Ti substituted nano-crystalline Cu$_3$N thin films

A. Rahmati, H. Bidadi, K. Ahmadi, F. Hadian

Abstract Ti:Cu$_3$N thin films were deposited on Si(111), quartz, and glass slide substrates by DC magnetron sputtering in molecular nitrogen ambient. The structural properties of Ti:Cu$_3$N thin films were studied by X-ray diffraction (XRD) analysis. XRD measurements show diffraction band with peaks close to the (100) and (200) diffraction lines of cubic anti-ReO$_3$ structure of Cu$_3$N. The Ti:Cu$_3$N nano-crystalline size is in the range 22–27 nm. Lattice constant expansion reflects Ti incorporation causing the excess nitrogen to occur. Surface morphology shows that the N richness suppresses the grain growth. The optical absorption spectra indicate a remarkable shift to higher energies of the absorption edge due to higher N concentration and quantum size effect. Photoluminescence (PL) measurement shows interstitial N excess and Ti impurity produce shallow and deep levels, respectively. Thermal stability of the Ti:Cu$_3$N films annealed at 300 and 400°C is improved in comparison with that of Ti free Cu$_3$N films.

Keywords N excess, Ti incorporation, Quantum size effect, Shallow and deep levels

Introduction

Cu$_3$N thin films have been successfully used to fabricate write-once optical recording media,\textsuperscript{1-3} for generating microscopic copper lines by maskless laser writing\textsuperscript{4} and as an insulating barrier in magnetic tunnel junctions.\textsuperscript{5} Indeed, copper nitride is thermally unstable and decomposes into copper and nitrogen. The decomposition temperature is around 250°C.\textsuperscript{6,7}

The potential interest in reactive magnetron sputtering process relies on the possibility of producing thin films with new properties, markedly different from those corresponding equilibrium bulk phases. This is even more so when considering nano-crystalline and nano-composite thin films that can be formed.\textsuperscript{8,9} Nano-crystalline semiconductors are very interesting materials to study due to the changes occurring in the fundamental properties of the matter when the carriers are confined to quantum size.\textsuperscript{10}

There is an easy approach for the determination of optical constants, which depends on single transmittance measurement. The refractive index $n$ and the extinction coefficient $k$ as well as the thickness $d$ of polycrystalline Ti:Cu$_3$N thin films studied here were determined from transmittance data by only using PUMA approach and code described by Birgin et al.\textsuperscript{11} This method implements the complex optical equations, shown below derived and formulated by Heavens\textsuperscript{12} and Swanepoel.\textsuperscript{13}

The transmittance $T$ of a thin absorbing film deposited on a thick transparent substrate is given by:

$$T = \frac{A'x}{B' - C'x + D'x^2},$$

where

$$A' = 16s(n^2 + k^2),$$

$$B' = [(n + 1)^2 + k^2][(n + 1)(n + s^2) + k^2]$$

$$C' = [(n^2 - 1 + k^2)(n^2 - s^2 + k^2)$$

$$- 2k^2(s^2 + 1)]2\cos \phi - k[2(n^2 - s^2 + k^2)$$

$$+ (s^2 + 1)(n^2 - 1 + k^2)]2\sin \phi$$

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\[ D' = [(n - 1)^2 + k^2][(n - 1)(n - s^2) + k^2], \]

\[ \phi = \frac{4\pi nd}{\lambda}, \quad x = \exp(-2d), \quad a = \frac{4\pi k}{\lambda} \]

where \( s \) is the refractive index of the substrate, \( n \) and \( k \) are, respectively, the real and imaginary parts of the refractive index of the film, \( d \) is the film thickness, \( \lambda \) is the wavelength of the incident light, and \( x \) is the absorption coefficient of the film. Birgin et al.\(^{11} \) presented that the continuous least square solution of the estimation problem is the solution \((d, n, k)\) of

\[
\begin{align*}
\text{Minimize} & \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \left| T(\lambda, s(\lambda), d, n(\lambda), k(\lambda)) - T_{\text{meas}}(\lambda) \right|^2 d\lambda. \\
\end{align*}
\]

subject to some physical constraints.

Quartz substrate is sufficiently thick such that the addition of interference effects resulting from multiple reflections in the substrate is eliminated.

The experimental transmittance data are compared with theoretical values, in PUMA code. The difference between the two values is minimized until a best solution is achieved for the refractive index \( n \), the extinction coefficient \( k \), and the film thickness \( d \). Poelman et al.\(^{14} \) have reviewed and tested PUMA approach and shown it to produce excellent estimate of optical constants of thin films.

Most publications have dealt with reactive magnetron sputter deposition and the characterization of the physical properties of the Cu\(_3\)N films as a function of deposition parameters: nitrogen (partial) pressure in the gas mixture,\(^{15,17} \) substrate temperature,\(^{7,18} \) and sputtering power.\(^{19,20} \) Although Cu\(_3\)N has been widely studied, little information is available in the literature concerning transition metal-doped Cu\(_3\)N. Recently, some ternary compound based Cu\(_3\)N have been grown; (Pd, Cu)\(_3\)N,\(^{21} \) (Ti, Cu)\(_3\)N,\(^{22} \) and (Ag, Cu)\(_3\)N.\(^{23} \) Also, Moreno-Armenta et al.\(^{24} \) have theoretically studied the effect of metal insertion (M = Ni, Cu, Zn, Pd, Ag, and Cd) at the center of Cu\(_3\)N unit cell on electronic structure. In this study, Ti has been included to the cubic anti-ReO\(_3\) structure of Cu\(_3\)N. The choice of Ti is due to the fact that this element strongly reacts with nitrogen and locally increases nitrogen concentration in the Cu\(_3\)N films. (Ti, Cu)N coatings are formed by reactive DC magnetron sputtering under pure nitrogen ambient. The structure, morphology, electrical resistivity, optical bandgap, as well as thermal stability of the deposited films are investigated.

**Experimental**

Copper nitride thin films with titanium content were deposited by a balanced DC magnetron sputtering from a TiCu single multicomponent target (13 at.% Ti) on ultrasonically cleaned Si(111) single crystals, quartz, and glass slide substrates in the presence of nitrogen atmosphere at sputtering powers of 60 and 80 W. The sputtering powers of \( \leq 100 \) W are optimum to produce nearly stoichiometric Cu\(_3\)N, and the films formed at powers higher than 100 W are mixed phases of Cu and Cu\(_3\)N.\(^{19,20} \) The working chamber of the sputtering system was pumped down via a rotary pump and a turbomolecular pump allowing a base pressure of \(< 7 \times 10^{-4} \) Pa to be maintained. The total gas pressure, substrate temperature, and the target-substrate distance were kept constant at 1.0 Pa, 150°C and 19 cm, respectively.

Structural characterization was done ex situ by XRD diffractometer (Siemens D5000) with a Cu K\(_\alpha\) radiation source in 2\( \theta \) scan mode. The mean size of nanocrystallites \( D \) was estimated from the full width at half maximum of the strongest peak by using a modified Scherrer formula,\(^{25} \) neglecting peak broadening due to residual stress in the films

\[
D = \frac{0.94\lambda}{(\beta - b)\cos\theta} 
\]

where \( \beta \) is the FWHM of the diffraction peak, \( \lambda \) is the wavelength of the incident Cu K\(_\alpha\) X-ray, \( \theta \) is the Bragg diffraction angle, and \( b \) is the standard instrumental broadening (0.08°).

Films morphology and their chemical composition were determined using coupled scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX, Philips XL30). Optical studies were performed by measuring transmittance in the wavelength region 300–1100 nm using spectrophotometer (Shimadzu, UV-1700 Pharma Spec) at room temperature. These measurements allowed us to obtain the complex refractive index, \( n_c = n + ik \), where \( n \) and \( k \) are the refractive index and extinction coefficient, respectively. The optical bandgap energy was obtained by extrapolating the absorption edge line to the abscissa to the low energy. The photoluminescence (PL) was measured at room temperature using an Xe 350 nm lamp as the excitation source. The electrical resistivity of the films at room temperature was deduced from measurement using four point probe method.

**Results and discussion**

**Structural properties**

In Fig. 1 are shown the XRD profiles for the as-deposited Ti:Cu\(_3\)N films on Si(111) substrates, one grown with sputtering power of 60 W and the other with sputtering power of 80 W. The films exhibit only Cu\(_3\)N phase and the peaks correspond to (100) and (200) reflections. A rough estimation of the mean crystallite size was obtained from the Cu\(_3\)N (100) diffraction peak versus sputtering power using
modified Scherrer formula. This indicates that the size of crystallites is 22 and 27 nm for sputtering power of 60 and 80 W, respectively. The Ti:Cu3N films are composed of these nano-crystallites.

In most works, the stoichiometry of Cu3N thin films has been deduced from XRD data (having a change in the lattice parameter). The lattice constant has been estimated from the position of the Cu3N (100) diffraction peak. The evolution of the film lattice constant is due to the variation in nitrogen stoichiometry. However, there is no information about the position of excess nitrogen in the Cu3N unit cell. Due to sensitivity of chemical composition to characterization method, lattice constant of Cu3N is regarded as a good qualitative criterion for composition determination. The Ti:Cu3N lattice constant is 0.3828 and 0.3851 nm for sputtering powers of 60 and 80 W, respectively. The Ti:Cu3N films are over-stoichiometric (N-rich).

Surface morphology

The surface morphology of Ti:Cu3N films prepared at two different sputtering powers is shown in Fig. 2. As it is seen the films have granular structure with clear grain structure and sharp grain boundaries. The granularity of the films decreases for sample prepared at sputtering power of 80 W relative to that of 60 W due to the enhanced surface diffusion of the adatoms at higher sputtering power. The Ti doped Cu3N films have spherical-like morphology in contrast to Ti free Cu3N films with pyramidal-like grains. The Ti:Cu3N films are similar to those having the zone transition (T) microstructure of Thornton’s model. The zone T films have a very smooth surface and high density.

Grain size of the films is determined from SEM images. From grain size determination, radius of each spherical grain along XY plane is determined. The effective grain size is calculated by taking the average of 10–12 grains in each SEM image. The effective grain size of Ti:Cu3N lattice is 108 and 58 nm for sputtering power of 60 and 80 W, respectively. The size of the apparent grains decreases with the sputtering power. It
is believed that the extra nitrogen atoms which surround the titanium atom (TiN<sub>x</sub> precipitation) suppress the growth of the grains. As seen from SEM images, grains size and nitrogen concentration (or equivalently lattice constant) have inverse trend.

**Chemical composition**

In order to estimate the atomic Ti:Cu ratio in films, we make the following assumptions:

- difference in throw distance of any sputtered component in target-substrate spacing,
- difference in nitriding kinetics on target surface of any component,
- difference in angular distribution of any sputtered component, and
- difference in sticking coefficient of any sputtered component on substrate are excluded. The atomic Ti:Cu ratio can roughly be calculated by

\[
\text{Ti : Cu} = \frac{c_b^{\text{Ti}}}{1 - c_b^{\text{Ti}}} \cdot \frac{Y_N}{Y_{\text{Cu}}},
\]

where \(c_b^{\text{Ti}}\) is Ti concentration in target surface. \(Y_N\) and \(Y_{\text{Cu}}\) are Ti and Cu sputtering yield, respectively, due to \(N^+\) ion bombardment (same as two separate \(N^+\) ions). Sputtering yield depends on energy and angular distribution of sputtered atoms, so

\[
Y(E, \theta) = Y(E, 0) \cdot S(\theta),
\]

where \(E\) is the energy of incident ions and is approximately equal to \(eV_d\) and \(\theta\) is the ejection angle of sputtered atoms with respect to the surface normal. Energy dependent part is given by Eckstein et al.\(^{31}\) as

\[
Y(E) = q\nu E_{\text{th}}^{\mu} \left( \frac{E}{E_{\text{th}}} - 1 \right)^{\nu},
\]

where \(q, E_{\text{th}}, \mu,\) and \(\lambda\), which are material-dependent parameters, listed in Table 2. \(E_{\text{th}}\) and \(\nu\) are threshold energy for sputtering and nuclear stopping power, respectively. Angular distribution of sputtered atoms was proposed by Yamamura et al.\(^{32}\) which follows a relation of the type

\[
S(\theta) = \cos(1 + \beta \cos^2 \theta),
\]

where \(\beta\) is a fitting parameter. The fitting parameter depends on the mass and binding energy of the target material, mass and ion energy. It may be expressed as

\[
\beta = B\ln Q - B_c \quad \text{and} \quad Q = \frac{M_t E_{\text{sb}}}{M_b E_{\text{sb}}},
\]

where \(M_t\) is the mass of the sputtered atom and \(E_{\text{sb}}\) is binding energy of the sputtered material (Table 2). The values of \(B\) and \(B_c\) are, respectively, approximated as 0.488 and 2.44. Using the Eq. 4 and under nearly normal ejection, the Ti:Cu atomic ratio for different nitrogen pressures is evaluated to be \(~0.068\). Owing to the uncertainty of EDX method in determining the nitrogen concentration and thermal instability of copper nitride, only the Ti:Cu atomic ratio is presented in this article. Atomic Ti:Cu ratio of the deposited Ti:Cu:N films on Si(111) substrates is averagely evaluated to be 0.067 and 0.074 for sputtering power of 60 and 80 W, respectively. The Ti:Cu ratios are generally lower than atomic Ti:Cu ratio of Ti<sub>13</sub>Cu<sub>87</sub>, namely, 0.15. There is a good agreement between the experimental and calculated values for Ti:Cu atomic ratio.

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**Fig. 2:** SEM images of deposited films at sputtering powers of (a) 60 and (b) 80 W
It was known that the sputtering yield ratio of Ti to Cu is nearly 0.6 according to the calculated values from Eq. 5 for all sputtering power. Also, when Ti is sputtered in an N₂ atmosphere, the sputtering yield is decreased because a part of Ti on the target surface is nitrided. This effect is weaker for the Cu because it is more difficult to nitride Cu than Ti due to weaker Cu–N bonding. After being sputtered for some time the Ti:Cu ratio on the target surface will reach an equilibrium so that the ratio of the sputtered yield of the two materials are less than their ratio in the bulk target. Thus, it is likely that the difference between the composition in the target and film is caused by their different throw distance, nitriding kinetics, angular distribution of any sputtered components and different absorption rates on the film surface. Also, the energetic neutral N ions from plasma atmosphere, which are dissociatively reflected by the target, might be the source of Ti re-sputtering and deficiency in Ti:Cu₃N films with respect to target composition.

In as-deposited films Ti can attract N into the Cu₃N lattice by direct Ti–N chemical bonding and by the increase in the solubility of N in the Cu₃N lattice, as discussed by Ding et al. The latter contribution is excluded and only the former one is considered. We assume the amount of N attracted by chemical bonding in the film is

\[ y = c \sum_i k_i x_i, \]  

where \( c \) is the Cu relative number per unit cell in Cu₃N lattice and is equal to 0.75, \( i = \text{Cu, Ti and } k_i \) is a dimensionless constant representing the average number of N atoms chemically bonded to each \( i \)th atom. \( x_i \) is mole fraction of each \( i \)th atom. In the unit cell of Cu₃N lattice, there is one N atom chemically bound to three Cu atoms, namely, \( k_{\text{Cu}} = 1/3 \). A Ti atom can attract three N atoms, because it has triplet valence. Any Cu substitution by Ti atom in the Cu₃N lattice causes there to be three excess N atoms. The N concentration is estimated to be 37.5 and 38.7% for sputtering power of 60 and 80 W, respectively, from the above simple model. The N concentration is around 25% in stoichiometric Cu₃N thin films.

### Optical properties

Figure 3 depicts the transmittance spectra of quartz substrate and deposited films at two different sputtering powers. Figures 4 and 5 show dispersion of the calculated refractive index \( n \) and extinction coefficient \( k \) as a function of wavelength in the 300–1100 nm range, respectively. The absorption coefficient of Ti:Cu₃N films is related to extinction coefficient through \( \alpha = 4\pi k/\lambda \). In the high absorption region (\( \alpha > 10^4 \text{cm}^{-1} \)), absorption coefficient can be presented by the relation

\[ \alpha(E) = B(E - E_g)^p / E, \]  

where \( B \) is a constant depending on transition probability, \( E_g \) is the bandgap, and \( p \) is an index that characterizes the optical absorption process and is theoretically equal 2, 1/2, 3, and 3/2 for indirect allowed, direct allowed, indirect forbidden, and direct forbidden transitions, respectively. The usual method for determining the values of the bandgap, \( E_g \), involves plotting a graph of \( (\alpha E)^{1/p} \) vs photon energy, \( E \), in accordance with Eq. 10. If an appropriate value of \( p \) is used to obtain linear plot, the value of \( E_g \) will be given by the intercept on the \( E \) axis. From fitting process, the best plot that cover the widest range of data may be obtained for the \( (\alpha E)^2 - E \) dependence. The \( E \)-axis interception \( (E_g) \) are shown in Fig. 6 and these results indicate direct allowed transitions dominant in

### Table 2: Materials dependent parameters presented by Eckstein et al. for Ti and Cu target atoms bombarded by nitrogen ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Target atom</th>
<th>( \lambda )</th>
<th>( q )</th>
<th>( \mu )</th>
<th>( E_{th} ) (eV)</th>
<th>( E_{sb} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N⁺</td>
<td>Ti</td>
<td>0.2321</td>
<td>1.8168</td>
<td>2.0297</td>
<td>16.5403</td>
<td>4.89</td>
</tr>
<tr>
<td>N⁺</td>
<td>Cu</td>
<td>0.1595</td>
<td>3.4102</td>
<td>2.1567</td>
<td>15.6567</td>
<td>3.52</td>
</tr>
</tbody>
</table>

Fig. 3: Transmittance spectra of quartz substrate and quartz plus deposited films at sputtering powers of 60 and 80 W

polycrystalline Ti:Cu$_3$N thin films. The values of direct allowed transition energy gaps are 2.79 and 3.34 eV for sputtering power of 60 and 80 W, respectively. These bandgap energies are considerably greater compared to those published for undoped Cu$_3$N in the literature where $1.2 \leq E_g \leq 1.9$ eV.$^{17}$

The lattice constant and crystallite size of Ti:Cu$_3$N, its bandgap energy, and grain size of the films increase for sample prepared at sputtering power of 80 W with respect to that of 60 W. For the as-deposited films there is a remarkable shift of the band edge absorption to lower energy as sputtering power decreases. These behaviors simultaneously illustrate two phenomena; first, the effect of N-richness in absorption process that causes the formation of electron acceptor centers associated with the interstitial nitrogen excess. Bandgap energy clearly increases from 2.79 to 3.34 eV for N rich film in accordance with hole-filling effect in the valance band.$^{37}$ This phenomenon may cause degeneracy near edge parabolic valence band and bandgap widening (Burstein-Moss shift).$^{38}$ Second, nano-crystalline dimension of the Ti:Cu$_3$N causes transitions to occur between discrete energy levels resulting from quantum confinement effects. If the Ti:Cu$_3$N nano-crystallite size is of the order of the Bohr exciton radius, then it corresponds to intermediate confinement regime of the Efros et al. model for describing the relationship between the quantized energy levels and the crystallite size.$^{39}$

$$E_g = E_{gb} + \frac{(\pi \hbar)^2}{2R^2m} - 2.438 \frac{e^2}{eR},$$

where $m$ is the carrier effective mass, $E_{gb}$ is the bulk bandgap energy, $R$ is the mean radius of the nanocrystallite, $E_g$ is the energy of the electronic transition between the quantized states in the conduction and valence band, and $\varepsilon$ is the semiconductor dielectric constant. Quantum confinement effects and interstitial N excess induce remarkable bandgap widening of Ti:Cu$_3$N in comparison to that of Ti free Cu$_3$N. According to Eq. 11 and crystallite size, it is expected that the bandgap energy of as-deposited films at sputtering power of 80 W to be less than that of
60 W. However, bandgap widening due to N richness overcomes bandgap shrinkage due to the nano-crystalline growth of films deposited at sputtering power of 80 W relative to those of 60 W.

Room temperature photoluminescence (PL) measurement results of Ti:Cu$_3$N films are shown in Fig. 7. In addition to band edge emission at 447 and 375 nm, related to as grown film at sputtering power of 60 and 80 W, respectively; there are two re-emission mechanisms for Ti:Cu$_3$N films; first, as discussed in, interstitial nitrogen excess acts as electron acceptor centers. The PL peak at 486 and 411 nm for as grown films at sputtering power of 60 and 80 W, respectively, are related to a band to acceptor re-emission. The N acceptor energy, $E_A$ can be estimated according to the following equation:

$$E_A = E_g - E_{PL} + k_B T/2,$$

(12)

where $k_B$ and $T$ represent the Boltzmann constant and absolute temperature, respectively. Using the related bandgap energy at room temperature, the $E_A$ is estimated to be 245 and 328 meV for as grown film at sputtering power of 60 and 80 W, respectively. Thus, interstitial N excess indicates shallow acceptor center. The second mechanism for PL measurement might be due to the doping of Ti and its corresponding defect state. The distinct PL peaks around 669 and 701 nm are due to Ti defect center for as grown film at sputtering power of 60 and 80 W, respectively. The Ti defect state produces a deep level in forbidden bandgap.

**Electrical properties**

Electrical resistivity at room temperature of Ti:Cu$_3$N films deposited on glass slide substrates is 530 and 490 $\mu$Ω cm for sputtering power of 60 and 80 W, respectively. The crystalline quality of sample prepared at sputtering power of 80 W is higher than that of the sample grown at 60 W (see XRD in Fig. 1). It is obvious; the electrical resistivity of the former film is lower than the latter film. The films electrically show quasi-metallic behavior. The addition of Ti- to Cu$_3$N-based films induces a strong decrease in their electrical resistivity at room temperature. Depending on the deposition conditions, the resistivity of Cu$_3$N films reported by Pierson is $<10^5$ $\mu$Ω cm.

**Thermal stability**

The thermal stability of films was studied by heat treatment at temperatures of 300 and 400°C in vacuum condition. Figures 8 and 9 show XRD diagrams of...
Ti$_3$Cu$_n$N films which were annealed at 19010/C0 for 2 h at 300 and 400/C176 respectively. As it is seen Ti:Cu$_3$N films deposited at sputtering power of 60 W have excellent stability in comparison with those deposited at sputtering power of 80 W and annealed at 300 and 400/C. The as-deposited Ti:Cu$_3$N films illustrate Cu$_3$N (100) preferred orientation, but annealed films have Cu$_3$N (100) and Cu$_3$N (211) mixed orientation.

**Conclusion**

This article is devoted to a study of Ti:Cu$_3$N films deposited by reactive DC magnetron sputtering of a titanium copper single multicomponent target in N$_2$ ambient. The structure, surface morphology, chemical composition, optical bandgap, electrical properties, and thermal stability of these films have been investigated. Under the conditions used in this study, Ti addition does not change the cubic anti-ReO$_3$ structure of Cu$_3$N. XRD analysis showed the presence of a nano-crystalline phase for the Ti:Cu$_3$N ternary alloys and using the Scherrer’s formula we were able to estimate the mean crystalline size to be around 22 and 27 nm. Ti incorporation in Cu$_3$N unit cell leads to over-stoichiometric in nitrogen (N-rich). Surface morphology shows agglomeration of grains. Ti:Cu atomic ratio in these films is less than that of the original target. Study of optical properties shows Ti:Cu$_3$N films are of direct type semiconductor. Their bandgap energy is typically 2.79 and 3.34 eV depending on N concentration. Quantum size effect and formation of electron acceptor centers associated with interstitial N excess considerably increase the bandgap energy of Ti:Cu$_3$N relative to undoped Cu$_3$N. The PL spectra show PL band with emission attributed to transition from the band to acceptor. The films electrically show quasi-metallic behavior. Compared with the Ti free Cu$_3$N film, the Ti:Cu$_3$N films possess higher thermal stability in vacuum.

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**References**