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Growth of stoichiometric Cu_3N thin films by reactive magnetron sputtering

A.L. Ji*, R. Huang, Y. Du, C.R. Li, Y.Q. Wang, Z.X. Cao

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, P.O. Box 603, Beijing 100080, China

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Abstract

Copper nitride (Cu_3N) is a thermally unstable material; therefore both the deposition of a stoichiometric sample and the reliable characterization of its properties constitute a big challenge. We reported here the growth of stoichiometric Cu_3N films on Si (1 0 0) wafer by reactive magnetron sputtering of Cu target using pure nitrogen as working gas. At a low substrate temperature (60 °C), a combination of high working pressure (>0.7 Pa) and low RF power supply (<150 W) favors the formation of stoichiometric deposits. With the pressure at 0.9 Pa and the RF power below 100 W, the deposits are [0 0 1]-oriented and consist of cubic Cu_3N grains, which are typically 40 nm in dimension. The lattice constant is 0.383 nm as determined by both X-ray diffraction and transmission electron microscopy; and the electrical resistivity measurement reveals a typical deficit semiconductor behavior in the cubic Cu_3N . The thermal decomposition temperature, being reported within 100–470 °C, was determined to be ~350 °C as indicated by the presence of Cu (1 1 1) and (0 0 2) reflections after prolonged annealing.

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1. Introduction

There is an increasing interest in exploring new materials and process technology for optimizing the electrical interconnections in ultralarge-scale integrated circuits. The binary compound Cu_3N in the cubic anti- ReO_3 structure is an indirect band-gap semiconductor with high resistivity at room temperature, which readily decomposes into metal Cu at an elevated temperature. Cu_3N is therefore a candidate for the production of deep sub-micrometer sized copper lines by direct laser- or electron beam writing [1–4] without involving a photolithography processes. Notably, the thermal decomposition of Cu_3N also brings about a remarkable change in its optical properties, which also provides the possibility of being used in write-once optical recording applications [3–5]. Towards

these aims, Cu dots arrays or lines have been fabricated via local decomposition of copper nitride by several researchers [1–7], but the preparation of stoichiometric copper nitride films remains an essential issue to be resolved.

The poor thermal stability of copper nitride is a factor both for the sample preparation and for the characterization of its physical properties. Since its first synthesis by Juza and Hahn [8], a variety of methods [1–3,5–17] have been employed in the growth of copper nitride, mostly in the form of thin films; and many experimental data have been established for this material. However, the physical properties of the copper nitride films reported in literature are inconsistent. For example, the reported lattice constant of cubic Cu_3N ranges from 0.3815 to 0.3885 nm [9,10], the optical band gap varies from 0.25 to 1.9 eV [11–13,18,19], the electrical resistivity spans a large range from 2.6×10^{-5} to 1000 Ωm [2,9,12,19–21], and the thermal decomposition temperature is believed to be between 100 and 470 °C [1,2,4–6,22]. The large discrepancy in the aforementioned

*Corresponding author. Tel.: +86 01 82648094; fax: +86 01 82649228.
E-mail address: alji@aphy.iphy.ac.cn (A.L. Ji).

data, besides the uncertainty originating in the analyzing methods, lies in the unstable nature of copper nitride. Nitrogen in Cu_3N is prone to reemission due to the weak N–Cu bond. Samples can differ greatly in composition and microstructure, generally a compound of Cu_3N plus pure metallic Cu inclusions. Moreover, under irradiation of energetic particle beams used in some forms of materials characterization, the samples undergo immediate changes. Consequently, a measured physical property depends sensitively on the sample condition and the relevant characterization processes. As for the growth of stoichiometric copper nitride by reactive magnetron sputtering, dynamic processes on both the growing surface and the target surface can influence the composition of the deposits. With argon as the working gas, which is generally used to stabilize the plasma, it is difficult to obtain a stoichiometric sample [13]. The use of increased RF power to enhance the degree of ionization of nitrogen can result in the presence of more pure-Cu inclusions in the deposited film. In this paper, stoichiometric Cu_3N films, with ‘stoichiometric’ being defined as having a Cu below 75.6% so that the samples behave as a typical deficit semiconductor were prepared by using pure nitrogen as precursor. A low substrate temperature, high pressure and small power feed-in, hence smaller ion energy to bombard the Cu-target, are desirable in producing these materials. With stoichiometric samples, more reliable and reproducible data for the physical properties such as the atomic structure, thermal stability and electrical resistivity have been obtained.

2. Experimental details

Copper nitride thin films were deposited onto Si (100) wafers in a custom-designed reactive magnetron sputtering system at a base pressure of less than 1×10^{-4} Pa, using the high-purity (5N) nitrogen as working gas. In order to prevent the nitrogen reemission from deposits, the substrate temperature was maintained at 60°C and the working pressure was raised to 0.9 Pa. As the controlling parameter, the RF power fed to the Cu-target ($\Phi 60$) was tuned from 150 to 50 W. Typical film thickness lies within 1.0–1.5 μm . To study the thermal stability of the as-deposited films, the samples were annealed in the same chamber under the nitrogen environment at 0.9 Pa for 20 min in the temperature range from 220 to 420°C . The morphology and structure of both the as-deposited and the annealed films are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Complementing the X-ray photoelectron spectroscopy, the energy-dispersive X-ray analyzer attached to the SEM was also used to determine the chemical composition of the deposits. The temperature dependence of electrical resistivity of the deposits was measured by the conventional four-point probe method over the temperature range from room temperature to 5 K. Due to the sensitive nature of the

copper nitrides, repeated measurements of electrical resistivity and structural analysis of the as-deposited and annealed samples by XRD have to be performed on the films freshly prepared under the identical conditions.

3. Results and discussion

The low substrate temperature allows for the preparation of copper nitride, which can be well reproduced. This is very important for the subsequent analysis of this unstable material since the energetic beam-based analyses and heating are generally destructive and repeated measurements must be carried out on the equally fresh samples. A low substrate temperature and higher working pressure can effectively suppress the formation of the pure Cu phase in the deposits. Figs. 1(a) and (b) display the XRD patterns for the samples deposited with various RF powers, and under two working pressures for comparison. It can be seen that the films have a typical anti- ReO_3 structure, showing strong peaks from the (001), (002) and (111) reflections. The presence of pure Cu crystallites is disclosed by the minor Cu-(111) reflection at $2\theta = 43.32^\circ$. The detection limits for the compositional and structural

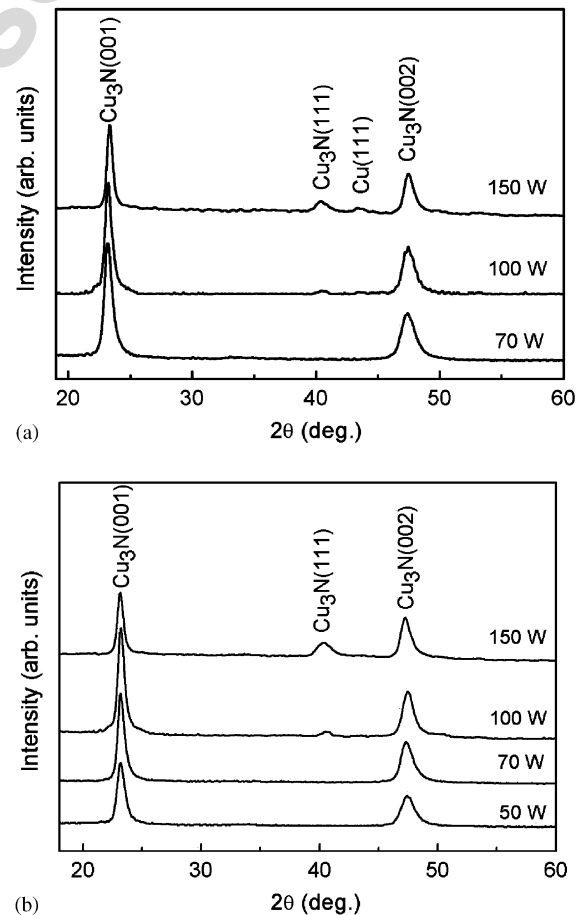


Fig. 1. (a). XRD patterns for the copper nitride deposits prepared at different RF powers. The working pressure was (a) 0.7 Pa and (b) 0.9 Pa, respectively.

characterization techniques used here are approximately a 1% volume fraction within the probed volume. The higher deposition pressure and the lower RF power favor the formation of deposits of the pure Cu_3N phase in a competitive way. At 0.7 Pa, the Cu-(111) reflection is visible in the deposit prepared with an RF power of 100 W; at 0.9 Pa, however, it is still absent when the RF power was raised to 150 W. Both the higher pressure and lower RF power can reduce the energy of nitrogen ions bombarding the Cu-target. By reactive magnetron sputtering the copper nitride is only likely to occur on the target surface, therefore very large ion energy is unfavorable for the formation of Cu–N bonds in the sputtered particles. Generally speaking, to obtain nearly stoichiometric copper nitride at a preset low substrate temperature, the gas pressure and the power should be chosen in a way that the density of nitrogen ions is sufficiently high and the ion energy has to be low so as not to decompose any Cu–N bonded species present on the sputtering target. A strict specification of the process parameters demands a thoughtful mass-resolved analysis of the bombardment products. Remarkably, in addition to the [001]-orientation, the larger RF power also leads to the occurrence of the [111]-orientation for the Cu_3N crystallites. Fig. 1 indicates that the copper nitride of pure Cu_3N phase in the predominantly [001]-orientation can be obtained in a considerably wide parameter window, so long as the combination of pressure and RF power allows the formation of Cu–N at the target surface.

The stoichiometric Cu_3N samples were further characterized by SEM and TEM techniques. For the sample prepared at 0.9 Pa and at 70 W, SEM image reveals a flat morphology composed uniformly of distinct morphological regions in a typical dimension of about 40 nm (Fig. 2). The HRTEM image of the stoichiometric sample exhibits well-aligned $\{001\}$ fringes, shown in Fig. 3, which confirms the purity of crystallographic orientation of the deposit. The planar distance for the $\{001\}$ -planes, i.e., the lattice constant, measures 0.383 nm in the TEM image, which is in good agreement with the results of XRD measurement.

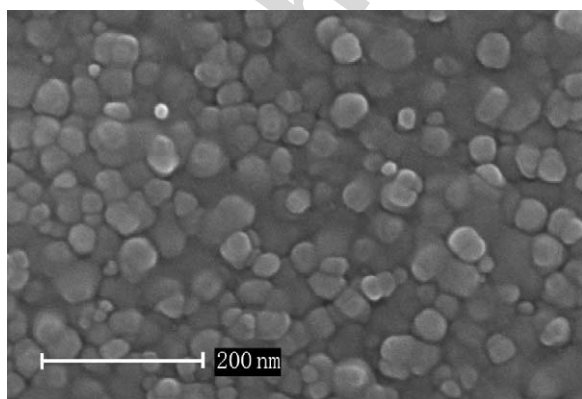


Fig. 2. Plain-view SEM image for the sample grown at the working pressure of 0.9 Pa and with an RF power of 70 W.

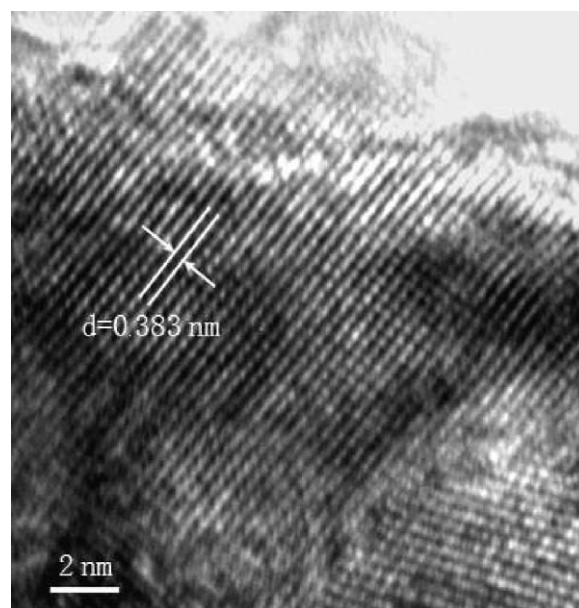


Fig. 3. TEM image of the same sample referred to Fig. 2.

Copper nitride even in the pure Cu_3N phase still possesses a minor deficiency of nitrogen. This is to say that in the stoichiometric samples we presented here, the content of Cu is somehow larger than 75.0%. In fact, from the energy-dispersive X-ray analysis and photoelectron spectroscopic data, the lowest Cu content is about 75.6% to the accuracy of the methods. The nearly stoichiometric copper nitride sample should be a typical deficit semiconductor, as seen from the temperature-dependence of the electrical resistivity, see Fig. 4(a). A slight increase of the content of Cu to $\sim 76.0\%$ can totally eliminate this characteristic behavior of a deficit semiconductor characterized by a resistivity first decreasing irregularly with the decreasing temperature, and below 50 K steeply increasing (not shown). In the Cu-rich sample with 78.8% of Cu, due to the presence of distinct Cu particles [13], the electrical resistivity shows characteristic metallic behavior in which the electrical resistivity increases linearly with the temperature rising from 5 to 300 K (Fig. 4(b)). According to the equation $\rho(T) = \rho_0[1 + \alpha(T - T_0)]$, the temperature coefficient α is determined to be 7.54×10^{-4} , much less than that the value $1/232$ for pure Cu. This can be explained by the fact that in the Cu-rich copper nitride, the conduction path is made of both Cu nanoparticles and the Cu_3N nanoparticles enclosed in the Cu-terminated $\{111\}$ -planes. The stoichiometric Cu_3N sample manifests a typical semiconductor character, the temperature dependence of electrical resistivity (Fig. 4(a)) can be approximately fitted by the equation $\rho(T) = C \exp(-E_a/kT)$, with the activation energy E_a being approximately 8.59×10^{-2} eV. For comparison, E_a is 1.47×10^{-2} eV that was reported in Ref. [12].

As the reports of the Cu_3N electrical resistivity, its thermal decomposition temperature is also uncertain since

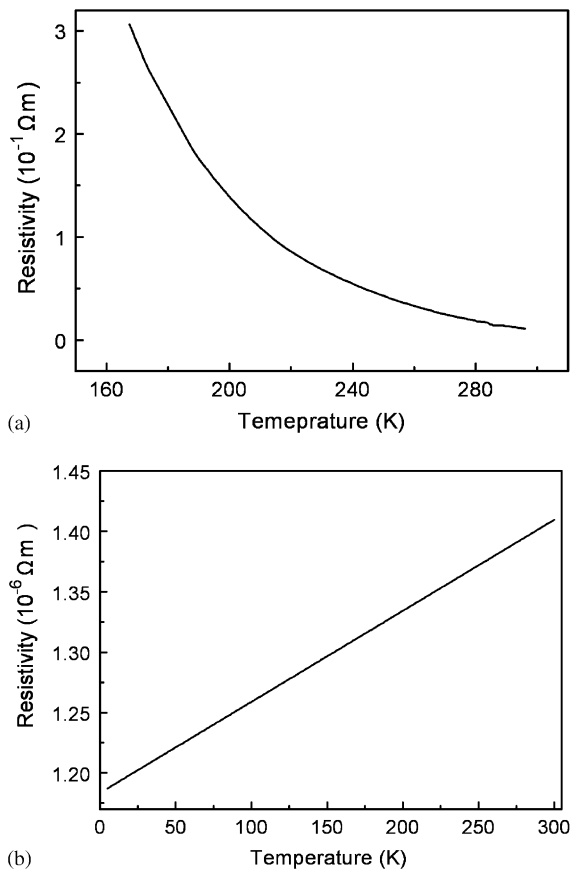


Fig. 4. Temperature dependence of electrical resistivity for a stoichiometric Cu_3N sample (a) and for a Cu-rich sample (b).

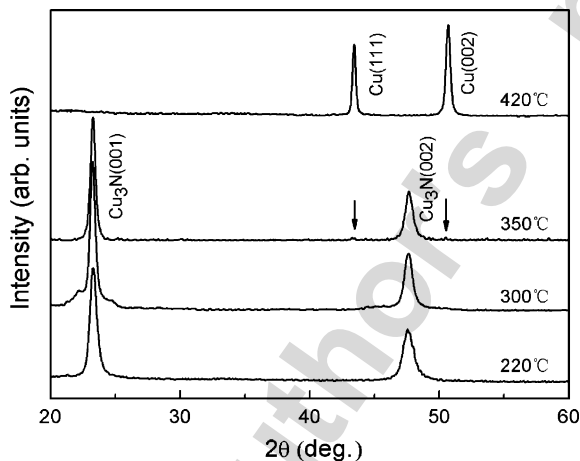


Fig. 5. XRD patterns of the Cu_3N films after annealing at temperatures varying from 220 to 420 °C.

the composition and structure of the reported samples are highly variable. We investigated the thermal stability of Cu_3N by XRD analyses on the stoichiometric, [001]-oriented sample annealed at different temperatures. The as-deposited sample displays on the (001) and (002) reflection (Fig. 5). Annealing for 20 min at 220 and 300 °C does not lead to any discernible changes to the diffraction pattern. After annealing at 350 °C, two small peaks appear

in the XRD spectra at $2\theta \approx 43.32^\circ$ and $\approx 50.55^\circ$ (arrowed) which can be assigned to the (111) and (002) reflections of a pure Cu phase. The appearance of the Cu (111) and (002) reflections unambiguously signifies the onset of thermal decomposition of Cu_3N . After annealing at 420 °C, only strong Cu peaks were observed with the Cu_3N completely decomposed. Although the current experimental data does not allow for a precise value of decomposition temperature, stoichiometric Cu_3N , as determined by XRD, decomposes measurably only upon annealing at a temperature of $\sim 350^\circ\text{C}$ under the nitrogen at a pressure of 0.9 Pa.

4. Conclusions

In summary, stoichiometric Cu_3N thin films as a deficit semiconductor can be grown by reactive magnetron sputtering using pure nitrogen as working gas. A higher working pressure and a low RF power are desirable for the formation of weak Cu–N bond at the sputter target surface, which is critical for the obtaining of stoichiometric samples. At a pressure of 0.9 Pa and an RF power below 70 W, the deposits are entirely [001]-oriented. Using stoichiometric samples, the lattice constant for cubic Cu_3N was determined to be 0.383 nm. The semiconductor character of the films was verified by resistivity measurements. The thermal decomposition temperature was found to be at $\sim 350^\circ\text{C}$. These results help clarify the controversies about the physical properties of this thermally unstable material.

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