolid materials such as Cu-2p [74], Au-4f [75], and Ta-4f [76].

Figure 2-21 XPS Cu 2p spectra from Cu overlayers deposited at 300 K; the average Cu coverages are indicated [74]

As plotted in Figure 2-21, Cu 2p_{3/2} binding energy increases from 932.7 eV to 933.7 eV when the Cu coverage decreases from 20 to 0.2 Å. Actually Cu coverage means the same as the grain size. Grain size increases with the increase of Cu coverage or film thickness.

2.9 Nanocomposite thin films

Nanocomposites are new concepts of nanocrystalline materials. They may own novel structures and new attractive physical properties due to the size effect and mixing of different phases with different properties. They are films consisting of more than one phase, in which the dimension of at least one of the phases is reduced to nanoscale [77].

At present, many studies have been conducted with special emphasis on ceramic composites composed of two or more immiscible components with nano-sized metal particles dispersed in a ceramic or metal matrix [5], such as Cu-Al₂O₃ [53], TiN-Ag [59], Co-ZnO [60] and so on. Introduction of nano-sized metal particles into ceramic or metals has been found to result in the evolution of a new innovative material. So far, most efforts have been made to investigate the optical [51, 78], magnetic [57] and mechanical properties [79, 80], with much less attention on the electrical properties.

2.9.1 Preparation

Nanocomposite thin films have been produced by various methods such as ion implantation [81, 82], chemical synthesis [83], plasma enhanced CVD [84], sol-gel [85], and magnetron sputtering [86, 87, 88]. Among them, the sputtering method has been widely used because of its simplicity in process, flexibility in the materials combination and controllability in size distribution. There are two different alternatives in the sputtering process, co-sputtering and alternating sputtering.

2.9.2 Electrical properties

It has been proved that physical properties of nanocomposites can be altered in a wide range by changing the metal volume fraction x . They may undergo an insulator or semiconductor to metal transition as x accedes a critical value of x_c for composite thin films [88]. It was also found that the magnitude of the electrical resistivity and hence conductivity in composites can be changed by altering the size of the electrically conducting component. For example, by changing the Fe particle size and volume fraction occupied by Fe, the electrical properties can be varied in a continuous fashion in Fe-SiO₂ system. Only by changing the volume fraction, the electrical conductivity could be increased by 14 orders of magnitude. So far, several studies on electrical properties were performed on oxide-matrix composites [89], and few reports on nitrides-matrix composites.

2.9.3 Mechanical properties

As discussed in section 2.5, compared with coarse-grained materials, thin films own higher hardness. By recent study, it was found that nanocomposite thin films can exhibit even higher hardness. Hard nanocomposite coatings can be formed in two ways: one way is nc-MN/hard matrix and the other is nc-MN/soft matrix. Here, MN is the metal nitride. The nanocomposite coatings with a 'hard' matrix represent a new class of superhard coatings with high Young's modulus. The films made by the first way are very hard but also very brittle. On the contrary, the nanocomposite coatings with a 'soft' matrix represent a new class of hard coatings with higher toughness [90]. The nanoscale grain size can also cause a 4-5 times increase in the strength and hardness over the coarse grained material.

2.9.4 Study of Ta-N-Cu system

Figure 2-22 the calculated Gibbs free energy diagram of the Cu-Ta system [91]

So far, several studies were made on Ta-Cu or Ta-N-Cu thin film system [92, 93, 94]. F. Zeng has formed an immiscible Cu-Ta system with positive heat of mixing by ion beam assisted deposition technique [91]. Figure 2-22 is the calculated free energy diagram of the system at 300 K. Considering the relationship between the composition and free energy, it is predicted that amorphous alloy may be realized around $\text{Cu}_{20}\text{Ta}_{80}$ and $\text{Cu}_{40}\text{Ta}_{60}$ if it is subject to a driving force provided by Ar^+ ion beam. In other studies by Aylesworth and Oh, the composition range for amorphous alloy formation has been extended to 60-90 at. % Ta and 55-95 at. % Ta respectively [92, 93]. It was also reported by Nikola Radic that the amorphous alloys of Cu-Ta are more stable than solid solutions in certain composition range [95].

Figure 2-23 Isothermal section at 700°C from the ternary Ta-N-Cu phase diagram [96]

Another important study was done by T. Laurila [96] who set up a ternary Ta-N-Cu phase diagram in his research about tantalum carbide and nitride diffusion barriers for Cu metallization, which is shown in Figure 2-23. From this phase diagram, various co-existing phases can be determined when concentrations of Ta, N, and Cu are specified respectively. This finding is very useful in our study of Ta-N-Cu nanocomposite thin films by suggesting the possible phases existing in the films.

2.10 Summary

In this chapter, a simple description of thin film including its definition, application, preparation, was discussed first. The electrical, mechanical, and piezoresistive properties of thin films were then talked about with more emphasis on electrical resistivity, TCR, and TCR tuning. Next, a detailed review of Ta-N thin film regarding

its system, preferred orientation, effects of thermal annealing, and its conduction mechanism was presented. Finally, nanocomposite materials including nanocrystalline thin films (its synthesis, structure and electrical properties), behaviors of nano-sized metal particles, nanocomposite thin films (preparation, electrical and mechanical properties) and study of Ta-N-Cu thin films were reviewed. Emphasis was paid on the properties of nano-sized metal particles and electrical properties of nanocomposite thin films.

Chapter 3 Experimental Details

3.1 Introduction

In this chapter, the preparation of Ta-N and Ta-N-Cu thin films and the characterization techniques were discussed in details. Thus, this section presents various techniques used for this project. They are: (1) the sputter coater used to fabricate the Ta-N and Ta-N-Cu nanocomposite thin films; (2) Rapid Thermal Processing (RTP) used to anneal the thin films; (3) Four-point probe used to measure the sheet resistance (R_s) and TCR; and (4) Nanoindenter applied for hardness and young's modulus measurement. The whole experimental procedure is shown blow in Figure 3-1.

Figure 3-1 Flow chart of the whole experiments

For the first step, Ta-N thin films were prepared using reactive sputtering. After deposition, rapid thermal annealing (RTA) at 400°C was applied to anneal the Ta-N thin films. For the second step, Ta-N-Cu nanocomposite thin films were deposited by reactive and co-sputtering method. After deposition, a Surface Profilometer was used to measure the thickness of the thin films. XRD (X-ray diffraction pattern) was applied to identify the crystal phase existing for both the as-deposited and annealed samples. TEM (transmission electron microscopy) was adopted to study the microstructures of Ta-N and Ta-N-Cu thin films before and after annealing. XPS (X-ray photoelectron spectroscopy) was used to

characterize the concentrations and to identify the chemical states of different elements: Ta, N, and Cu. Four-point probe attached by a hot stage was used to measure the sheet resistance (R_s) and TCR of the films. Nanoindenter was applied for the measurement of hardness and Young's modulus.

3.2 Sample preparation

3.2.1 Sputter coater

As mentioned in Chapter 2, Ta-N and Ta-N-Cu nanocomposite thin films in this project were synthesized by the reactive sputtering and reactive co-sputtering PVD method respectively. The sputter coater applied for the preparation of thin films is the Penta Vacuum sputtering system, which has three separately magnetron-controlled targets for the purpose of co-deposition. Each target has a tilt of 30° . The distance between target and substrate holder is 15 cm. The substrate holder is provided with water cooling.

3.2.2 Si substrate preparation

Figure 3-2 Steps for the preparation of Si substrates

The substrates used in the deposition are n-type single crystalline Si (100). The preparation of the Si substrates before sputter deposition is introduced as follows: First, the Si substrate was put into the acetone and cleaned ultrasonically for 10 minutes to remove the solvents from the Si surface, then cleaned by flowing ethanol and dried by blowing N₂. Second, before deposition, plasma cleaning was applied to clean the substrate for 15 minutes for further cleaning of Si to enhance the adhesion ability of thin films with Si. The preparation of Si was summarized as Figure 3-2.

3.2.3 Preparation of Ta-N thin film

Table 3-1 Parameters for Ta-N thin film deposition

Base pressure (torr):	6×10^{-6}
Process pressure (torr):	5.5×10^{-3}
Ar gas (sccm):	60
N ₂ gas (sccm):	0, 2, 4, 6, 8, 10, 12 sccm
Power of tantalum target (W):	250
Substrates:	Si (100) with size of 1.5 cm×3 cm
r. f. bias applied (W):	40
Deposition time (s):	2700

The deposition parameters for Ta-N thin films were summarized as Table 3-1. In this step, Ta-N thin films were prepared by using d. c. magnetron reactive sputtering with pure tantalum target in the plasma of N₂ and Ar. Before deposition, the process chamber was pumped down to about 6×10^{-6} Torr or less by a turbo pump backed up with a mechanical pump. The working gas Ar (60 sccm) was then introduced into the chamber to generate plasma at a pressure of 5.5×10^{-3} Torr. The reactive gas N₂ (0~12 sccm) was fed into the plasma 60 s in advance before the deposition started. During deposition, the power of Ta was kept at 250W. A r.f. bias of 40W was applied to the substrate. The substrates were not rotated or heated intentionally during the deposition. The deposition time for all the samples was 45minutes. The Si (100) substrates in this experimental step have the dimension of 1.5cm×3cm.

3.2.4 Preparation of Ta-N-Cu thin film

Table 3-2 Parameters for Ta-N-Cu thin film deposition

Base pressure (Torr):	6×10^{-6}
Process pressure (Torr):	$5.5 \sim 7.5 \times 10^{-3}$
Ar gas (sccm):	60
N ₂ (sccm):	0, 2, 4, 6, 8
Power of Ta, Cu (W):	250, 40
Substrates:	Si (100) with size of 1.5 cm×1.0 cm
r. f. bias applied (W):	40
Deposition time (s)	2700

The deposition parameters for Ta-N-Cu thin films were shown above in Table 3-2. Both Ta and Cu targets have a purity of 99.995%. Each target has a diameter of 100 mm and was tilted by 30°. The distance of target-to-target and target-to-substrate was 200 mm and 150 mm respectively. Before deposition, the process chamber was first pumped down to 6×10^{-6} . Ar gas (60 sccm) was then introduced to fill the chamber up to 5.5×10^{-5} Torr. During deposition, the power of tantalum was kept at 250 W; while copper was set at 40 W. To introduce nitrogen into the films, N₂ gas was added at various amounts relative to Ar gas ranging from 0 sccm to 8 sccm. The Si substrates have a size of 1.5cm×1.0cm. For each N₂

flow rate, 8 pieces of Si (sample 1 to sample 8) were placed at different locations of substrate holder with a distance interval of 1.0 cm to allow various concentrations distributed in each sample. A schematic drawing is shown in Figure 3-3.

Figure 3-3 Schematic drawing of Si substrates displacement during deposition

3.2.5 Rapid thermal annealing of thin films

Rapid thermal annealing (RTA) has been widely used in semiconductor industry for diverse applications. The great advantages of this method are the high ramp rate, short annealing time and its relative simplicity as compared with the conventional furnace annealing. A typical temperature profile of RTP is shown in Figure 3-4.

Figure 3-4 Typical temperature profile of RTP

RTA used in this study is the RTP (JIPLEC, JETFIRST) with the rising temperature from 25°C to 1200°C, and the maximum heating rate is 100°C/s. The working condition is under vacuum of 1×10^{-2} Torr with the chamber filled with Ar as the protective atmosphere. The system chamber consists of a quartz jacket with 30 tungsten halogen lamps arranged on the top and bottom serving as a heat source with Ar or N₂ as the ambient atmosphere. The samples are placed on a 4-inch silicon wafer, and the temperature is monitored using a thermocouple placed underneath the wafer when annealing temperature is below 400°C and a pyrometer placed above the wafer when annealing temperature is higher than 400°C.

After deposition, RTA was applied to anneal the as-deposited Ta-N and Ta-N-Cu samples at 400°C for 2, 4, and 8 minutes to stabilize the Ta-N thin films and to induce the nucleation and grain growth of Cu nanoparticles from Ta-N matrix. Ar gas acts as the protective gas to prevent the oxidation of the samples during the annealing process. Annealing parameters applied were summarized in Table 3-3.

Table 3-3 Parameters for RTA processing of thin films

Ramp rate (°C/s)	75
Annealing temperature (°C)	400
Annealing time (s)	120, 240, 480
Chamber pressure (mbar)	997~999
Protective gas	Ar

3.3 Thin film characterization

Modern material characterization is based on the measurement of particles and radiation that emerge from a solid that is irradiated by X-ray photons, electrons, or heavy particles. Due to various collision and scattering processes, the penetration depth of the incident particles and the escaping length of the scattered particles are very limited. The specimen thickness that contributes to the measurement is only of several atomic layers, which are the basis of the sensitivity of thin film analysis, for example, SEM, TEM, and XPS, all of which are very surface sensitive techniques. Since the above characterization techniques have been generally understood, only those applied for characterization of electrical and mechanical properties in this study are briefly described here.

3.3.1 Measurement of resistivity and TCR using Four-Point Probe

A common way to calculate thin film resistivity values is in terms of sheet resistance (R_s) with units ‘ohms per square.’ To understand this property and the units involved, consider the film with length l , width w , and thickness d as shown in Figure 3-5. If the film resistivity is ρ , the film resistance is $R = \rho l / wd$ (according to $R = \rho \frac{l}{A}$). Thus, in the special case of a square film ($l = w$),

$$R = R_s = \rho / d \quad (\Omega/\square) \quad (3-1)$$

$$\rho = R_s \cdot d \quad (\mu\Omega \cdot cm) \quad (3-2)$$

where R_s is independent on film dimensions other than thickness. Any square, irrespective of size, would have the same resistance.

Figure 3-5 Thin film conductor with length l , width w , and thickness d

A general way to measure R_s of a film is to lightly press a four-point metal-tip probe assembly into the surface as shown in Figure 3-6. The outer probes are connected to the current source, and the inner probes detect the voltage drop. Electrostatic analysis of the electric potential and field distributions within the film yields

$$R_s = KV/I \quad (3-3)$$

where K is a constant dependent on the configuration and spacing of the contacts. Normally, $K=4.53$.

Figure 3-6 Four-point probe method for measuring sheet resistance

In this project, for measuring the resistivity and TCR of our films, a four-point probe station (Singatone, S-1060R), attached by four equally spaced tungsten metal tips (radius: 100 μm) and a sample holder stage which can be heated, was used to measure the sheet resistance R_s and TCR. A good ohmic contact between metal W tips and our TaN or TaN-Cu thin films was formed and the contact resistance was negligible. A Singatone Model S-

1060R power supply was used to provide a variable power. This power supply can control the precise temperature at the same time. The temperature used was from 25°C to 150°C. The four-point probe was enclosed in a cabinet filled with Ar gas to protect the oxidation of Cu during the measuring process at high temperature. For the calculation of TCR, we follow its definition in Equation (2-13). The resistance at 25°C and 150°C was measured respectively and value was used to calculate the TCR at 25°C.

3.3.2 Determination of hardness by Nanoindenter

‘Nanoindentation’ technique has been widely used to characterize the mechanical properties of thin films. It is a miniaturized version of the Vickers hardness test for bulk materials. It can evaluate the thin film with feature less than 100 nm across, as well as thin films less than 5 nm thick. When the indentation depth is less than one tenth of the thickness of the films, the effect of substrate on the hardness can be neglected. In this work, we use Nano Indenter[®] XP (MTS Cooperation, USA) to characterize and compare the hardness and elastic modulus of the as-deposited and annealed Ta-N-Cu thin films, and the films with different Cu concentrations. A Berkovich (3-face pyramid) indenter was used to measure the load-displacement relation of the film. The measurement is done at the mode of ‘hardness at a depth’ with a constant depth of 50 nm.

3.4 Preparation of specimens

3.4.1 Plain view TEM specimens

Ta-N and Ta-N-Cu coated Si chips with a size of 3mm×3mm were prepared first and glued onto a pair of stainless steel columns which allows free rotation of inner column around the outer one. The Si substrate was then hand-ground and polished by SiC sand paper to reach a thickness of 100 nm. Then the sample was taken off and a Cu ring was glued onto the Si side, and finally was thinned by ion milling from the Si side until an electron transparent area at the center of sample was obtained. The whole process was shown in Figure 3-7.

Figure 3-7 Plain view TEM specimens preparation process

3.4.2 Samples for other characterization tests

- (1) For XRD experiments, including both the as-deposited and the annealed samples were made using the same procedure as the normal thin film samples, with the same sizes of 1.5 cm×3 cm. A schematic drawing of our sample is shown in Figure 3-8.

- (2) For XPS experiments, there is no special requirement for the samples, expect that the samples must be high vacuum compatible. The sample preparation was the same as the normal thin film samples, but the sample was cut into much smaller pieces according to the length and width of the loading bar.
- (3) For nanoindentation test and four-point probe resistivity and TCR measurement, thin film thickness must be thick enough to avoid the influence from Si substrates. The deposition time thus for these samples is extended to 60 minutes. The size is the same as the normal samples.

Figure 3-8 Schematic drawing of our samples for characterization tests

Chapter 4 Study of Ta-N Thin Films

4.1 Introduction

Ta-N thin films were fabricated by using magnetron d. c. reactive sputtering. After thin film deposition, rapid thermal processing (RTP) was applied to anneal the films at 400°C for 2, 4, 8 minutes. The microstructures and electrical properties were then characterized. In this chapter, the relationship between microstructures, electrical properties (ρ and TCR) and N_2 flow rate is mainly discussed. The effect of annealing time on the microstructures and electrical properties was also studied. The experimental results reveal that when N_2 flow rate is 8 sccm, stoichiometric TaN was formed and exhibits most semiconductor-like properties compared with the other films. Thus, N_2 flow rate of 8 sccm was chosen for deposition and study of Ta-N-Cu thin films in chapter 5.

4.2 Deposition rate

Using an Alpha-step surface profilometer (DEKTAK³), the thickness of Ta-N thin films was found to vary from 517 nm to 234 nm when N_2 increases from 0 sccm to 12 sccm. The deposition time for all the films is 45 minutes. The deposition rate (d. r.) calculated by film thickness over deposition time, sheet resistance (R_s) and resistivity values (ρ) were listed in Table 4-1.

Table 4-1 List of the thickness, deposition rate (d. r.), sheet resistance and resistivity of d. c. reactively sputtered Ta-N thin films grown on the Si substrate

N ₂ gas flow (sccm)	0	2	4	6	8	10	12
Thickness (nm)	517	328.5	324	279	261	256.5	234
d. r. (nm/min)	11.4	7.3	7.2	6.2	5.8	5.7	5
R_s ($\Omega/\square$)	0.6	0.7	1.4	1.9	3.2	4.6	8.1
Resistivity ($\mu\Omega\text{cm}$)	306	224	450	528	823.7	1175.6	1811.7

(a)

(b)

Figure 4-1 Deposition rate (a) and sheet resistance (b) of Ta-N thin films deposited at different N₂ gas flow rate

The deposition rate calculated by thin film thickness over deposition time at varied N₂ flow rate ranging from 0 sccm to 12 sccm is plotted in Figure 4-1 (a). It can be seen that the deposition rate decreases dramatically from 11.5 nm/min to 7.3 nm/min when N₂ flow rate increases from 0 sccm to 2 sccm, which indicates the switch of sputtering mechanism from ‘metallic mode’ to ‘covered mode’. In this case, with the introduction of 2 sccm N₂ into the chamber, the pure tantalum target would be ‘poisoned’ by a thin layer of semiconductor-like tantalum nitride formed on the target surface. The semiconductor-covered target results in the decrease of the sputtering rate or the sputtering yield and hence the deposition rate was decreased. From 4 sccm to 12 sccm, the deposition rate decreases gradually, which implies more tantalum nitride formed on the surface of the

target and results in more opening sites of the tantalum target surface to be covered by the tantalum nitride compounds. Other researchers also reported the similar trend of deposition rate variation with N₂ flow rate [35, 97, 98].

On the other hand, with the increase of N₂ flow rate, sheet resistance of the films increases gradually when N₂ is less than 6 sccm, but quickly when N₂ reaches to 8 sccm or higher. This is mainly due to the more and more prevailing of semiconductor-like TaN phase formed in the films with increase of N₂ flow rate, which owns higher resistance value.

4.3 Study on microstructure

4.3.1 XRD analysis

The crystalline structures of the as-deposited films were measured by using $\theta - 2\theta$ XRD (Philips, PW 1830) with a Cu K α source working at 30kV and 20mA. The scanning angle is from 20° to 90° with a step size of $\Delta 2\theta = 0.02^\circ$ and a measuring time of 1.25 s per step. Figure 4-2 presents the XRD patterns of the as-deposited Ta-N films with N₂ flow rate ranging from 0 to 12sccm.

Figure 4-2 XRD patterns of the as-deposited Ta-N films versus N_2 flow rates

Without introduction of N_2 gas into the process chamber, the pattern reveals two peaks at 37.39° and 63.59° , which refer to (202) and (631) crystal planes of tetragonal β -tantalum respectively [99]. This β -tantalum phase can also be identified from the resistivity value shown in Table 4-1, since β -tantalum phase always owns higher resistivity value compared with α -tantalum or cubic phase.

When N_2 flow rate of 2 sccm was introduced, three diffraction peaks at 35.4° , 41.3° , and 60° appear, which can be indexed as (111), (200) and (220) crystal planes of *f.c.c.* TaN phase respectively.

It can also be observed that those three peaks in curve (b) are very broad and short. One explanation is the TaN crystal size is very fine. To estimate the grain size D , the

well-known Scherrer formula [100] can be applied by measuring the full width at half-maximum (FWHM) of the diffraction peaks at the angle of interest:

$$D = \frac{C\lambda}{FWHM \cdot \cos \theta} \quad (4-1)$$

Where C is a constant ($C=0.91$), λ is the wavelength of X-ray, θ is the diffraction angle or Bragg angle, FWHM in radian is the peak width at half-maximum peak height, and D is the crystallite dimension normal to diffraction planes. For (111) peak in curve (b), it spans 5° , calculated by Scherrer formula, D approximates to 1.7 nm.

Another explanation for the broad (111) peak is that the film may contain other phases that exhibit the very close peak positions to TaN (111), like Ta (202) peak, and Ta(N) alloy phases with nitrogen atoms distributed in the tantalum interstitial lattice may also exist. The medium intensity suggests that small amount of stoichiometric TaN phase is formed inside the film due to the small N_2 gas flow rate.

With more N_2 introduction (> 2 sccm), the films exhibit changes in the intensity, position and shape of diffraction peaks, and these changes were caused by the variation in the microstructures. The (111) peak begins to dominate, implying that the crystalline grains in the films begin to be oriented along the (111) direction, which was also reported in other studies [37, 45]. At the same time, TaN (111) peak shifts to the smaller angle because of the distortion and expansion of crystal lattice constant, which was caused by the nitrogen atoms incorporation at the interstitial positions. This phenomena was also observed by some researchers [44, 45]. It was reported in [45] that the lattice constant of

the films increases by 1.4 % from 4.365 Å to 4.427 Å when N₂ partial pressure increases from 7.5 % to 30 %.

With N₂ increasing further to 12 sccm, TaN (111) becomes even more prominent, exhibiting very sharp and high intensity peak. Peak (200) almost disappears and (222) begins to appear. This means more dominant (111) preferred orientation and better crystallinity in the films. Calculated by Scherrer formula, when N₂ is 8 sccm, the crystal size is 4 nm, increased by 57.5 % relatively compared with that of the film at 2 sccm of N₂ flow rate. Through all of the above analysis, the possible phases existing in the films observed by XRD can be summarized in the following table.

Table 4-2 Possible phases existing in Ta-N thin films

N ₂ flow rate (sccm)	0	2~6	8	10~12
Possible phases	β-Ta	Ta-rich Ta(N)	Stoichiometric TaN	N-rich TaN

However in this study, only β-tantalum and *f. c. c.* TaN were observed by using XRD. No Ta₂N or other N-riched compounds could be identified. From literature review, Ta₂N may be formed at very low N₂ partial pressure of 2.5 % [38]. Other Ta-N phases can also be formed besides pure tantalum, Ta₂N and TaN phases, since Ta-N system is extremely rich [38, 101]. Besides the equilibrium phases of *b.c.c.* α-Ta, solid-solution α-Ta(N), *f.c.c.* TaN, and hexagonal γ-Ta₂N, a variety of metastable phases have been reported. These include tetragonal β-Ta, *b.c.c.* β-Ta(N), hexagonal Ta₅N₆, and tetragonal Ta₄N₅. M. Stavrev has reported the existence of β-Ta, β-Ta & Ta(N), *b.c.c.*-Ta(N), *f.c.c.*-TaN

when N_2 flow increases from 0 sccm to 5 sccm [37]. H. B. Nie [45] has obtained similar results to those achieved in this study. Riekkinen achieved the phase change from Ta_2N to TaN as the N_2 partial flow increased from 5% to 15% [40]. C. S. Shin reported the phase transition from $TaN_{0.1}$, Ta_4N , Ta_2N , TaN, to TaN_x with N_2 fractions ranging from 0.013 to 1 [38].

After deposition, RTP was applied to anneal some of the thin films (N_2 : 8 sccm) at 400°C for 2, 4, 8 minutes. The XRD result is presented in Figure 4-3.

**Figure 4-3 XRD patterns for TaN thin film after annealing for 2, 4, and 8 minutes
(N_2 : 8sccm)**

In this case, stoichiometric *f.c.c.* TaN was formed in the film, together with a little amount of $TaN_{0.8}$ as indicated by the weak peaks at 47.5° (101) and 62.5° (002). No

much change in the intensity and shape of TaN (111) peak can be observed. During annealing, the film may undergo recovery of the crystal defects and release of the intrinsic stress inside the as-deposited films. However, annealing temperature of 400°C is too low to cause obvious grain growth of Ta-N thin films, since the melting point is as high as 3087°C.

On the other hand, corresponding to the change in TaN phase after annealing, the electrical properties must undergo changes. Due to the formation of more stoichiometric and semiconductive TaN phase, it can be concluded that the film resistivity will be higher and TCR will be more negative, which will be proved in next section.

4.3.2 TEM observation

Figure 4-4 Bright-field TEM image of an as-deposited TaN film (N₂: 8 sccm)

Figure 4-4 is the bright-field TEM image of an as-deposited Ta-N thin film (N₂: 8 sccm). Notice that only tiny TaN particles, represented by the small dark clusters, can be

observed. Since the highest resolution for the TEM applied is 1 nm, the cluster boundary and the cluster size can not be identified clearly. From the electron diffraction pattern, only the diffraction rings from TaN (111), (200), (220) appear. The preferred orientation of TaN (111) examined by TEM was not so obvious as that by XRD due to poor crystallinity.

4.3.3 XPS study

Figure 4-5 Concentrations of Ta and N vary as a function of N₂ flow rate for the as-deposited Ta-N thin films (N₂: 0~12 sccm)

As determined from XPS results, the change of Ta and N concentrations in the films versus N₂ flow rate can be obtained, as shown in Figure 4-5. It can be concluded that

stoichiometric TaN with atomic ratio of Ta over N equal to 1:1 can only be formed in the film when N₂ is 8 sccm. Lower than 8 sccm, substoichiometric TaN was formed; and if larger than 8 sccm, N-riched Ta-N phase was formed.

With the increase of N₂ flow rate from 0 sccm to 12 sccm, the atomic concentration of Ta decreases gradually from 100 at. % to 42.3 at. %, while N concentration increases monotonically from 0 at. % to 57.7 at. %. When N₂ is 0 sccm, 100 % tantalum dominates in the film, and as analyzed by XRD, it is β -Ta phase. At 2 sccm of N₂, the atomic ratio between N and Ta is near 1:2, and the phase most possibly is Ta₂N. However, by previous analysis of XRD, when N₂ is 2 sccm, the phase may be non-stoichiometric TaN or a combination of pure β -Ta, TaN and Ta(N). The difference between XPS and XRD results may arise from the preferred sputtering of the light element when Ar etching was applied in XPS [26, 102]. With the increase of N₂ flow rate, the difference between N and Ta concentration becomes smaller. Only when N₂ is 8 sccm, the atomic ratio between Ta (49.9 at. %) and N (50.1 at. %) reaches to 1:1, which indicates the formation of stoichiometric TaN phase. This result matches well with the XRD and TEM results, which shows the formation of the nanocrystalline TaN phase when N₂ is 8 sccm. When N₂ is even larger, the atomic ratio between N and Ta becomes larger than 1:1, and increases with increase of N₂ flow rate. Analyzed by XRD, the phases existing in the films are still f.c.c. TaN phase. Thus, it can be concluded that nitrogen may react with tantalum to form f.c.c. TaN or N-rich phase, like Ta₃N₅ or Ta₅N₆ with small amount.

(a)

(b)

Figure 4-6 XPS core level spectra of (a) Ta 4f and (b) N 1s for as-deposited Ta-N thin films (N₂: 0~12 sccm)

The chemical states of tantalum and nitrogen in the films were determined using XPS under mono-Al K α X-ray irradiation. Figure 4-6 shows the XPS core level spectra of Ta 4f (a) and N 1s (b) photoelectrons for the as-deposited Ta-N thin films (N₂: 0~12 sccm). All binding energy values have been corrected for the charging effect with reference to the adventitious carbon 1s peak at 285 eV [47]. It can be observed that with the increase of N₂ flow rate from 0 sccm to 6 sccm, both Ta 4f 5/2 and Ta 4f 7/2 shift to the right side with higher binding energies and become stabilized at 8 sccm of N₂ or higher, which indicates the phase transition and gradual domination of TaN phase in the films, which owns higher binding energy of core level electrons to the atom core. Another reason may be attributed to the smaller thickness with the increase of N₂ flow rate. The thickness effect on the energy shift has been reported by other researchers [72].

Without N₂, the binding energy of Ta 4f_{7/2} photoelectrons was determined to be 22.3 eV, while little nitrogen signal was found. For the N-doped films, when N₂ reaches to 8 sccm or higher, the binding energies of Ta 4f_{7/2} and Ta 4f_{5/2} become stable at 23.3 eV and 25.2 eV respectively, which were consistent with the stoichiometric TaN reported by Sasaki [103]. The binding energy of Ta 4f_{7/2} photoelectrons for b.c.c. Ta and stoichiometric f.c.c. Ta-N compounds were once reported to be 21.9 [104] and 22.6 eV [105] respectively. Chang [106] once reported the binding energy of Ta 4f_{7/2} photoelectrons of pure Ta and low-N incorporated Ta(N) at 22.8 eV and N-doped Ta-N at 23.5 eV. The discrepancy between our results and reported values is presumably due to the structure difference in the films that were prepared under various deposition parameters.

(a)

(b)

Figure 4-7 XPS core level spectra of (a) Ta 4f and (b) N 1s for as-deposited and annealed TaN thin films (N_2 : 8sccm)

Figure 4-7 presents Ta 4f (a) and N 1s (b) photoelectron spectra for the as-deposited and annealed TaN thin films (N_2 : 8 sccm). The binding energies of Ta 4f_{7/2} and Ta 4f_{5/2} keep almost unchanged at 23.0 eV and 24.8 eV respectively even after annealing, which implies that the chemical bonding does not undergo much change before and after annealing, even for longer time. The only difference is the higher peak intensity with longer annealing time. This can be attributed to the better crystallinity of the films after annealing. For N 1s, which overlaps with Ta 4p, the only change is the lower and broader peak after annealing compared with the as-deposited one. This may be due to the escaping of nitrogen atoms during annealing. On the other hand, annealing time doesn't have any effect on the peak position of N 1s, which means the unchanged bonding of nitrogen with tantalum.

4.4. Resistivity and TCR

The resistivity ρ and TCR of the as-deposited and annealed Ta-N films were measured using a standard four-point probe equipment with a temperature-control stage. The testing temperature is adjustable from 298 K (25°C) to 423 K (150°C).

Figure 4-8 shows the resistivity and TCR change versus N_2 flow rates for the as-deposited Ta-N thin films. Without N_2 , the resistivity of the pure Ta film was measured to be 306 $\mu\Omega\cdot\text{cm}$, which is higher than that of α -Ta. Chang reported a resistivity value of only 60 $\mu\Omega\cdot\text{cm}$ for pure α -Ta [106]. Riekkinen obtained a β -Ta phase with resistivity value of 166 $\mu\Omega\cdot\text{cm}$ [40]. Nie has pointed out that β -Ta phase generally has a higher resistivity value compared with α -Ta phase in his study [45]. According to Schauer's

result, b.c.c. α -Ta phase normally has a resistivity value of 25~95 $\mu\Omega\cdot\text{cm}$, and that of β -Ta phase will be higher [107]. These reports are further proof to support our XRD results, and suggest that the film without nitrogen incorporation is most possibly β -Ta phase.

When applying a N_2 flow rate of 2 sccm, the resistivity value remains almost the same as that of pure tantalum, implying a metallic behavior with low resistivity value. This indicates that in the film, a metallic phase, possibly Ta(N), still contributes greatly to the conductivity of the film and results in a resistivity value close to that of the pure β -Ta film. The similar observation was also presented by other researchers [45].

Figure 4-8 Resistivity and TCR change for the as-deposited Ta-N thin films as a function of N_2 gas flow rate

With further increase of N_2 flow rate from 4 sccm to 10 sccm, the resistivity increases monotonically from $450 \mu\Omega\cdot\text{cm}$ to $1100 \mu\Omega\cdot\text{cm}$. The increase in resistivity value can be mainly attributed to the high resistivity of the TaN phase formed in the films, which exhibits semiconductor-like electrical properties ($\rho_{\text{TaN}}=200\sim300$) [45, 46, 106, 108]. The resistivity goes up sharply to as high as $1800 \mu\Omega\cdot\text{cm}$ when N_2 flow rate increases from 10 sccm to 12 sccm. This abrupt increase may also be attributed to the domination of TaN and N-riched semiconductor phases like Ta_3N_5 with higher resistivity ($\rho_{\text{Ta}_3\text{N}_5}=10^6 \mu\Omega\cdot\text{cm}$).

The results of the present work are consistent with the general characteristic of resistivity for the Ta-N film system. Normally the Ta-N system undergoes successive appearance of Ta-rich and N-rich phases when an increasing N_2 flow is introduced into the plasma, and thus the conduction has gradual change from metallic conduction to semiconductive conduction. However, some studies showed a constant level of film resistivity over a rather wide range of nitrogen partial flow rates. For example, $\rho \approx 300 \mu\Omega\cdot\text{cm}$ for 33-45% N_2 [109], $\rho \approx 220 \mu\Omega\cdot\text{cm}$ for 20-27% N_2 [110], and $\rho \approx 250 \mu\Omega\cdot\text{cm}$ for 10.5-20.6% N_2 flow [40].

On the other hand, corresponding to the phase transition in the Ta-N films from metallic β -Ta to semiconductor-like f. c. c. TaN phase, TCR is also associated with a change from metallic ($\text{TCR}>0$) to semiconductor-like ($\text{TCR}<0$) conduction behavior, as shown in Figure 4-8. With the increase of N_2 flow rate, the TCR value shifts from positive value to negative values gradually. At 0 sccm, TCR is + 250 ppm/ $^\circ\text{C}$ for β -

tantalum phase, exhibiting normal metal behavior. Then it decreases continuously from almost 0 ppm/°C at 2 sccm of N₂ to – 250 ppm/°C at 8 sccm of N₂, indicating the transition from metallic phase to semiconductor-like one. A sharp decrease from –500 ppm/°C to -1700 ppm/°C occurs when N₂ flow rate decreases from 10 sccm to 12 sccm, implying the domination of semi conductive behavior. This result matches well with the dramatic increase in the resistivity when N₂ increases from 10 sccm to 12 sccm. This phenomenon, as explained previously, may be due to the formation of some other N-rich phases, like Ta₃N₅. Both the resistivity and TCR changes reflect the variation of microstructures and transition of phases in the films when N₂ flow rate changes.

Figure 4-9 shows the resistivity and TCR change with N₂ flow rate for Ta-N films before and after annealing at 400°C for 2 minutes. It can be seen that the resistivity value will increase after annealing except the film without nitrogen incorporation (N₂: 0 sccm). This can be attributed to the better crystallinity of Ta phase after annealing. In this case, within the crystal lattice, the conduction electrons can move more freely, reducing the chance of colliding with randomly distributed vacancies or defects in the as-deposited film.

For the other films with nitrogen incorporation, the resistivity value is higher than that before annealing. This is due to the escaping of nitrogen atoms entrapped inside the interstitial lattice positions which act as donors to contribute conduction electrons [110]. During deposition, excessive nitrogen atoms can be trapped in the interstitial positions of crystal lattice and grain boundaries, which can serve as donors to provide more conduction electrons to improve the conductivity of the film. However, during annealing, the trapped nitrogen atoms could obtain enough thermal energy to be thermally activated

and escape from the film surface, causing the less number of donors and higher resistivity for annealed films compared with the as-deposited ones. Similar findings have been reported in other studies [41, 58].

Figure 4-9 Resistivity and TCR change as a function of nitrogen flow rate for Ta-N thin films before and after-annealing

Regarding the change of TCR, it can be seen that when N₂ is 0 sccm and 2 sccm, TCR will become more positive after annealing at 400°C for 2 minutes. This may be due to the release of intrinsic stress, recovery of crystal defects and better crystallinity after annealing. However, at 2 sccm, TCR also transforms to a positive value. As explained in

the previous, when N_2 is 2 sccm, metallic Ta and Ta(N) still dominate mainly in the microstructure.

With 4 sccm of N_2 , TCR falls from -36 ppm/ $^{\circ}C$ to -107 ppm/ $^{\circ}C$, indicating the transformation from metallic to semi-conductive conduction in the film after annealing. TCR was reduced further at 6 sccm and 8 sccm of N_2 , suggesting most prevailing of the semiconductor-like phase in the films. Due to the biggest change at 8 sccm, this flow rate was chosen for the investigation of TaN-Cu nanocomposite thin films.

Figure 4-10 Resistivity and TCR change with annealing time for Ta-N thin film (N_2 : 8 sccm) before and after annealing for 2, 4, 8 minutes

Figure 4-10 depicts the change of resistivity and TCR change with annealing time for the film deposited at N_2 flow rate of 8 sccm. It can be seen that the resistivity increases

from $859 \mu\Omega\cdot\text{cm}$ to 907, 913, and $911 \mu\Omega\cdot\text{cm}$ respectively after annealing for 2, 4, 8 minutes. It undergoes little change after annealing for 2, 4, 8 minutes, implying the stable microstructure after annealing and it won't change much even for longer annealing time. Contrary to the resistivity change, TCR decreases quickly from $-243 \text{ ppm}/^\circ\text{C}$ to -840 , -857 , and $-853 \text{ ppm}/^\circ\text{C}$ respectively. It also keeps almost stable even after longer annealing time, arising from the stable crystalline phase formed in the film.

Figure 4-11 Sheet resistance varies with temperature for Ta-N film after annealing for 2 minutes (N_2 : 8 sccm)

Figure 4-11 describes the sheet resistance change vs. temperature for the annealed film when N_2 flow rate is 8 sccm. The result indicates very stable and semi-conductive properties of stoichiometric TaN within the testing temperature range from 25°C to

150°C. It shows a stable negative TCR (~ -1000 ppm/°C). The similar trend showing the change of sheet resistance as a function of temperature was also obtained for the other films ($N_2=4, 6, 10, 12$ sccm), indicating the domination of semiconductor-like phases in the films.

4.5. Summary

In this study, Ta-N thin films were prepared by d.c. magnetron reactive sputtering method. During deposition, N_2 flow rates were varied, ranging from 0 sccm to 12 sccm. After deposition, rapid thermal annealing was applied to anneal the films at 400 °C for 2, 4, 8 minutes. Both the crystal structures and electrical properties were then characterized.

The results indicate that:

1. With the increasing of N_2 flow rate, the phase would transit from pure β -Ta to f.c.c. TaN, and when N_2 was 8 sccm, stoichiometric TaN phase was formed. No Ta_2N phase could be observed. Annealing at 400°C did not change the structure of Ta-N thin films much.
2. The resistivity increased with the increase of nitrogen flow rate, mainly due to the phase transition from pure metallic tantalum to semi-conductive tantalum nitride. TCR decreased with the increase of nitrogen flow rate, which can be attributed to the domination of more semi-conductive TaN phase.

3. After annealing, the resistivity increased further due to the escape of trapped nitrogen atoms that acted as donors to contribute conduction electrons. On the other hand, TCR decreased to a more negative value. This is caused by the stabilization and formation of semiconductor-like TaN phase.

Chapter 5 Microstructure of Ta-N-Cu Nanocomposite Thin Films

5.1 Introduction

This chapter deals with the characterization of microstructures of TaN-Cu thin films by TEM, XRD and XPS. It is important since the properties are the direct reflection of thin film microstructure and will only depend on it. TEM was used for the observation of the microstructures and electron diffraction patterns. XRD was applied for the analysis of crystalline structures and phases. XPS was applied for the determination of chemical compositions and chemical states of Ta, N, and Cu. In TEM and XRD analysis, cases with different Cu concentrations and annealing time were studied. In XPS study, chemical compositions were measured as a function of N₂ flow rate, and chemical states were analyzed as functions of Cu concentrations and annealing time.

The Ta-N-Cu thin film preparation has been described in detail in Chapter 3. After deposition, RTP was applied to anneal the films for inducing the nucleation and grain growth of Cu nano-clusters from the TaN matrix. In order to determine the annealing temperature, DSC (Differential Scanning Calorimetry) test on a TaN-rich film (2.1 at. % Cu) was carried out. According to the DSC result shown in Figure 5-1, Cu begins to crystallize from 300°C and finish at 400°C. The phenomenon of phase transition can be determined by the drop of heat flux. For full crystallization of Cu, 400°C was thus determined. As observed by TEM and analyzed by XRD, Cu nano-clusters were precipitated after annealing from the matrix. They were called secondary Cu (Cu II). According to the results of XPS analysis, the precipitated Cu II nanoparticles exist as

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metallic Cu. The Cu phase formed right after deposition in Cu-rich films was called primary Cu (Cu I). The difference between Cu I and Cu II is that Cu II shows higher binding energies of 2p core level than that of Cu I. The experimental results discussed in chapter 6 proved that Cu II had significant influence on the electrical properties of TaN matrix.

Figure 5-1 DSC curve for an as-deposited TaN-Cu (2.1 at. % Cu)

5.2 TEM results for microstructures

**Figure 5-2 Bright field TEM image of an as-deposited TaN-rich thin film
(Cu=36.5 at. %)**

Figure 5-2 shows the bright field TEM image of an as-deposited TaN-rich thin film s3 (Cu=36.5 at. %) with its electron diffraction pattern (EDP). Only from the plane view, no Cu or TaN particles can be found clearly. This can be explained by two possibilities. One is due to the extremely fine particles of TaN and amorphous Cu existing in the film analyzed by the XRD results; the other is due to the low resolution (1 nm) of conventional TEM that was applied.

From the EDP, the rings from center to the outside are TaN (111), (200), (220), (222) and (311), respectively. All the rings are in a certain degree diffused, implying the very fine TaN particles. This corresponds well with the following XRD result, which shows very broad and low intensity diffraction peaks. No diffraction rings from the Cu crystal planes can be found, suggesting that Cu phase exists in an amorphous

state. This observation also matches well with the XRD result that no Cu diffraction peaks observed from this film.

Figure 5-3 Bright field TEM image of an annealed TaN-rich film (Cu=36.5 at. %) at 400°C for 2 minutes

Figure 5-3 is the bright field TEM image of the above specimen after annealing at 400°C for 2 minutes. Obviously, the Cu clusters begin to form appearing as the dark clusters. These Cu were called secondary Cu or Cu II. They arise from the Cu atoms that were first trapped in TaN matrix and diffuse out to form nano-clusters after annealing. Cu II nano-clusters are distributed almost uniformly in the films. Due to the 1 nm resolution of TEM, the precise particle size can not be estimated. The diffraction rings formed by the electron beams diffracted by the Cu crystal planes can also be detected with very weak intensity. As previously reviewed, when the grain size of metal is less than 10 nm, it will not show the normal metal behavior but semiconductor behavior. In this case, the energy band will be in a discontinuous state, instead of a continuous one as in the bulk metal materials [111]. The energy gap between the conduction band and the valence band becomes larger. With grain size

larger than the critical size (10 nm), the nano-particles will show normal metal behavior [112]. However, the fact is that different metals will have different critical sizes, but for most of the metal, the critical size is about 10 nm [113].

Figure 5-4 Bright field TEM image of an annealed TaN-rich film (Cu=36.5 at. %) at 400°C for 4 minutes

Figure 5-4 shows the bright field TEM image and its diffraction pattern for the above film after annealing for 4 minutes. With longer annealing time, Cu particles grow larger with the average grain size of 5~8 nm. These nano-sized Cu particles will also give rise to the higher resistivity and more negative TCR due to the quantum size effect. Another possible effect caused by the continuous Cu particles precipitation is that TaN matrix will become looser, which may also cause the increase of resistivity and decrease of TCR [55]. The diffraction ring coming from Cu is more obvious than that from the as-deposited film and the film after annealing for 2 minutes. This can be due to the grain growth of Cu nano particles.

Figure 5-5 Bright field TEM image of an annealed TaN-rich film (Cu=36.5 at. %) at 400°C for 8 minutes

Figure 5-5 shows the bright field TEM image and its diffraction pattern of the above film after annealing for 8 minutes. It can be seen that some Cu particles with the astonishing grain size of 100 nm~120 nm were presented, which corresponds to big diffraction spots from these large Cu particles. However, the diffraction spots are embedded on the continuous diffraction rings. The continuous Cu diffraction rings indicate that the grain size of Cu is small. However, by the conventional TEM, the much smaller Cu particles contributing to the continuous diffraction rings cannot be detected. This TEM result also corresponds with the XRD result that shows the combination of a sharp Cu diffraction peak and a broad base line for the above film (section 5.3).

These large Cu particles (100~120 nm) will decrease the resistivity and increase TCR compared with the nano-sized Cu particles, since they will exhibit normal metal behaviors. In these Cu particles, the energy band is continuous and the conduction electrons can move freely and the chance of scattering within the crystal lattice is

much less. At the same time, the surface to volume ratio becomes smaller with the grain growth, the grain boundaries scattering contributing to the resistivity will be reduced. So, the grain growth of Cu particles and the reduced surface to volume ratio will give rise to the decrease of resistivity and increase of TCR.

Figure 5-6 Bright field (a) and dark-field (b) TEM images of an as-deposited Cu-rich film (Cu=67.5 at. %)

Figure 5-6 shows (a) bright and (b) dark field TEM images of s8 (Cu=67.5 at. %). The primary Cu particles (Cu I) can be observed clearly. The particle size ranges from several nanometers to more than 15 nm. The average grain size was calculated to be around 10 nm. According to the XRD result, the average grain size obtained by

Scherrer equation is about 6~7 nm. There is only acceptable difference between the TEM and XRD results.

Figure 5-7 Bright field TEM image of a Cu-rich film (Cu=67.5 at. %) after annealing at 400°C for 8 minutes

Figure 5-7 shows the bright field TEM image and diffraction pattern of a Cu-rich film (Cu=67.5 at. %) after annealing at 400°C for 8 minutes. It is clearly that there are two different types of Cu particles co-existing in the film, Cu I and Cu II. Cu I was first formed right after the deposition. After annealing for 8 minutes, it has large grain size ranging from 15 to 25 nm, some of which even get together to be larger than 100 nm. Cu II comes from the atoms embedded in TaN matrix and have an average grain size of about 10 nm. These conclusions can also be proved in the XRD results discussion. These two kinds of Cu particles will exhibit different properties due to different particle sizes. In the previous review, when metal particle size reaches to a critical size, specific nano-size effect like small size effect, quantum size effect, surface effect, tunneling effect, etc, will impose on the particles [53, 111].

5.3 XRD results for crystal phase

The position of Si substrates during the deposition of Ta-N-Cu nanocomposite thin films has been plotted using a schematic drawing in Chapter 3. There are eight pieces of Si substrates in one batch. From sample (1) to (8), the composition of the as-deposited thin films shifts continuously from TaN-rich to Cu-rich, due to the relative distance between the Si substrates and the Cu/Ta targets. The precise compositions obtained by XPS analysis for all films with an 8-sccm N₂ flow during the deposition were shown in Table 5-1. This precise concentration will be helpful for us to understand the XRD results.

Table 5-1 Compositions for as-deposited Ta-N-Cu thin films (N₂: 8 sccm)

	1	2	3	4	5	6	7	8
Cu (at. %)	2.161	5.937	36.516	55.167	58.403	60.51	63.352	67.456
Ta (at. %)	45.269	42.332	25.186	14.624	12.777	9.94	11.021	9.247
N (at. %)	44.479	45.614	25.924	14.912	9.927	9.52	9.624	8.712

Figure 5-8 X-ray diffraction patterns of the as-deposited Ta-N-Cu thin films (N_2 : 8 sccm). From (1) to (8), Cu increases from 2.16 at.% to 67.5 at.%

The numbers in brackets represent samples from 1 to 8 with continuously changed Cu contents. The identification of the diffraction peaks was done by comparing the peak positions with diffraction data from the JCPDS-International Center for Diffraction Data.

From Figure 5-8, only sample (1) with 2.1 at. % Cu reveals a strong peak at 35.7° , which can be indexed as (111) of stoichiometric f. c. c. TaN phase. A broad and low peak at 74° corresponds to (311) of f. c. c. TaN. The high intensity ratio between (111) and (311) indicates a highly TaN (111) preferred orientation for this film with only 2.1 at. % Cu. This XRD result for sample (1) is very similar to pure f. c. c. TaN phase obtained in Chapter 4. This indicates that such a low Cu at. % addition is not high

enough to cause the obvious change in the crystalline structure of TaN matrix. For sample (1), no Cu peaks can be observed, which may be due to a very low Cu concentration (2.1 at.%). In this case, Cu phase may exist as nanocrystalline grains or in amorphous state embedded in TaN matrix [114].

For sample (2) with 5.9 at. % Cu, a sharp decrease in TaN (111) peak intensity has been observed, implying the disappearance of TaN (111) preferred orientation and smaller grain size when 5.9 at. % of Cu was incorporated into TaN matrix. This can be due to the mixing effects by incorporation of Cu into TaN matrix, and other researchers also reported this phenomenon [115, 116]. It has been reported by Musil that the addition of a second element to a base material strongly affects the mechanism of its formation and can be used as an efficient way to control the structure and grain size of sputtered films. The changes would depend on greatly the type and quantity of the second element [116, 117].

From sample (3) to (6), the co-existence of TaN phase and Cu phase is evident since diffraction peaks of both TaN (111) and Cu (111) could be clearly seen. The peak at 43.2° can be indexed as f. c. c. Cu (111). For sample (7) and (8), no peaks from TaN can be observed, and only Cu (111) at 43.2° can be observed. In this case, TaN may exist as very fine nano-crystals or in amorphous state embedded in Cu matrix. Another peak at 50.4° from Cu crystal plane can be indexed as f. c. c. Cu (200) and can only be found in sample (8). Similar f. c. c. Cu phase appearing in Ta-low Ta-Cu alloys was also reported by Kim [118]. With the increase of Cu content, Cu (111) becomes more dominant, but the degree of preferred orientation at Cu (111) is much lower than TaN (111) in sample (1). This may be caused by different mutual solubility

of Cu in TaN matrix and TaN in Cu matrix. For TaN-rich thin films, TaN acts as the matrix; while for Cu-rich thin films, Cu will act as the matrix.

On the other hand, from sample (2) to (8), all the diffraction peaks are very broad and weak. Based on the basic X-ray diffraction theory or Scherrer equation, it can be concluded that very fine grain size or amorphous phases were formed in the as-deposited films. Some papers concerning characterization of Ta-Cu amorphous alloy films had been published [92, 93, 94], but very few studies on Ta-N-Cu ternary system so far. In reference [93], it reported that Ta_xCu_{1-x} films are in glassy or amorphous state when $0.55 \leq x \leq 0.95$. In some studies, the amorphous phase has been proved to contribute to the negative TCR [112]. As reviewed in Chapter 2, the extremely fine crystals with only several nanometers, the amorphous and near-amorphous solids will cause the “weak-localization” of the conduction electrons, with each crystal acting as a potential well with boundary (interface) as a barrier. As a result, a large fraction of conduction electrons is localized within this well, causing the decrease of effective density of conduction electrons [55], thus the higher resistivity and negative TCR.

Figure 5-9 X-ray diffraction patterns of Ta-N-Cu thin films (N_2 : 8 sccm) after annealing at 400°C for 2 minutes

Figure 5-9 is the plot of X-ray diffraction patterns for the above eight samples after annealing at 400°C for 2 minutes using RTP. Compared with the as-deposited thin films shown in Figure 5-8, the annealed samples show comparatively higher and sharper TaN and Cu peaks. This indicates better crystallinity and larger grain sizes after annealing. It was expected that during the RTA process, Cu clusters begin to nucleate from TaN matrix where the Cu atoms were originally trapped, and these precipitated Cu clusters after annealing are called secondary Cu (Cu II). The Cu phase right after deposition as detected by XRD shown in Figure 5-8 are called primary Cu (Cu I). It has been observed by TEM that Cu I and Cu II co-exist in Cu-rich film after annealing. Cu I and Cu II will grow larger with longer annealing time. Thus, for Cu-

rich thin films, after annealing, Cu peaks will be composed of two separate peaks: one from the original Cu I and the other one from thermally induced Cu II. However, because of the low resolution of XRD, it is difficult to discriminate between these two types of Cu particles clearly.

On the other hand, TaN phase only undergoes the release of intrinsic stress and re-crystallization, which results in the higher intensity of TaN diffraction peaks. However, due to the high melting point of TaN (3087°C) [119], the annealing temperature at 400°C is too low to cause the grain growth of TaN. The possible phases existing in Ta-N-Cu thin films before and after annealing are listed in the below table (Table 5-2). According to the definition of nanocomposite thin films described in chapter 2 and the experimental results of XRD and TEM, the TaN-Cu thin films produced with an 8-sccm N₂ flow rate are proposed to be nanocomposite thin films.

Table 5-2 Possible phases existing in Ta-N-Cu thin films before and after annealing (N₂: 8 sccm)

	Cu: 2.1 at. %~36.5 at. %	Cu: 36.5 at. %~67.5 at. %
Before annealing	Nanocrystalline TaN+ Trapped Cu atoms+ Amorphous phase	Primary Cu (Cu I)+ Nanocrystalline TaN+ Trapped Cu atoms+ Amorphous phase
After annealing	Nanocrystalline TaN+ Fine Cu particles (Cu II)+ Amorphous phase	Primary Cu (Cu I)+ Nanocrystalline TaN+ Fine Cu particles (Cu II)+ Amorphous phase

Figure 5-10 X-ray diffraction patterns of a TaN-rich film (Cu=36.5 at. %) before and after annealing at 400°C for 2, 4, 8 minutes

Figure 5-10 shows the X-ray diffraction patterns of sample 3 (Cu=36.5 at. %) before and after annealing for 2, 4, 8 minutes respectively. It is obvious that Cu (111) and Cu (200) peaks become sharper and higher when annealing time increases from 2 minutes to 4 and 8 minutes. However, little change in the intensity and shape on TaN peaks can be found even with longer annealing time. This result matches well with the XRD results presented in Chapter 4. Accordingly, annealing at 400°C has a more obvious effect on the grain growth of Cu than that on TaN phase [120].

What can also be observed is that Cu (111) and Cu (200) peaks actually can be separated into two parts, the broadened base line and the sharp top line, suggesting the existence of two types of Cu particles. One is the larger size Cu I phase contributing

the sharp top peak, and the other one is the very fine Cu II particles causing the broadened base peak. However, due to the partial overlapping of TaN (200) with Cu (111), the grain size can't be obtained by using the Scherrer's equation.

The co-existence of Cu I and Cu II has been proved by TEM photo shown in Figure 5-7. The Cu II nano-clusters were formed after annealing. Nano-sized Cu II clusters can cause the quantum size effect. The precipitation of Cu II particles may also make the TaN matrix become porous, giving rise to more vacancies and holes left inside the matrix. The vacancies and holes will lead to the reduction of effective conduction area, creating the extrinsic increase of resistivity and decrease of TCR [56, 121].

Figure 5-11 X-ray diffraction patterns of a Cu-rich film (Cu=67.5 at.%) before and after annealing at 400°C for 2, 4, 8 minutes

Figure 5-11 shows the XRD patterns of s8 (Cu=67.5 at. %) before and after annealing for 2, 4, 8 minutes. Just like sample 3, with the increase of annealing time, Cu (111) and Cu (200) peaks become sharper and higher, especially the Cu (111) peak.

This result indicates better crystallinity, higher degree of Cu (111) preferred orientation and larger grain size of Cu. Similar to sample 3, no significant change in the intensity and shape of TaN peaks was found even for a longer annealing time due to the low annealing temperature. It can also be seen that after annealing, Cu (111) peak actually can be separated into two peaks, one broad base line and one sharp top line as discussed in Figure 5-11. In order to explain this phenomenon clearly, a schematic drawing was plotted and shown in Figure 5-12.

Figure 5-12 Schematic drawing of Cu (111) peak for the Cu-rich film (Cu=67.5 at. %) after annealing at 400°C for 2 minutes

From Figure 5-12, the sharp and high peak arises from primary Cu phase (Cu I) with larger grain size (14~15 nm calculated by Scherrer's equation). The broad and short peak is contributed by secondary Cu phase (Cu II) with very fine grain size (2~3 nm calculated by Scherrer's equation). Due to different grain size, secondary Cu

particles (Cu II) may create much different effects compared with the primary Cu (Cu I) [59]. Therefore, the ultimate effect on the electrical behaviors of TaN-Cu nanocomposite thin films caused by these two types of Cu particles would be the competitive or the combination effect between Cu I and Cu II.

Figure 5-13 X-ray diffraction patterns of an as-deposited pure TaN and a TaN-rich TaN-Cu (Cu=5.9 at. %)

Figure 5-13 shows the comparison of X-ray diffraction patterns between a pure TaN and a TaN-rich TaN-Cu film (Cu=5.9 at. %). Firstly, pure TaN exhibits sharp and high TaN (111) peak that indicates the columnar structure in the film as explained by Saha [21]. Comparatively, TaN (111) and TaN (200) from TaN-Cu (Cu=5.9 at. %) are much broader and shorter. No Cu peaks can be observed. This result suggests that TaN-rich film has nanocrystalline TaN structures with near-amorphous Cu particles embedded in. The similar phenomenon has also been reported by other researcher

[116]. This is due to the mixing effects as explained in reference [86]. Cu incorporation results in the decrease of grain size of TaN phase. Another difference between TaN and TaN-Cu (Cu=5.9 at. %) is that the preferred orientation of TaN (111) disappears after mixing with Cu.

5.4 XPS results for chemical state analysis

As is well known that XPS is a very useful and superior technique for thin film characterization in compositions, chemical states or chemical shifts, depth profiling, thin film thickness, and imaging and so on [122]. In this study, XPS was also applied for composition, chemical state and depth profiling of different elements (Ta, N and Cu), before and after annealing. Both survey (wide) scan and detailed (narrow) scan were performed. Through survey scan from 1280 eV to 0 eV, the elements existing on the film surface can be identified by using the elemental library. While doing detailed scan on Cu 2p, O 1s, N 1s, C 1s, Ta 4f, the information about the chemical states of each element can be obtained. From Cu 2p binding energy difference caused by small size effect [123], Cu I phase and Cu II phase can be discriminated. Depth profiling was also performed by using Ar ion etching to investigate the distribution of elements in the bulk material before and after annealing. The operation of the depth profiling consisted of the repetition of the Ar etching for 300 s followed by an XPS detailed scan until the total sputtering period reached 30 minutes [124].

5.4.1 Survey scan

(a)

(b)

Figure 5-14 Survey scan for an as-deposited (a) TaN-rich (Cu: 5.9 at. %) and (b) Cu-rich (Cu: 67.5 at. %) sample

Survey scans from 1280 eV to 0 eV on an as-deposited TaN-rich (Cu: 5.9 at. %) and a Cu-rich (Cu: 67.5 at. %) sample with a step size of 1 eV were performed on the film surface. For the TaN-rich film, Ta 4f, C 1s, N 1s, and O 1s were detected, while no Cu 2p could be detected. However for Cu-rich film, only C 1s, O 1s and Cu 2p were collected, while no Ta 4f or N 1s were detected.

5.4.2 Concentrations

(a)

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(b)

(c)

Figure 5-15 Atomic concentrations of eight as-deposited Ta-N-Cu thin films deposited with (a) N₂=2 sccm, (b) N₂=4 sccm, (c) N₂=8 sccm. The substrates were placed in sequence on substrate holder

Figure 5-15 shows the atomic concentration of Cu, Ta and N for eight as-deposited and sequentially placed Ta-N-Cu samples with 2, 4, and 8 sccm of N_2 added into the chamber during deposition. Substoichiometric TaN is formed in the films deposited with 2 and 4 sccm of N_2 , while stoichiometric TaN is formed when deposited with 8 sccm of N_2 . It is also observed that the ratio of Ta to N is not affected by Cu concentration.

5.4.3 Chemical states

Figure 5-16 Cu 2p core level spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes

Figure 5-16 is the Cu 2p spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes. With the increase of Cu content continuously from s1 to s8, Cu 2p 3/2 and Cu 2p 1/2 shifts to the left side very slightly with lower binding energies. Cu 2p 3/2 reaches to the highest value at 933.5 ± 0.1 eV for s1 and the minimum value at 932.5 ± 0.1 eV for s8. Cu 2p 3/2 and Cu 2p 1/2 become higher in the intensity and narrower in its shape with the increase of Cu content from 2.1 at. % to 67.5 at. %.

Figure 5-17 Ta 4d core level spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes

Figure 5-17 is the plot for Ta 4d spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes. Just contrary to the change of Cu 2p peaks, Ta 4d 3/2

and Ta 4d 5/2 decrease in the intensity with the increase of Cu content. The samples of s1 and s2 show the highest peak intensity. From s3 to s8, Ta 4d 3/2 and Ta 4d 5/2 peaks can be observed to be broader in full width at half maximum (FWHM) and lower in peak intensity due to relatively low Ta concentration in the films. In most of the papers, Ta 4f was collected and studied [30, 47, 125], however, there is few reports on Ta 4d.

Figure 5-18 N 1s core level spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes

Figure 5-18 is the N 1s spectrum of as-deposited Ta-N-Cu thin films after Ar ion etching for 12 minutes. The sharp and high peak with lower binding energies at the left side comes from Ta 4p 3/2 photoelectrons. The binding energy of Ta 4p 3/2 is so

close to N 1s that these two peaks overlaps with each other. The similar results were also reported in other studies [42, 123]. Corresponding to Ta 4d, N 1s can be detected from s1 and s2 with highest intensity and smallest FWHM. Other films show comparatively weak signal. The binding energy of N 1s at 397.2 eV matches with that of TaN and close to the value reported by [30].

Figure 5-19 Cu 2p core level spectrum for s1 (Cu=2.1 at. %) after annealing at 400°C for 2, 4, and 8 minutes

Figure 5-19 plots Cu 2p core level spectrum for s1 (Cu=2.1 at. %) after annealing at 400°C for 2, 4, and 8 minutes. So it can be clearly seen that the binding energy of Cu 2p 3/2 is 933.5 ± 0.1 eV for the film after annealing for 2 minutes (particle size: 3~5 nm), and that of the same film after annealing for 4 and 8 minutes is almost the same

at 932.7 ± 0.1 eV and closer to bulk Cu at 932.0 eV~932.2 eV due to the growth of Cu clusters [126]. (particle size: 5~8 nm and 15~16 nm respectively). This special phenomenon was also reported by other researchers [74, 126, 127]. Martin [126] reports that Cu 2p $3/2$ spectra shifted towards higher binding energies from 932.2 eV in pure Cu to 933.0 eV in amorphous $\text{Cu}_{31}\text{Y}_{69}$ thin films, which is so similar to our results. In [74], Wu reports the change of Cu 2p as a function of Cu coverage on the substrate, that is Cu 2p $3/2$ binding energy increases from 932.7 eV to 933.7 eV when Cu coverage decreases from 20 Å to 0.2 Å. Sun [73] even points out that the core level binding energy of a nanosolid shifts inversely with the particle radius.

Figure 5-20 Cu 2p core level spectrum for s8 (Cu=67.5 at. %) before and after annealing at 400°C for 2, 4, and 8 minutes

Figure 5-20 plots Cu 2p core level spectrum for s8 (Cu=67.5 at. %) before and after annealing at 400°C for 2, 4, and 8 minutes. The spectrum were collected after Ar ion etching for 10 minutes in order to eliminate the oxidation and contamination on the film surface. There is little shift on Cu 2p 3/2 peak before and after annealing, which can be attributed to the larger Cu particle size for the as-deposited film (~10 nm). These Cu particles own the same physical properties as bulk Cu and won't show the size effect any more. After annealing for 2, 4 and 8 minutes, Cu particles grow larger with almost unchanged Cu 2p_{3/2} binding energy of 932.5 eV. In [128], Yang said that the binding energy of Cu clusters shows strong size dependence and he plotted a line showing the Cu 2p_{3/2} binding energy shift (relative to 932.6 eV for bulk Cu) as a function of the average cluster size. In his result, when cluster size is larger than 10 nm, the binding energy shift will be close to zero, which matches well with our results.

From the above study, the binding energies of Cu 2p_{3/2} for TaN-rich (Cu=2.1 at. %) and Cu-rich (Cu=67.5 at. %) films before and after annealing can be listed in Table 5-3. It can be concluded that for TaN-rich film, Cu 2p_{3/2} decreases to smaller value with the increase of annealing time from 2 minutes to 4 and 8 minutes. This is due to the grain growth of Cu II nano-clusters. Higher binding energies are caused by the size effect of Cu nano-clusters. However for Cu-rich film, there is almost no change on binding energy of Cu 2p_{3/2}. This is due to the larger grain size of 10 nm for Cu I formed in the as-deposited Cu-rich film and grows even larger after annealing. There is no size effect exhibited by Cu I. Thus, the binding energies of Cu particles (≥ 10 nm) approach to those of bulk Cu.

Table 5-3 Binding energies of Cu 2p_{3/2} for a TaN-rich and a Cu-rich sample before and after annealing at 400°C for 2, 4, and 8 minutes

Annealing Cu 2p _{3/2} (eV)	As-deposited	400°C-2 min.	400°C-4 min.	400°C-8 min.
TaN-rich (Cu=2.1 at. %)	932.8	933.5±0.1	932.7±0.1	932.7±0.1
Cu-rich (Cu=67.5 at. %)	932.5	932.5	932.5	932.5

5.4.4 Cu I and Cu II

From the above XRD and TEM analysis on Cu-rich films, it is known that primary Cu phase (Cu I) co-exists with secondary Cu (Cu II) after annealing. However, XRD and TEM results can only give us a qualitative analysis. In order to get a quantitative concentration of Cu I and Cu II, a deconvolution of Cu 2p spectrum for s8 after annealing for 8 minutes was shown to show the co-existence of Cu I and Cu II with different binding energies (as shown in Figure 5-21).

Figure 5-21 Deconvolution of Cu 2p for s8 (Cu=67.5 at. %) after annealing at 400°C for 8 minutes

Figure 5-21 is the deconvolution of Cu 2p for s8 (Cu=67.5 at. %) after annealing at 400°C for 8 minutes. By curve fitting, Cu 2p_{3/2} can be separated into two peaks. The sharp and high peak at 932.5 eV corresponds to Cu I according to the value of sample 8 (Figure 5-16). The short and broad one at 933.5 eV arises from Cu II according to the value of sample 1 (Figure 5-16). It has been found by Wu that the FWHM of Cu 2p_{3/2} peak becomes broader as the Cu coverage on the substrate decreases [74]. Martin also compared the FWHM of Cu 2p peak of crystalline Cu with that of amorphous Cu; and he obtained an increase in FWHM with the increase in the degree of amorphous

state [126]. By deconvolution, the ratio between Cu I and Cu II components can be determined. By calculation, Cu I occupies 82.5 % of the total Cu, and 17.5 % of Cu II.

Figure 5-22 Comparison of Cu 2p_{3/2} for as-deposited pure Cu, Cu-rich and TaN-rich thin films

For observation of Cu 2p_{3/2} peak shift with change of Cu concentration (Cu particle size), three typical thin film specimens were selected: pure Cu, Cu-rich (Cu=67.5 at. %), TaN-rich (Cu=5.9 at. %). The result was shown in Figure 5-22. With the increase of Cu concentration, Cu 2p_{3/2} shifts to the lower binding energy from 932.5 eV for TaN-rich film (Cu=5.9 at. %) to 932.3 eV for Cu-rich and pure Cu films. Our result matches well with the reported studies.

5.4.5 Cu distribution

Figure 5-23 Depth profile of Cu 2p for as-deposited s1 (Cu=2.1 at. %). The time labeled at the right side is the etching time

Figure 5-23 plots the depth profile of Cu 2p for as-deposited s1 (Cu=2.1 at. %) after Ar ion etching for 30 minutes. It can be concluded that Cu distributes along the film thickness uniformly with the Cu 2p 3/2 binding energy at 933 eV consistently, due to almost the same intensity after etching for various cycles. Cu 2p 3/2 from the surface before Ar ion etching shows higher binding (934 eV) energy, mainly due to the oxidation of Cu on the surface after deposition. On the other hand, much lower binding energy of Cu 2p_{3/2} at 933 eV indicates Cu exists in metallic state.

Figure 5-24 Depth profile of Cu 2p for s1 (Cu=2.1 at. %) after annealing at 400°C for 8 minutes

Figure 5-24 depicts the depth profile of Cu 2p for s1 after annealing at 400°C for 8 minutes. Even after annealing for 8 minutes, the distribution of Cu along the film thickness is still uniform, as indicated by almost the same Cu 2p intensity. The chemical state of Cu (BE=932.5 eV) still exists as free Cu, however it is lower than that of the as-deposited thin film (BE=933 eV) with the same Cu concentration, due to the larger grain size after annealing. The similar results were also obtained for Ta 4f and N 1s spectrum and won't be shown here. For Cu-rich films, Cu has the same distribution as TaN-rich films and was shown in Figure 5-25.

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(a)

(b)

Figure 5-25 Depth profile of Cu 2p for s8 (Cu=67.5 at. %) (a) As-deposited, (b) after annealing at 400°C for 8 minutes

Figure 5-25 plots the depth profile of Cu 2p for s8 (Cu=67.5 at. %) for (a) as-deposited and (b) after annealing for 8 minutes at 400°C. Cu distributes uniformly

along the film thickness before and after annealing just like TaN-rich film. Cu under the film surface exists as metallic Cu ($\text{Cu } 2p_{3/2}=932.5 \text{ eV}$), while the surface Cu was oxidized ($\text{Cu } 2p_{3/2}=933.5 \text{ eV}$). Thus, Cu phase distributes uniformly along the film thickness. On the other hand, either Cu in bulk TaN-rich film or bulk Cu-rich film exists in metallic state and Cu doesn't react with nitrogen to form any compound, while co-existing as free Cu with TaN phase.

5.5 Summary

From the above discussion, the crystal phases, microstructures, compositions, and chemical states analyzed by XRD, TEM, and XPS respectively for Ta-N-Cu nanocomposite thin films can be summarized as the following:

1. By TEM, for the as-deposited TaN-rich film ($\text{Cu}=36.5 \text{ at. } \%$), no Cu particles were observed by conventional TEM. After annealing for 2 minutes, tiny Cu particles shown as dark clusters were formed. After annealing for 4 minutes, Cu particles grew to the average size of 5~8 nm. After annealing for 8 minutes, the average particle size increased to 15~25 nm, and some even increased to 100~120 nm.
2. For Cu-rich films, after annealing for 8 minutes, besides the large Cu I particles, secondary Cu II could also be clearly observed with the average size of 10 nm. Cu atoms that were first trapped in TaN crystal lattice were induced during the annealing process to form Cu II.
3. Analyzed by XRD, when N_2 flow rate was 8 sccm, different nanocrystalline TaN and Cu phases were formed in the films. When Cu was less than 36.5 at.

%, only TaN phase could be detected. TaN phase and primary Cu phase (Cu I) co-existed when Cu was more than 36.5 at. %. According to the definition of nanocomposite thin film, TaN-Cu thin films belonged to it.

4. Analyzed by XRD, most of the as-deposited films showed very broad and low intensity TaN and Cu peaks, indicating the existence of very fine crystalline grains or the near-amorphous phase. With the increase of Cu content, Cu peaks (111) and (200) became higher, implying the better crystallinity and larger grain size. After annealing at 400°C, the Cu peaks became stronger and sharper with the increase of annealing time. However, no much change in the intensity and shape of TaN peaks was observed.
5. Cu (111) peak for Cu-rich films after annealing could be divided into two separate peaks. One sharp and high peak came from primary Cu (Cu I), and the other broad and low peak arose from secondary Cu (Cu II).
6. By XPS, Cu 2p peaks shifted to lower binding energy and became sharper with the increase of Cu content in the film. Higher binding energy of Cu 2p from TaN-rich films was due to the size effect of nano-sized Cu particles. Binding energies of Cu 2p correspond to metallic Cu. Binding energies of Ta 4d and N 1s matched with TaN phase.
7. After annealing, Cu 2p showed the same trend as that caused by the increase of Cu content, that is, with the increase of annealing time, Cu 2p shifted to lower binding energies and at the same time became sharper due to the grain growth of Cu particles.

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8. By XPS peak deconvolution, for Cu-rich films after annealing, Cu 2p $3/2$ could be separated into two peaks. The lower binding energy came from primary Cu (Cu I), and the other higher binding energy arose from secondary Cu (Cu II). The relative components of Cu I and Cu II were also calculated.
9. By XPS depth profiling, Cu distributed uniformly along the film thickness as free metallic Cu before and after annealing for both the TaN-rich and Cu-rich films.

Chapter 6 Electrical Properties of Ta-N-Cu Nanocomposite Thin Films

This chapter composes of two parts: (i) investigation of electrical properties of Ta-N-Cu thin film in its resistivity and TCR, and (ii) its conduction mechanism behind. Compared with Ta-N thin films, the electrical properties of TaN-Cu nanocomposite thin films show very different electrical properties. The results reveal that both the resistivity and TCR are largely dependent on Cu content, nitrogen flow rates and annealing time. It is exciting that by precisely controlling those three parameters, a near-zero TCR could be achieved, since a zero-TCR is the most important and basic requirement for thin film resistors. On the other hand, with the variation of N₂ flow rate, a wide range of resistivity could be obtained. Thus, in this chapter, the effects of Cu content, N₂ flow rates and annealing time on the change of resistivity and TCR were discussed. A theoretical model based on the experimental results was set up to explain the conduction mechanisms for TaN-rich and Cu-rich films.

6.1 Effects of Cu content on the electrical properties

By putting Si at different locations on the substrate holder, TaN-Cu nanocomposite thin films with various Cu contents can be obtained. The experimental results suggest that Cu content has an obvious effect on the resistivity and TCR.

Figure 6-1 Resistivity change as a function of Cu content for the as-deposited thin films (N_2 : 8 sccm)

Figure 6-1 shows that the resistivity varies with Cu content for the as-deposited TaN-Cu nanocomposite thin films (N_2 : 8 sccm). The resistivity seems to follow the Nordheim's rule for the randomly mixed two elements which suggests the maximum resistivity value at almost 50 at. % of two metal materials [129]. In our experiments, a maximum resistivity value is also found when Cu atomic concentration is around 50 at. %. With further increase of Cu content, the resistivity decreases gradually. This is mainly due to the switching of the continuous TaN matrix, a semi-conductive phase with a much higher resistivity value, to Cu, a metallic phase with a lower resistivity value. The same trend has been found in other cases when the films are deposited under varied nitrogen flow rates (N_2 : 0, 2, 4, 6 sccm).

When Cu is less than 60 at. %, the resistivity value for TaN-Cu nanocomposite thin films is much higher than that of pure TaN phase ($823.7 \mu\Omega\cdot\text{cm}$). This is mainly due to the co-existence of Cu nano-clusters and certain degree of amorphous phase formed in the film. It was reported that in the case of alloy systems, the disordered structure would increase the overall resistivity but at the same time lower the resistivity dependence on temperature [130]. It is often the case that some amorphous phase could be formed when two immiscible phases are mixed together by some non-equilibrium synthesis methods, like sputtering, evaporation, sol-gel and so on [131, 132].

On Cu-rich sides, the resistivity value is much lower than that of TaN-rich films, but it is still higher than that of the pure Cu phase. When Cu is 80 at. %, the resistivity value is about $120 \mu\Omega\cdot\text{cm}$, while the resistivity value for pure Cu is only $2.5\sim 7 \mu\Omega\cdot\text{cm}$ [133]. This can be attributed to two factors. One is the film contains a little amount of TaN phase, which has a higher resistivity value. Another one is certain amount of amorphous phase may exist in the film, which can also cause the increase of the resistivity.

Figure 6-2 TCR change as a function of Cu content for the as-deposited thin films (N_2 : 8 sccm)

Figure 6-2 shows the TCR variation with Cu content for the as-deposited films (N_2 : 8 sccm). With the increase of Cu content, TCR climbs up to the positive side. Thus, it is not surprising that a zero TCR will be obtained finally. This is mainly due to the formation of larger Cu clusters with the increase of Cu content. In this case, a zero TCR is achieved when Cu is about 75 at. %. It can be concluded that the negative TCR caused by the TaN phase can be gradually compensated by the positive TCR of Cu phase. The similar change of TCR, when the second metal element was incorporated into the semiconductor or ceramics matrix, can also be found in the references [134, 135].

However, when Cu content is less than 60 at. %, the TCR value is much more negative than that of pure TaN phase ($\text{TCR} = -823 \text{ ppm}/^\circ\text{C}$). This is mainly caused by the existence of amorphous phase. Amorphous phase was known to contribute negatively to the total TCR due to its weak localization effect [71, 136].

When Cu concentration is higher than 60 at. %, TCR increases from $-500 \text{ ppm}/^\circ\text{C}$ to $0 \text{ ppm}/^\circ\text{C}$ when Cu increases from 65 at. % to 75 at. %, and finally to $340 \text{ ppm}/^\circ\text{C}$ at about 80 at. %. Within this compositional range, the films begin to show a metallic behavior with positive TCR, which can be explained by the fact that the matrix has undergone a transition from the semi-conductive TaN phase to metallic Cu phase.

On the other hand, even Cu content is close to pure Cu ($\text{Cu} = 80 \text{ at. \%}$), TCR value of TaN-Cu is still much lower than that of pure bulk Cu phase ($\text{TCR} \approx 4300 \text{ ppm}/^\circ\text{C}$). This can be attributed to two factors. One is the films still contain a little amount of TaN phase, which offset the positive TCR value of Cu; the other one is that certain amount of amorphous phase exists, which also causes the negative TCR.

6.2 Effects of N_2 on the electrical properties

During the deposition of Ta-N-Cu nanocomposite thin films, N_2 was introduced into the process chamber with varied flow rates ranging from 0 sccm to 8 sccm. The electrical property tests also reveal that N_2 flow rate also has an obvious effect on the resistivity and TCR. Figure 6-3 shows the resistivity change as a function of Cu content at various N_2 flow rates of 0, 2, 4, 6, 8 sccm for the as-deposited thin films.

Figure 6-3 Resistivity change as a function of N_2 flow rates for the as-deposited thin films

From Figure 6-3, it can be observed that a maximum value can always be found at a certain point for all the cases. Furthermore, with the increase of N_2 flow rates, the maximum resistivity value moves to the right side with more Cu concentration in the films. When N_2 flow rate is 8 sccm, the maximum value has been found at 50 at. % of Cu. It is also interesting to find that the resistivity values when N_2 is 2 sccm are smaller than those when N_2 is 0 sccm. What can also be observed is that with the increase of the N_2 flow rates, the overall resistivity value would increase. This is similar to the resistivity change of pure Ta-N phase with increase of N_2 .

Figure 6-4 Resistivity change as a function of N₂ flow rate (Cu: 40 at. %) for the as-deposited thin films

Figure 6-4 shows the resistivity change as a function of N₂ flow rates at a constant Cu content of 40 at. %. With the increase of N₂ flow rates, the resistivity increases. There is a sharp increase when N₂ increases from 6 sccm to 8 sccm. A small decrease is observed at 2 sccm. This may be attributed to the domination of a metallic phase with small amount of N atoms trapped acting as the donors of conduction electrons.

The trend of resistivity change, varying with N₂ flow rates for Ta-N-Cu thin films, is very similar to that for pure Ta-N thin films. The only difference is the resistivity of Ta-N-Cu is much higher than that of Ta-N due to the amorphous phase formed in Ta-N-Cu thin films, which is due to the mixing effect of Ta-N and Cu, as discussed in the above.

Figure 6-5 TCR change as a function of N_2 flow rates for as-deposited thin films

Figure 6-5 shows the TCR change as a function of Cu content with the increase of N_2 flow rates for the as-deposited Ta-N-Cu thin films. It can be seen that more nitrogen will result in more negative TCR. This is also due to the formation of stable semi-conductive TaN phases in thin films with the increase of N_2 flow rates. Ta-N phases own negative TCR and become more negative with the increase of nitrogen concentration in Ta-N thin films as described in chapter 4. When N_2 is 0 sccm, TCR doesn't change greatly with Cu content. It is exciting to find that for each N_2 flow rate, a zero-TCR can always be achieved. Normally zero-TCR point approaches to Cu-rich side.

Figure 6-6 TCR change as a function of N₂ flow rates at Cu content of 40 at. % for as-deposited thin films

The above Figure 6-5 shows the overall TCR change as a function of Cu content with the increase of N₂ flow rate from 0 sccm to 8 sccm. The TCR change versus N₂ flow rates at a constant Cu content of 40 at. % was shown in Figure 6-6. With the increase of N₂ flow rate from 0 sccm to 8 sccm, TCR will decrease sharply from 60 ppm/°C at 0 sccm to -1823 ppm/°C at 8 sccm. This exhibits the same trend as that for pure Ta-N phases.

It can be seen that more nitrogen will give rise to more negative TCR. On the other hand, from the previous discussion, more Cu causes TCR to move to the positive side and finally a zero TCR can be achieved. Combining these two factors, some conclusions can be drawn. That is, less nitrogen and more Cu will result in less

negative TCR. More Cu is needed to compensate the negative effects by nitrogen. A zero-TCR can be obtained only when the competitive effect between negative TCR by TaN phase and positive TCR by Cu phase reaches to a balance.

6.3 Effects of annealing time on the electrical properties

After deposition, rapid thermal annealing was applied to anneal the films at 400°C for 2, 4, 8 minutes in Ar ambient, in order to cause the nucleation and grain growth of Cu. It was found that the resistivity and TCR changed after annealing due to the competitive effects among the normal metallic behavior caused by Cu I, quantum size effect caused by Cu II nanoparticles, weak-localization effect caused by the amorphous phase. The biggest increase in the resistivity was found after annealing for 4 minutes, and the biggest decrease in TCR also occurred after annealing for 4 minutes. After for 8 minutes, the resistivity decreased a little while TCR increased. In order to achieve a near-zero TCR, a suitable combination of annealing time, Cu concentration, and N₂ flow rate is required.

Figure 6-7 Resistivity of the TaN-Cu films (N_2 : 8 sccm) versus Cu concentrations before and after annealing at 400°C for 2, 4, 8 minutes

The effect of annealing time on resistivity ($N_2=8$ sccm) is shown in Figure 6-7. It was found that the resistivity seems to follow Nordheim's rule for the randomly mixed phases as studied previously. A maximum resistivity value is found when Cu is about 50 at. % for all the films.

For TaN-rich films, the resistivity is further increased after annealing for 2 minutes and reaches to the maximum value when annealing for 4 minutes. This could be attributed to the formation of nano-sized Cu clusters (Cu II) analyzed by XRD and TEM. As analyzed previously, Cu II exhibits quantum size effect, resulting in higher resistivity and lower TCR. Generally, TCR and resistivity normally follow the general trend of increasing resistivity and decreasing TCR [130]. After annealing for 4

minutes, Cu II nano-clusters become larger with an average size of 5~8 nm (analyzed by XRD and TEM), which also cause the quantum size effect. Another possible reason is the looser matrix density after Cu precipitation. After annealing for 8 minutes, Cu II particles grow to be larger than 10 nm, showing metal behavior and resulting in the decrease of resistivity [120]. These electrical behaviors match well with the microstructures observed by XRD and TEM.

For Cu-rich thin films, the resistivity is nearly not affected by annealing time. This result could be due to the switching of the matrix from TaN to Cu. For Cu-rich films, TaN nano-particles are embedded in Cu matrix, which is a reverse situation to the TaN-rich films. The temperature (400°C) used for annealing the films may not be high enough to cause significant grain growth of TaN particles. As analyzed in Chapter 4, TaN doesn't change much with the increase of annealing time. Thus, the decrease in resistivity caused by Cu I may offset the increase in resistivity caused by Cu II. Therefore, annealing may not change the resistivity of Cu-rich films significantly.

Figure 6-8 TCR of the TaN-Cu films ($N_2=8$ sccm) versus Cu concentrations before and after annealing at 400°C for 2, 4, 8minutes

Figure 6-8 shows the change of TCR versus Cu content as a function of annealing time. When Cu is less than 50 at. %, the as-deposited TaN-Cu films have far more negative TCR values than that of pure TaN (-823 ppm/°C). This could be due to the formation of nano-sized Cu clusters and amorphous phase, which can cause quantum size effect and weak localization effect respectively. With the increase of Cu content, Cu particles begin to form, making TCR shift towards the positive side. Eventually, a near-zero TCR point is found at Cu=75 at. %. Cu, as a metal, normally has a much more positive TCR in contrast to semi-conductive TaN. Therefore, it is not surprising to find the zero-TCR point.

Figure 6-8 also shows that annealing for 2 and 4 minutes will cause the TCR values of TaN-rich thin films ($\text{Cu} \leq 50$ at. %) to become more negative, and TCR reaches to the minimum value after annealing for 4 minutes. Apparently, quantum size effect caused by the nano-sized Cu II (≤ 10 nm) results in the negative TCR [112]. Another possible reason could be due to the decrease of matrix density. It was reported by Qin that lower specimen density contributes negatively to TCR [56, 136].

However, when annealing for 8 minutes, TCR will increase due to the further grain growth of Cu with larger grain size (15~25 nm) and better crystallinity. With the increase of annealing time, the near-zero TCR point will shift to the left side with less Cu concentration, due to the stronger offset effect by larger-size Cu particles.

However, for Cu-rich films ($\text{Cu} > 50$ at. %), TCR increases with the increase of annealing time, exhibiting normal metallic behavior. It is also found that annealing will have an obvious effect on TCR at $\text{Cu} = 65$ at. % (≈ 50 vol. %). At this point, the TCR increases from -500 ppm/ $^{\circ}\text{C}$ for as-deposited film to 0 ppm/ $^{\circ}\text{C}$ after 2 minute annealing, then 500 ppm/ $^{\circ}\text{C}$ after annealing for 4 minutes, finally 1250 ppm/ $^{\circ}\text{C}$ after annealing for 8 minutes.

Figure 6-9 TCR of the TaN-Cu films versus Cu concentrations after annealing at 400°C for 2minutes, with the variation of N₂ flow rates

The above figure shows the TCR change versus Cu concentration for Ta-N-Cu films after annealing at 400°C for 2 minutes when N₂ is from 0 sccm to 8 sccm. It can be seen that TCR values are affected by both Cu content and N₂ flow rates. More Cu and less nitrogen in the film resulted in less negative TCR. With the increase of N₂ flow, the zero-TCR point is shifting toward Cu-rich side, which means more Cu is needed to compensate the negative effect of nitrogen. For instance, when N₂ is 2 sccm, the zero-TCR was found at 32.7 at. % of Cu, and when N₂ increases to 8 sccm, the zero-TCR point shifts to 66 at. % of Cu. However, no matter what the N₂ flow rate is, a zero-TCR can be found.

Table 6-1 lists the compositions of TaN-Cu (N₂: 8 sccm) with zero-TCR before and after annealing for 2, 4, and 8 minutes. It can be concluded that with the increase of annealing time, less Cu is needed to reach a zero-TCR.

Table 6-1 Compositions of TaN-Cu (N₂: 8 sccm) with zero-TCR before and after annealing for 2, 4, and 8 minutes

TaN-Cu Films	Cu (at. %)	Ta (at. %)	Resistivity ($\mu\Omega$ -cm)
As-deposited	74	13	300
2 min. annealing	66	17	1450
4 min. annealing	62	19	2550
8 min. annealing	57	21.5	1700

Table 6-2 summarizes the compositions of all the elements for all the zero-TCR points. The films were annealed for 2 minutes at 400°C. From this table, it can be clearly concluded that to reach zero-TCR point, more Cu is needed to offset the negative effect caused by higher N₂ flow rates.

Table 6-2 Compositions of Ta-N-Cu films annealed for 2 minutes, with near-zero TCR values

N ₂ flow rate (sccm)	Ta (at.%)	N (at.%)	Cu (at.%)	Resistivity ($\mu\Omega$ -cm)
0	82.4	0	17.6	226
2	44.9	22.4	32.7	161
4	23.1	18.8	58.1	350
6	21.2	19.5	59.3	364
8	17	17	66	1450

Figure 6-10 Sheet resistance change as a function of temperature for (a) a TaN-rich film (b) zero-TCR film and (c) Cu-rich film after annealing at 400°C for 2 minutes

Figure 6-10 shows the sheet resistance changes with temperature for (a) TaN-rich (b) zero-TCR and (c) Cu-rich films after annealing at 400°C for 2 minutes. From curve (a), it is easily known that the sheet resistance decreases almost linearly with the temperature, suggesting the constant TCR (gradient of the line) value and thus the very stable semiconductor-like electrical properties of TaN-rich film. For TaN-rich film with only 2.1 at. % of Cu, its TCR value can reach to as low as $-2400 \text{ ppm}/^\circ\text{C}$ after annealing. Obviously, this value is not suitable for thin film resistor application that requires not only as stable as TCR value but also as small as TCR value. However this film shows promise in use as thin film thermal sensor, which requires as high (low) as TCR values.

Curve (b) shows the sheet resistance changes with temperature for the film with zero-TCR after annealing for 2 minutes. TCR is very stable within the testing temperature range from 25°C to 150°C, with a fluctuation smaller than 5 ppm/°C. It is evident that TCR almost equals to zero within the testing temperature range. It suggests that this film with near-zero TCR meets well with the basic requirement of a thin film resistor. On the other hand, it can also prove our concept that by mixing a metallic phase with a ceramics phase, like Cu and TaN, a stable zero-TCR can be obtained. It is very promising that TaN-Cu nanocomposite thin film with zero-TCR can be applied to thin film resistors [137].

The sheet resistance change with temperature for the Cu-rich film (80 at. % of Cu) is shown in curve (c). It can be seen that with the temperature increasing from 25°C to 150°C, the sheet resistance also increases almost lineally with the temperature. This indicates that Cu-rich film exhibits a positive TCR and shows normal metal behaviors. TCR of the Cu-rich film remains almost unchanged within the testing temperature range, that is 1745 ppm/°C, obtained from the nearly linear change of sheet resistance with temperature.

From curve (a), (b) and (c), clear difference can be obtained for three films with different compositions. For TaN-rich film, TCR is negative and remains the same with the increase of temperature, exhibiting semi-conductive electrical properties. For the film with zero TCR, TCR is also almost unchanged with the temperature, showing very attractive and stable electrical properties. This film is very suitable for thin film resistor applications. For Cu-rich film, TCR is positive and remains unchanged with temperature, which indicates the metallic behaviors. So, with varied compositions, the films will be under control of different conduction mechanisms: (a) semi-conductive

conduction with negative TCR, (b) combination of semi-conductive and metallic conduction with zero TCR, and (c) metallic conduction with positive TCR. The most important thing is that a stable and zero-TCR has been achieved in TaN-Cu nanocomposite thin films in this study.

6.4 Conduction mechanism

This study was focused on the achievement of a zero-TCR and its mechanism behind. Experimentally, a zero-TCR has been obtained by a new concept of material, nanocomposite, with the co-existence of semiconductor-like TaN phase and metallic Cu phase in the film. By controlling the N₂ flow rate, Cu concentration and annealing conditions, a zero-TCR was successfully achieved. This will be of great importance in industry when the TaN-Cu is used as thin film resistors. On the other hand, building of a theoretical model behind the physical phenomena will be very helpful in explaining and predicting the experimental results. In building the theoretic model, the case with nitrogen set at 8 sccm was chosen for the study.

What we observed in this study was that the nano-sized Cu particles would change the electrical properties greatly, depending on its particle size and content. For TaN-rich films, Cu particles formed with size of less than 10 nm after annealing will cause the higher resistivity and more negative TCR. Based on our experimental results, the calculation for the resistivity and TCR of the nanocomposite thin film can be concluded,

$$\rho_c = x_{TaN} \rho_{TaN} + x_{Cu} \rho_{Cu} \quad (6-1)$$

$$TCR_c = \frac{\rho_{TaN}}{\rho_c} x_{TaN} TCR_{TaN} + \frac{\rho_{Cu}}{\rho_c} x_{Cu} TCR_{Cu} \quad (6-2)$$

where ρ_c is resistivity of the composite thin film, TCR_c is TCR of the composite thin film. χ is the volume fraction. In Cu-rich side, a zero-TCR may be obtained and after annealing, there exists two kinds of Cu, primary Cu and secondary Cu exhibiting contrary properties. Another model was set up with consideration of Cu I and Cu II at the same time.

$$\rho_c = x_{TaN}\rho_{TaN} + x_{CuI}\rho_{CuI} + x_{CuII}\rho_{CuII} \quad (6-3)$$

$$TCR_c = \frac{\rho_{TaN}}{\rho_c} x_{TaN} TCR_{TaN} + \frac{\rho_{CuI}}{\rho_c} x_{CuI} TCR_{CuI} + \frac{\rho_{CuII}}{\rho_c} x_{CuII} TCR_{CuII} \quad (6-4)$$

The theoretical model was based on the classic resistivity mixture rules (or the series rule of mixture). The calculation for a random mixture of phase α and phase β is represented by the following equation:

$$\rho = x_\alpha \rho_\alpha + x_\beta \rho_\beta \quad (6-5)$$

Where, ρ is the effective resistivity, x is the volume fraction, α and β are the two different phases. Since Cu II with nano-meter size behaves the same as in TaN-rich and Cu-riched films, we take a TaN-rich film (2.1 at. %) as an example. we use (6-1) and (6-2) to calculate the resistivity and TCR of Cu particles with different grain sizes. When doing this, we have an assumption that after annealing for 8 minutes, Cu with large grain size has the same electrical properties as bulk Cu: $\rho = 2.3 \mu\Omega \cdot cm$, $TCR = 4300 \text{ ppm}/^\circ\text{C}$. In the calculation, ρ_c and TCR_c after annealing for 8 minutes were measured directly by four-point probe; x_{TaN} and x_{Cu} were analyzed and

calculated by XPS, that is $1024 \mu\Omega \cdot cm$, $-2300 \text{ ppm}/^\circ\text{C}$, $97.9 \text{ at. } \%$ and $2.1 \text{ at. } \%$ respectively.

According to (6-1), after annealing for 8 minutes, ρ_{TaN} was calculated to be $1286 \mu\Omega \cdot cm$. Introducing ρ_{TaN} into (6-2) and TCR_{TaN} was calculated to be $-2288 \text{ ppm}/^\circ\text{C}$. Since TaN phase changes little with annealing time, thus we assume that its resistivity and TCR keep constant when annealing time increases from 2 minutes to 4 and 8 minutes (proved in Chapter 4). According to (6-1), after annealing for 2 minutes, $\rho_c = 1044 \mu\Omega \cdot cm$, $\rho_{TaN} = 1286 \mu\Omega \cdot cm$, $\rho_{Cu} = 850 \mu\Omega \cdot cm$. According to (6-2), $TCR_c = -2370 \text{ ppm}/^\circ\text{C}$, $TCR_{Cu} = -3550 \text{ ppm}/^\circ\text{C}$. Thus, after annealing for 2 minutes, Cu particles with particle size below 5 nm doesn't show metal behavior, but semiconductor behavior, with much higher resistivity value and a negative TCR value of $-3550 \text{ ppm}/^\circ\text{C}$.

For the film after annealing for 4 minutes, the same calculation method as the above, $\rho_{Cu} = 1869.3 \mu\Omega \cdot cm$, and $TCR_{Cu} = -5246 \text{ ppm}/^\circ\text{C}$. The calculated results for the resistivity and TCR of Cu II for TaN-rich films were listed in Table 6-3.

By calculation, it can be further proved that secondary Cu particles (Cu II) exhibit semi-conductive behavior when particle size is smaller than 10 nm. Cu II nano-clusters result in the much higher resistivity and more negative TCR for TaN-rich films compared with pure TaN thin film. In Cu-rich film with zero-TCR, Cu II acts together with TaN and Cu I. They compete with each other and achieve a balance of zero-TCR.

Table 6-3 Calculated resistivity and TCR of Cu II for TaN-rich films after annealing for 2, 4, and 8 minutes

	2 minutes	4 minutes	8 minutes
Resistivity (Cu II)	850 $\mu\Omega\cdot\text{cm}$	1869.3 $\mu\Omega\cdot\text{cm}$	2.3 $\mu\Omega\cdot\text{cm}$
TCR (Cu II)	-3550 ppm/ $^{\circ}\text{C}$	-5246 ppm/ $^{\circ}\text{C}$	4300ppm/ $^{\circ}\text{C}$

6.5 Summary

All the electrical behaviors exhibited by TaN-Cu thin films are the results of the competitive counteractions or the combinations of all the conduction mechanisms and phenomena. In a specific case, one mechanism will be the dominant factor, which is called as the competitive effect. For TaN-rich films, the electrical behavior is mainly dominated by the **weak localization effect** by amorphous phase, the **quantum size effect** by Cu nano particles and the lower density of TaN matrix. However, for Cu-rich film, the **quantum size effect** caused by the Cu nanoparticles (**Cu II**) and **metallic conduction** contributed by the larger Cu particles (**Cu I**) act together. The main results can be summarized as the following lists:

1. With the increase of Cu content in the TaN-Cu nanocomposite thin films, the resistivity increased and reached to a maximum value at about 50 at. %, and then decreased. The resistivity seemed to follow the Nordheim's rule for two randomly mixed phases. For TCR, it increased monotonically from negative value to positive one. Thus, a zero-TCR could be achieved on Cu-rich side.

2. With the increase of N₂ flow rate from 0 sccm to 8 sccm, the total resistivity increased. A maximum value can always be found at a certain Cu content for all the N₂ flow rates. Furthermore, with the increase of N₂ flow rates, the maximum resistivity value moved to the right side with more Cu concentration in the films. For TCR change, more nitrogen caused more negative TCR. To reach a zero-TCR, more Cu was needed in the film deposited with larger N₂ flow rate.

3. For TaN-rich films, after annealing for 2 and 4 minutes, the resistivity increased and reached to the maximum after annealing for 4 minutes. After annealing for 8 minutes, the resistivity decreased but still higher than that of the as-deposited films. This was mainly due to the **quantum size effect** caused by the **Cu II**, and the **weaklocalization effect** caused by the **amorphous phase**. The stabilization of TaN matrix also contributed to the increase of resistivity after annealing for 2 minutes.

4. For TaN-rich films, TCR was far more negative than that of pure TaN phase. This was mainly due to the **amorphous phase** formed in the films, which caused the **weaklocalization effects**. After annealing for 2 and 4 minutes, TCR decreased to more negative values and reached to the minimum after annealing for 4 minutes. This can be attributed to the **quantum size effect** caused by **Cu II**. After annealing for 8 minutes, it increased a little.

5. For Cu-rich films, after annealing, the resistivity didn't change much. This was due to the balance between the quantum size effect by Cu II and semi-

conductive conduction by TaN that resulted in the increase of resistivity, and the metallic conduction by Cu I that resulted in the decrease of resistivity.

6. As a summary, when Cu content, N₂ flow rate, and annealing time reached to a balance, a zero-TCR could always be achieved.

Chapter 7 Piezoresistive & Mechanical Properties of TaN-Cu Nanocomposite Thin Films

7.1 Introduction

From the discussion in Chapter 6, it is found that the emergence of Cu nanoparticles (Cu II) after RTA can further decrease or increase the negative TCR value of TaN, depending on the particle size. Zero or near-zero TCR can always be achieved if Cu concentration, N₂ flow rate and annealing time were controlled well. These thin films with zero-TCR meet the basic requirement of near-zero TCR for TFR applications.

In this chapter, strain gauge factors of the thin films were also evaluated on the thin films with near-zero TCR, since it is expected that these TFRs would have little resistance change when under external force. The gauge factor value was found to be affected by annealing time and Cu concentration, but not N₂ flow rate. An equipment based on three-point bending was made and applied for the measurement. On the other hand, in order to know more about the mechanical properties of these nanocomposite thin films, hardness and Young's modulus were also tested by using nanoindentation technique. The results show that the highest hardness and Young's modulus can only be achieved in case of very low Cu concentration.

7.2 Piezoresistive properties

TaN thin-film resistors have a wide variety of applications. The films have a wide range of electrical resistivity (ρ) and TCR that can vary with nitrogen content or

thermal annealing process after deposition [138]. So far, many efforts have been spent to determine the material structures and electrical properties of these films [139].

On the other hand, nanocomposite thin films have recently become a popular research area due to their promising optical, electrical, magnetic and mechanical properties [140]. Among those films, the metal clusters with characteristic sizes on the order of a few nanometers embedded in a ceramic matrix show many special properties which could be applied for numerous potential applications. This is mainly due to the large surface-to-volume ratio of nano-clusters. If the cluster size is smaller than the mean free path of electron, then the electrical resistivity and TCR are expected to change dramatically due to electron scattering [6].

Meanwhile, not only a low TCR, but also a small resistance change due to strain (the piezoresistance effect) is compulsory to an ideal TFR [22]. In contrast to the requirements of TFR, a strain gauge normally needs a large and stable piezoresistance effect. The commonly used metallic thin film strain gauges in pressure sensors and accelerometers exhibit gauge factors smaller than 6, while semiconductor-based strain gauges have large gauge factors (negative). TaN thin films, used as thin film resistors, have a small strain gauge factor of less than 3.5, which indicates its stability when stressed [23]. So far, no study has been reported on the piezoresistive properties of TaN-Cu composite films. In this section, the effects of N₂ flow rate, Cu content and annealing time on strain gauge factor (γ) were studied and analyzed.

The strain gauge factor γ can be calculated by the following equation [141]:

$$\gamma = \frac{1}{R_0} \frac{\Delta R}{\Delta \varepsilon} \quad (7-1)$$

where $\Delta R = R - R_0$. R is the resistance of the specimen, when stressed by a strain $\Delta\epsilon$, and R_0 is the unstrained resistance.

Figure 7-1 Resistance change as a function of longitudinal strain for three TaN-Cu thin films (N_2 flow rate = 8 sccm)

Figure 7-1 shows the resistance change as a function of physical strain for three as-deposited TaN-Cu thin films. Each of these films has a varied Cu concentration. The data show good linearity for every film. This indicates a constant strain gauge factor (slope of the line) for these films ($\gamma = 2.3, 2.9$, and 4.3). With the increase of Cu content, it can be observed that the gauge factor also increases, especially when Cu at. % = 64 %. At this particular composition, it is possible that Cu phase has become a

continuous matrix. Therefore, the value of gauge factor is close to that of Cu metal [114].

Figure 7-2 Strain gauge factor for a TaN-Cu film showing zero-TCR (Cu=75 at. %) before and after annealing for different time

Figure 7-2 shows the effect of annealing time on the strain gauge factor of a film with zero-TCR (Cu at. % $\approx$ 75 %). The maximum value of the gauge factor is found to be 4.4 which is obtained from the as-deposited thin film. The gauge factor then decreases to 3.0 after 2 minute annealing, and 3.1 after 4 minute annealing. This result suggests that the formation of nano-particles may decompress the gauge factor. Semiconductor materials often show negative gauge factor due to the distortion of energy band [142]. When annealed for 8 minutes (large Cu particles appear), the film

has a gauge factor increasing to 4.0. At present, more study on this effect is still in progress.

Figure 7-3 Strain gauge factor for annealed TaN-Cu thin films showing zero-TCR vs. N_2 flow rates

Figure 7-3 shows the strain gauge factors for films with zero-TCR values, but deposited with various nitrogen flow rates. The strain gauge factor fluctuates from a minimum value of 2.6 ($N_2=4$ sccm) to a maximum value of 3.3 ($N_2=6$ sccm). Since there is no obvious increasing trend in Figure 7-3, the results reveal that γ is affected by Cu content and annealing time, but not affected by N_2 content. Overall the gauge factors for the films showing near-zero TCR are stable and small, which satisfy one of the major requirements for a good TFR.

7.3 Mechanical properties

In this section, TaN-Cu nanocomposite thin films with Cu nanoparticles dispersed in TaN matrix were characterized by a nanoindenter (Nano Indenter[®] XP) with a Berkovich indenter. Consequently, hardness and Young's modulus values will increase or decrease with the increase of annealing time, depending on Cu content and TaN morphology (particularly, preferred orientation). The increase of N₂ concentration will result in higher hardness and Young's modulus due to the formation of stoichiometric TaN phase.

Many nitride thin films have been known to have excellent mechanical properties and used as protective coatings [20]. When these films are dense and the grain size is reduced to a certain degree, the mechanical properties in general can be improved [143]. Recently, it was found that the mechanical properties of these films could be improved even further when metal particles are embedded in the ceramic matrix. This discovery opens up a new research area for engineers and scientists.

Sputter-deposited TaN also exhibit excellent mechanical properties [30, 37], e.g. good wear resistance and oxidation erosion, high hot hardness, and good impact toughness. The maximum hardness value achieved by Yuan-Zhu is 18.8 GPa [144] and a hardness value as high as 32 GPa was reported by Ranjana [20] when partial pressure of N₂ is 0.1mTorr. However, it is not clear whether the film contains Ta₂N or not.

On the other hand, ceramic-matrix nanocomposite thin films with dispersed nano-sized metal particles composite is attracting much interest [5]. Although metals are usually soft, ductile, and tough while their nitrides are strong, hard, and brittle, it has

been shown that the mechanical properties of metal-ceramic composites can be improved significantly, when the size of embedded metal particles is reduced to less than a few nanometers [87]. In addition to the improved mechanical properties, the friction coefficient is found to be lower due to the incorporation of metal particles (especially Cu) [145].

Figure 7-4 Variations of hardness and young's modulus of TaN-Cu thin films with various Cu content which were deposited at different N₂ flow rates

Figure 7-4 shows the effects of N₂ flow rate on hardness values and Young's modulus of several Ta-N-Cu nanocomposite thin films deposited with various Cu content. All the samples were annealed by using RTA at 400 °C for 2 minutes. It was found that the hardness values and Young's moduli of TaN-Cu films deposited with 8 sccm N₂ are higher than those of TaN-Cu films deposited with N₂ flow rates at 2 and 4

sccm. It appears that the chemical stoichiometry of TaN can affect the mechanical properties of TaN-Cu nanocomposite thin films greatly. Figure 7-4 also shows that high hardness can only be obtained when the amount of Cu is less than 5 at. %. However, Young's modulus is less affected by the increase of Cu content. The reason is not clear at this moment [146].

Figure 7-5 Effect of annealing on the hardness values of three TaN-rich thin films. TaN is shown for comparison reason

Figure 7-5 depicts the effects of annealing on hardness values of TaN and TaN-Cu nanocomposite thin films. In this figure, three TaN-rich samples were investigated. For the sample with 2.1 at. % Cu, after annealing for 2 minutes, the hardness increases from 21.2 GPa to 27.5 GPa. The hardness reaches to the maximum value of 32 GPa after annealing for 4 minutes. However, after annealing for 8 minutes,

hardness decreases sharply to 20 GPa. The increase of hardness after annealing is not found in other two samples. According to Zeman et al. [16], nanocomposite thin films with a soft metal as their second phase may have significant increase in hardness after annealing only when (i) Cu content is low, and (ii) matrix is strongly oriented with dense columnar structure. Under these conditions, TaN or other nitride grains may be surrounded or separated by a thin and uniform layer of tiny Cu particles after annealing. This can result in a significant increase in hardness. From the XRD result in chapter 5, it was analyzed that the sample with 2.1 at. % Cu has a strong TaN (111) orientation. From the AFM topography pictures shown in Figure 7-6, the columnar structure can also be observed. Therefore, the effect of annealing on hardness for this sample is explained. Karvankova et al. [147], by studying ZrN-Ni, also reported that the formation of nanocomposite with soft metal particles could not increase the hardness. This could be due to high percentage of Cu in their samples. TaN structure can easily become randomly oriented when Cu percentage is more than 5 at. %. Consequently, no hardening enhancement can be seen on all the samples except the one that has Cu at. % = 2.1 %.

(a)

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(b)

Figure 7-6 (a) 2-D and (b) 3-D AFM topography of TaN-Cu nanocomposite thin film (Cu=2.1 at. %) before annealing

(a)

(b)

Figure 7-7 Young's modulus of (a) TaN-rich (2.1 at. % Cu) and (b) Cu-rich (67.5 at. %) as a function of annealing time

Figure 7-7 shows the young's modulus of a TaN-rich film (2.1 at. % Cu) and a Cu-rich film (67.5 at. % Cu) as a function of annealing time. For the TaN-rich film, young's modulus doesn't fluctuate much with increase of annealing time and only shows a little increase when annealed for 2 and 4 minutes. For Cu-rich films, with the increase of annealing time, young's modulus decreases much, mainly due to the larger grain size of Cu I.

According to the analysis of microstructures using XRD and TEM, it is found that the addition of Cu may cause the formation of nanocrystalline TaN or amorphous-like structure. Until Cu content reaches a critical value (>37 at. %), Cu is randomly trapped in the TaN lattice. The trapped Cu atoms will then emerge as Cu nanoparticles after annealing. The hardness enhancement of TaN-Cu nanocomposite

is dependent on Cu content, nitrogen content, preferred orientation of TaN, and annealing. For the sample with 2.1 at. % Cu, after annealing for 2 and 4 minutes, both hardness and Young's modulus will increase and reach to the maximum value. Other samples do not show any hardness enhancement after annealing. This may be explained by the theory proposed by Zeman et al [16]. In their theory, to achieve high hardness, fine TaN columnar structure with preferred orientation and little Cu is required. When 8 sccm of N₂ was added during deposition, the hardness values and Young's moduli of the thin films are higher than those deposited with 2 and 4 sccm of N₂, due to the formation of stoichiometric TaN phase.

(a)

(b)

Figure 7-8 Load-displacement curve for (a) Cu -rich and (b) TaN-rich film

Figure 7-8 shows a typical load-displacement curve obtained using nano indentation technique for a Cu-rich and a TaN-rich film. The film thickness is 700 nm and 550 nm respectively. From the load-displacement curve slope of these two films, it can be concluded that TaN-rich film is harder and stronger than Cu-rich film.

7.4 Summary

For piezoresistive properties of TaN-Cu nanocomposite thin films, the conclusions can be drawn as the following:

1. The resistance variation changed almost linearly with strain, indicating stable and constant strain gauge factors.

2. With the increase of Cu content, strain gauge factor value also increased to more positive value.
3. Strain gauge factor achieved its maximum value of 4.4 from the as-deposited film, and decreased to 3.0 and 3.1 after annealing for 2 and 4 minutes due to the size effect of nano-sized metal particles; and increased to 4.0 after annealing for 8 minutes due to the larger size Cu particles.
4. There was no significant trend for the change of strain gauge factor versus N_2 flow rate. However, the strain gauge factor values were small and stable, implying that these films could be applied to TFRs.

For hardness and Young's modulus of TaN-Cu nanocomposite thin films, the results could be summarized as the following:

1. Both the hardness and Young's modulus decreased to smaller value with the increase of Cu content; and increased to higher value with the increase of N_2 flow rate. The highest hardness could only be obtained from the film containing less than 5 at. % of Cu. Young's modulus was less affected by the increase of Cu content compared with hardness.
2. The hardening effects caused by the nano-sized metal clusters emerged after annealing could only be achieved for the films with less than 5. at. % of Cu. The hardness reached to the maximum value after annealing for 4 minutes for the film with only 2.1 at. % of Cu. For the other films with more Cu, there was no hardening effect observed.

Chapter 8 Conclusions

This project is composed of two main parts: Ta-N thin film study and Ta-N-Cu nanocomposite thin film study. In the study of Ta-N thin films, the effects of N₂ flow rate and annealing time on the microstructures and electrical properties of Ta-N thin films (resistivity and TCR) were investigated. It is the basis of Ta-N-Cu nanocomposite thin film study.

In the second part, the Cu phase was incorporated into TaN phase originally by co-sputtering to make a nanocomposite thin film for the purpose of tuning the negative TCR of TaN. It was exciting to find that metallic Cu phase can offset the negative TCR of semi-conductive TaN phase and a near-zero TCR could always be achieved only if the Cu concentration, N₂ flow rate and annealing time were controlled well. For the first time in research, it was proved that a zero-TCR could be achieved by tuning the semi-conductive phase (TCR<0) with a suitable metallic phase (TCR>0). The effects of Cu concentration, N₂ flow rate and annealing time on the microstructures and the electrical properties (resistivity and TCR) were investigated, as well as on the piezoresistive and mechanical properties.

The detailed experimental results for Ta-N and Ta-N-Cu thin films about the microstructures, electrical properties, piezoresistive and mechanical properties are summarized and listed in the following.

8.1 Ta-N thin films

1. With the increase of N₂ flow rate, the phase would transit from pure β -Ta phase to f.c.c. TaN phase directly as observed by XRD. By XPS, when N₂ was 8 sccm, stoichiometric TaN was formed since the binding energies of Ta 4f_{5/2} at 25.2 eV and N 1s at 398 eV correspond to that of TaN.
2. The resistivity increased from 306 $\mu\Omega\cdot\text{cm}$ to 1850 $\mu\Omega\cdot\text{cm}$ monotonically with the increase of N₂ from 0 to 12 sccm. Resistivity increased sharply when N₂ flow rate reached 10 sccm, mainly due to the prevailing of semi-conductive TaN phase and nitrogen-rich Ta-N compounds formed in the films.
3. TCR decreased from 250 ppm/°C to -1700 ppm/°C quickly with the increase of N₂ flow rate from 0 to 12 sccm. This result can also be attributed to the domination of semi-conductive TaN phase and nitrogen-rich Ta-N compounds formed in the films.
4. After annealing, the resistivity of all the films increased further while TCR decreased to a more negative value. This was due to the stabilization of semi-conductive TaN phase. Among all the films prepared under different N₂ flow rates, the film deposited with 8 sccm N₂ showed the most stable electrical properties of a semi-conductive material.

8.2 Ta-N-Cu nanocomposite thin films

8.2.1 Microstructures

1. For TaN-rich film (Cu=36.5 at. %) before annealing, no Cu particles could be observed by conventional TEM. After annealing for 2 minutes, the Cu particles shown as fine dark clusters can be observed. After annealing for 4 and 8 minutes, Cu particles increased to 5~8 nm and 15~25 nm, respectively.
2. For Cu-rich films (Cu=67.5 at. %), after annealing, besides the larger primary Cu particles (Cu I), secondary Cu particles (Cu II) with nano-meter size could also be observed.
3. From EDP, the diffraction rings from Cu became sharper with the increase of Cu content and annealing time, but no change in TaN diffraction rings could be observed. For all the as-deposited films, the diffused diffraction rings from TaN and Cu indicated the formation of very fine nano-crystals or amorphous phase.
4. Analyzed by XRD, when N₂ was 8 sccm, only nanocrystalline TaN and Cu phases were formed in the films. When Cu was less than 36.5 at. %, only TaN phase could be detected, while TaN phase and primary Cu phase (Cu I) co-existed when Cu was more than 36.5 at. %.
5. Almost all of the as-deposited films exhibited very broad and low intensity diffraction peaks. This result indicated nanocrystalline structures or the

existence of amorphous phase. Only the film with 2.1 at. % Cu showed a comparatively high and sharp TaN (111) peak.

6. With the increase of annealing time, Cu (111) became sharper, implying better crystallinity and larger grain size. However, no much change in TaN peaks was observed. Cu (111) for Cu-rich films after annealing can be divided into two separate peaks. One sharp and high peak was from primary Cu phase (Cu I), and the other broad and low peak was from secondary Cu phase (Cu II).
7. By XPS analysis, Cu 2p peaks shifted to lower binding energies and approached to the value of bulk Cu with the increase of Cu content and annealing time. Higher binding energies of Cu 2p were due to the size effect of nano-sized Cu clusters. Binding energies of Ta 4f_{7/2} and N 1s kept unchanged and matched well with TaN phase.
8. By XPS peak deconvolution, for Cu-rich films after annealing, Cu 2p_{3/2} can be separated into two peaks: one with lower binding energy was from primary Cu (Cu I), and the other with higher binding energy was from secondary Cu (Cu II).

8.2.2 Electrical properties

1. The resistivity of TaN-Cu was higher and TCR was more negative than those of the pure TaN, due to the **quantum size effect** of nano-sized particles and **weak-localization effect** of amorphous phase. With the increase of Cu content, the resistivity increased first and decreased after achieving a maximum, while TCR increased monotonically from negative value to positive one.

2. After annealing for 2 and 4 min., for TaN-rich films, the resistivity increased while TCR decreased due to the **quantum size effect** of nano-sized Cu II formed. After annealing for 8 min., the resistivity decreased and TCR increased due to the grown-up Cu II. With longer annealing time, less Cu was needed to compensate the negative TCR of TaN to reach a zero-TCR.
3. With the increase of N₂ flow rate from 0 sccm to 8 sccm, the overall resistivity increased and TCR became more negative. In order to obtain a zero-TCR, more Cu concentration was needed to offset the negative effect caused by more nitrogen incorporation.
4. Generally, to achieve a zero-TCR, more Cu content and a suitable annealing time were needed to balance the negative TCR caused by the increase of N₂ flow rate. A zero-TCR can always be achieved by controlling the Cu content, N₂ flow rate and annealing time as well.
5. Calculating by the theoretical model we set up, secondary Cu (Cu II) showed a much higher resistivity value than that of the bulk Cu and even negative TCR value. This result matched well with our prediction that Cu II particles with less than 10 nm would show semi-conductive behavior.

8.2.3 Piezoresistive and mechanical properties

1. The resistance changed almost linearly with strain for the films with various Cu concentrations, indicating stable and constant strain gauge factors. With the increase of Cu content, strain gauge factor value also increased to more positive values.

2. The strain gauge factor achieved its maximum value of 4.4 from the as-deposited film, and decreased to 3.0 and 3.1 after annealing for 2 and 4 min. due to the size effect of nano-sized metal particles; and increased to 4.0 after annealing for 8 min. due to the larger size Cu particles.
3. There was no significant trend for the change of strain gauge factor versus N₂ flow rate. However, the strain gauge factor values were small and stable, implying that these films can be applied to TFRs.
4. Both the hardness and Young's modulus decreased to smaller values with the increase of Cu content; and increased to higher values with the increase of N₂ flow rate. The highest hardness can only be obtained from the film containing less than 5. at. % Cu. Young's modulus was less affected by the increase of Cu content.
5. The hardening effects of nano-sized metal particles emerged after annealing for 2 and 4 min. can only be achieved for the films with less than 5.0 at. % Cu. The hardness reached the maximum value after annealing for 4 min. for the film with only 2.1 at. % Cu. For the films with more Cu, there was no hardening effect observed.

8.3 Recommendations

This project so far has focused on the characterization of electrical properties of Ta-N-Cu nanocomposite thin films, the achievement of near-zero TCR from these films, and the explanation of conduction mechanism behind a zero-TCR. However, the

conduction mechanism behind the zero-TCR phenomenon from Cu-rich films still needs to be studied thoroughly. We will continue on the following work:

1. To find out the critical size for nano-sized Cu particles. Beyond that value, Cu particles will act as metal and show normal metal properties. Below that value, Cu particles will behave as semiconductor and exhibit semiconductor properties.
2. To study the piezoresistive properties for TaN-rich films in order to see whether its strain gauge factor is large enough to be applied as strain gauge. If so, the TaN-rich film may be made into strain gauge, while Cu-rich film may be used as thin film resistor.
3. To investigate the long-term stability of the films with zero-TCR by extending the exposure time to several months at 25°C and 150°C respectively for its practical application as thin film resistor in the industry.
4. To build up a practical TFR using one zero-TCR TaN-Cu thin film to see its feasibility of production and test its performance.

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