

# Orogenic movement mechanism for the formation of symmetrical relief features in copper nitride thin films

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Nonequilibrium growth of crystals has revealed an astonishing variety of structures, resulting from the interplay of relevant factors such as atomic mobility, thermal effect, dynamic heterogeneity, etc. In preparing thin films of the thermally unstable copper nitride  $\text{Cu}_3\text{N}$ , growth proceeds with simultaneous nitrogen reemission, which both bestows a preferred, Cu-terminated  $\{111\}$  facet on the  $\text{Cu}_3\text{N}$  crystallites and limits their size to about 45 nm. The authors observed an orogenic movement of  $\text{Cu}_3\text{N}$  nanocrystals via glide along the  $\{111\}$  planes, resulting in a hollow, relief morphology primarily of round caps and later of mesoscale rosettes which often demonstrate a fivefold symmetry at the center. The area expansion in the thin film by a few percent is sustained through the rearrangement of nanocrystals into ragged steps and terraces, while the ongoing fast growth prevents the relief features from cracking. The results bear broad significance for the film growth of thermally unstable materials. © 2007 American Vacuum Society. [DOI: 10.1116/1.2433970]

## I. INTRODUCTION

Hard electronic devices based on wide-gap semiconductors such as SiC and GaN that are expected to operate at temperatures over 300 °C demand both innovative design and novel materials for the metallization of insulating layers and for the fabrication of electrical interconnects. For this, noble metal nitrides which are semiconductors or even metallic conductors promise to meet the requirements with their excellent properties, particularly when the compatibility with the base materials is of concern. Among the various candidates, copper nitride  $\text{Cu}_3\text{N}$ , which has an indirect band gap within 1.2–1.9 eV (Refs. 1–4) and can be directly made metallic in its Cu-rich allotrope,<sup>5</sup> has attracted much attention from researchers.

Copper nitride  $\text{Cu}_3\text{N}$  has an anti- $\text{ReO}_3$  structure with a lattice constant of  $\sim 3.80$  Å. It is thermally unstable since copper is a noble metal against nitrogen. A decomposition temperature in the range of 100–470 °C has been reported by various authors.<sup>1,6–8</sup> An immediate consequence of the thermal instability is that the deposits of copper nitride are generally Cu rich containing  $\text{Cu}_3\text{N}$  crystallites and Cu precipitates.<sup>9</sup> Though it can be exploited for beneficial applications in making write-once optical recording<sup>10</sup> and in fabricating microscopic copper wires,<sup>7,11</sup> the thermal instability of copper nitride is certainly a troublesome factor for the film growth practitioners.<sup>12</sup> In growing a film on a substrate material, a properly chosen substrate temperature is often required to improve the adhesion, to alter the microstructure, etc. For copper nitride, even a substrate temperature of 200 °C will provoke a considerable decomposition rate. The interplay of reactive growth and simultaneous decomposition—a weird situation that has rarely been discussed—not only poses some difficulties for the control of

film chemistry and/or microstructure but may also cause some unusual effects such as the formation of a textured morphology. In this work we report the observation of a relief morphology comprising of mesoscale rosettes which often show a fivefold symmetry in the central disk and ramify successively at an angle  $>74^\circ$  in the copper nitride thin films prepared at a substrate temperature as low as 70 °C. Based on the spectrometric and microscopic characterizations, it is found that it is the glide of the  $\{111\}$ -faceted nanocrystals, being a consequence of nitrogen reemission, that is responsible for the bewildering morphogenesis. An orogenic movement mechanism is put forth to illustrate the multiscale process for the formation of such a relief morphology.

## II. EXPERIMENT

Copper nitride films were grown on Si (001) wafers and quartz substrates in a custom-designed system using the reactive magnetron sputtering (rf power supply set at 150 W) of a copper target ( $\phi 60$  mm, 4N purity). Prior to the sample deposition, the substrates were ultrasonically cleaned successively in acetone and alcohol, and then rinsed with deionized water. For Si wafers, they had to be immersed in the 1.0% HF solution to remove the native oxide before final cleaning. For the growth of copper nitride that exhibits the relief morphology concerned below, the working pressure during deposition was maintained at a value between 1.0 and 1.3 Pa, while the total flow rate was kept at 4 SCCM (SCCM denotes cubic centimeter per minute at STP) with the flow ratio  $[\text{N}_2]/([\text{N}_2]+[\text{Ar}])$  being tuned within 60%–80%. A substrate temperature as low as 70 °C was chosen in order to restrain the possible nitrogen reemission from the deposits. With these given processing parameters, a growth rate of about 20 nm/min was achieved. Two groups of samples, each grown for 15 and 30 min, respectively, were taken for a comparative study. Morphology investigation was performed

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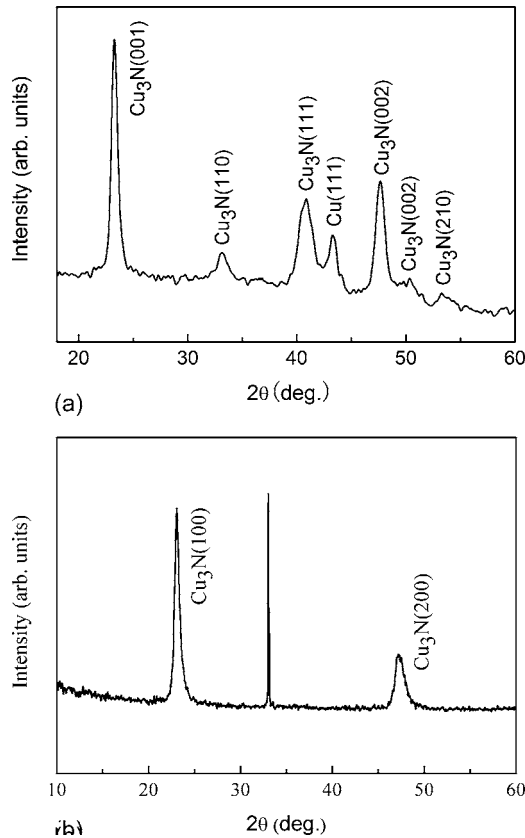


FIG. 1. (a) XRD pattern for the copper nitride film referred to in Figs. 2(b) and 2(c), in contrast to that for (b) a stoichiometric, compact film which shows only Cu<sub>3</sub>N (001) and (002) reflections in addition to the sharp peak from silicon substrate.

in an XL30 S-FEG scanning electron microscope (SEM) with attached energy-dispersive x-ray spectrometry facilities for chemical analysis operated at 10 keV. X-ray diffraction (XRD) (D/max-2400) using the Cu  $K\alpha$  irradiation was employed to characterize the crystalline structure of the samples.

### III. RESULTS AND DISCUSSION

The thermal instability of copper nitride makes the deposition of a stoichiometric sample with magnetron sputtering a great challenge. Samples obtained under given conditions generally contain both Cu<sub>3</sub>N and pure Cu crystallites. A typical XRD pattern is displayed in Fig. 1(a), which reveals three dominant peaks from the (001), (111), and (002) reflections of the cubic Cu<sub>3</sub>N phase and two minor peaks referring to the Cu (111) and (002) reflections. The significant broadening of the diffraction peaks indicates the nanocrystalline nature of the deposition that the crystallite size is estimated well below 100 nm. Furthermore, the lattice constant calculated from the Cu<sub>3</sub>N (001) reflection is 3.827 Å, which is larger than the standard value (3.814 Å) by 0.34%. Such a small deviation arises simply from the nanoscale dimension of the crystallites due to the atom relaxation at the boundaries; stress accumulation in the deposits is not found, which helps simplify the understanding of the unusual morphology

to be discussed below. To facilitate the discussion, the XRD pattern from a stoichiometric, compact Cu<sub>3</sub>N film, which was obtained with pure nitrogen as working gas at a reduced power supply (100 W),<sup>13</sup> is also presented for comparison [Fig. 1(b)].

With a power supply of 150 W, even the deposits prepared with pure nitrogen still contain tiny Cu particles; with increasing argon content in the precursor gas the situation becomes worse. The nearly stoichiometric sample exhibits a compact surface consisting of crystallites in rounded habit [Fig. 2(a)] and the SEM image looks nebulous due to the semiconducting nature of Cu<sub>3</sub>N. On the contrary, the samples with larger Cu content (>78%) manifest a compact surface with distinct Cu crystallites in cubic habit (not shown). Under the given conditions specified in Sec. II, the copper nitride films exhibit a very appealing morphology. In a 0.3 μm thick deposit, some round caps in a typical dimension of 5–6 μm are observed, and the coverage by these protruding features is about 20% [Fig. 2(b)]. With continued deposition the round caps grew larger and they began to ramify, turning into a rosettelike structure. At the same time, some new bulges evolved, adopting a rather irregular shape due to the strain field imposed by the surroundings. In Fig. 2(c) the rosettes on a film of ~0.6 μm in thickness have a quite uniform size with a lateral dimension around 23 μm, and now the coverage by the protruding features amounts to 70%. In a large scope of view, the rosettelike structures have a homogeneous, close-packed appearance. Of course, by saying this the geometrical rigor is absent. The averaged content of Cu in the films referred to in Figs. 2(b) and 2(c) was roughly 77.2%, manifesting explicitly the deficiency of nitrogen in the deposit. Later we will see that it falls in the range for percolation conduction to undergo via the Cu-rich {111} planes of the nitrogen-deficient Cu<sub>3</sub>N pyramidal crystallites (Fig. 5 below).

At first glance, this morphology reminds us of island formation as frequently encountered in growing crystalline films, which generally can be modeled with an atomistic view. But we find that this is not the case. Both the smaller round caps and the larger rosettes are hollow, as confirmed by the presence of some cracked entities [Fig. 2(d)]. When probing through the crack of a broken rosette, the energy-dispersive x-ray spectrometry detected a dominantly strong signal only for silicon and a weak signal for copper (not shown here)—the nitrogen is completely absent. This is to say that the protruding features are due to a complete local detachment of the film and in that process some tiny amount of copper is left behind on the Si substrate.<sup>14</sup> Nevertheless, such protruding structures cannot have developed from a previously well-deposited coating due to the accumulated stress. This point can be clarified by briefly examining the necessitated area expansion of the material for the formation of such hollow features. As a conservative estimation, consider a round cap 20 μm in lateral dimension and 1 μm high. This corresponds to an area expansion of ~5.0% with regard to the underlying circular base. Such a large area expansion coefficient is prohibitive for rigid materials such as

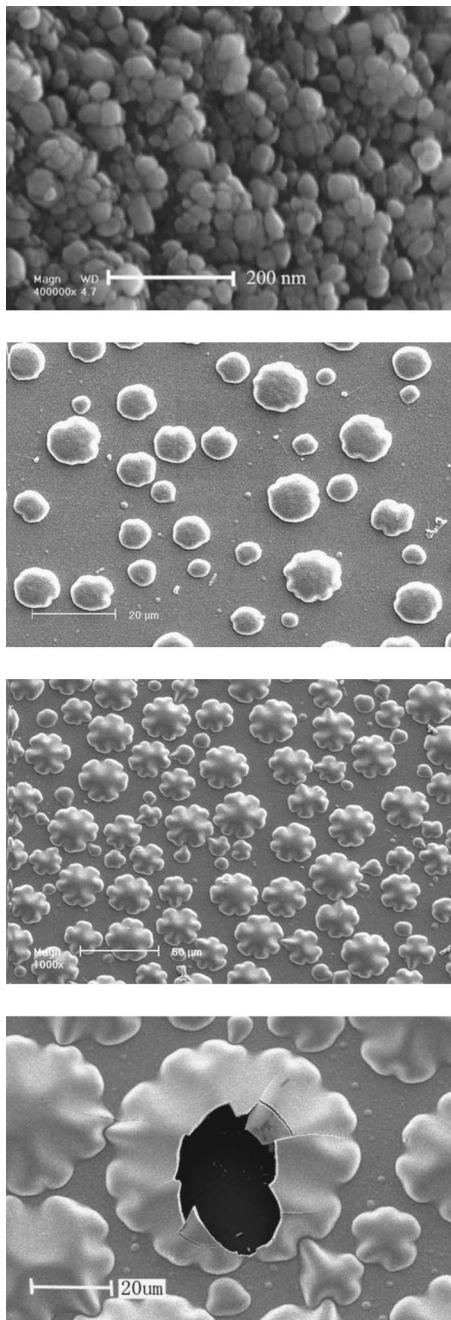


FIG. 2. Scanning electron micrographs of (a) a compact  $\text{Cu}_3\text{N}$  thin film and of [(b) and (c)] the deposits showing some protruding features. In (b) the film is  $0.3 \mu\text{m}$  thick and the protrusion has a round, convex morphology; in (c) the film grew to  $\sim 0.6 \mu\text{m}$  thick, and rosettes with bifurcated rays were observed. The rosettes are generally quintilobed; often fivefold symmetry can be identified at the center. (d) Cracked rosette revealing its hollowness.

the ionic copper nitride. Moreover, such a morphology is formed in the growth stage; postgrowth degradation of an originally flat film due to nitrogen reemission leaves behind a flat still surface, but Cu rich. The aging of films with a morphology in Fig. 2(b) in the ambient will not invoke any rosette structure as in Fig. 2(c).

The puzzle of the enormously expanded area of the rosettes with regard to the underlying base becomes immediately resolved with the aid of scanning electron micrographs

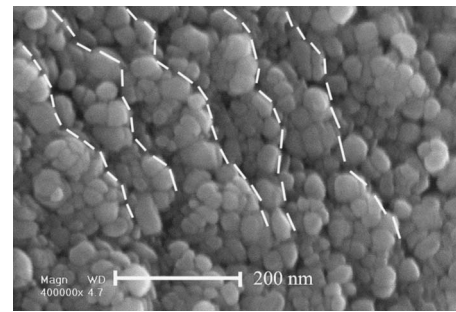


FIG. 3. Scanning electron micrographs at a large magnification from the rosette. Typical crystallite size is  $45 \text{ nm}$ . The dashed lines are plotted to guide the eye.

at enlarged magnification. The deposits are composed of distinct crystallites, around  $45 \text{ nm}$  in dimension. Figure 3 was taken on a rosette referred to in Fig. 2(c). In contrast to the compact, flat portion of the deposit in Fig. 2(a), the peculiarity in the way of crystallite stacking is obvious—in Fig. 3 the surface displays ragged steps and terraces, and it is thinner than the flat portion of the deposits. The typical terrace is about  $100 \text{ nm}$  wide comprising two or three crystallites. Such a morphology has not been reported to the best knowledge of the authors. We are inspired to speculate that the crystallites in a rosette have experienced a rearrangement process. The area expansion in due course of relief formation is sustained through the glide of the nanocrystals which is facilitated when the nanocrystals are clothed with the amorphized Cu-terminated  $\{111\}$  planes, and the ongoing fast growth prevents the film from cracking.

In order to fully understand the formation mechanism for such protruding features, we take a close look at the morphological profile of the rosettes. They have the shape of a starfish with rays, but these rays generally do not meet at the same point in the central disk. Occasionally, a symmetrically developed rosette could be found, in which a perfect pentagram is discernible at the center, as shown in Fig. 4(a). In fact, the sample also preferably breaks into pentagon pieces of micrometer sizes [Fig. 4(b)]. The rays show further bifurcations, and the offshoots extend generally at an angle of about  $74^\circ$ , a little larger than  $72^\circ$  as required by fivefold rotational symmetry, which in turn is a little larger than the wedge angle of a tetrahedron,  $\alpha \approx 70.53^\circ$ . This cannot be a coincidence, bearing in mind that the tetrahedral subcrystals do have the tendency to juxtapose at an angle of about  $72^\circ$  with a  $[110]$  orientation in order to fill the space, giving rise to a loosely fivefold symmetry.<sup>15,16</sup> Fivefold symmetry evolving from this construction mechanism has been confirmed in nanostructures of cubic metals Au, Ag, and Cu.<sup>15–18</sup>

Fivefold symmetry is prohibitive in the world of crystals, since it is incompatible with translation. But, in case that the requirement on translation symmetry is dropped, fivefold symmetry can be observed in quasicrystals<sup>19</sup> or in nanorods of a cubic metal which are often properly strained.<sup>15–18</sup> As we know, the  $\{111\}$  planes of the cubic  $\text{Cu}_3\text{N}$  comprise exclusively either Cu atoms or N atoms. When nitrogen reemits from a  $\text{Cu}_3\text{N}$  crystallite, it leaves behind crystallites with a

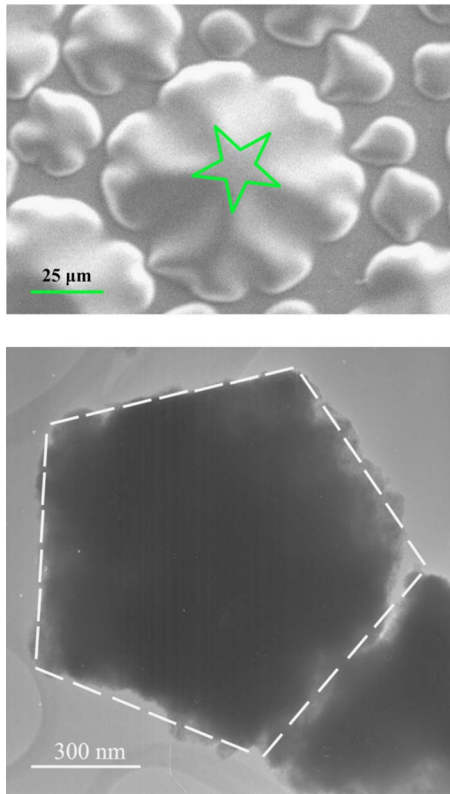


FIG. 4. Fivefoldness in the microstructure of a copper nitride deposit. (a) Rosette displaying perfect fivefold symmetry at the center. (b) Pentagonal assembly of the  $\text{Cu}_3\text{N}$  nanocrystals under transmission electron microscope.

soft clothing of amorphous Cu layer in a habit, not necessarily tetrahedral, but with facets joining at the wedge angle  $\alpha \approx 70.53^\circ$ . The soft Cu clothing facilitates the mutual gliding of the  $\text{Cu}_3\text{N}$  nanoparticles; its existence is also evidenced in the percolation behavior of electrical conductivity via this channel (Fig. 5) which occurs with an overall Cu concentration between 77.0% and 77.5%, covering the Cu concentration for the films concerned here (more Cu concentration leads to compact films showing Cu nanoparticles in cubic habit and in turn a current percolation via Cu nanoparticles). When driven by a sufficiently large stress, here initiated by the reemitted nitrogen gas from beneath, the nanocrystals

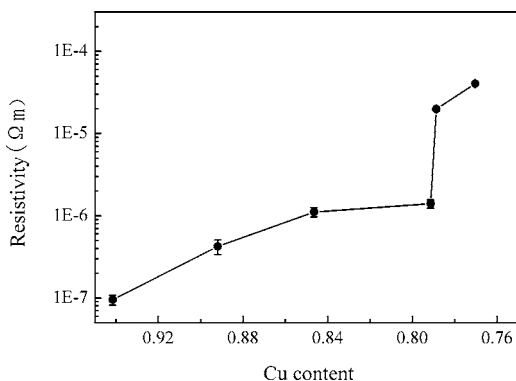


FIG. 5. Electrical conductivity of copper nitride films as a function of Cu concentration.

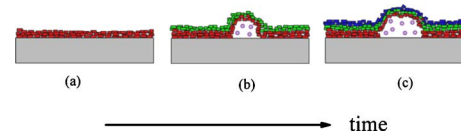


FIG. 6. Orogenic movement model for the formation of relief rosettes in copper nitride. (a) At the initial stage the film is compact. (b) With nitrogen (filled circles) accumulated beneath the film, local detachment occurs, and round caps come into view; in (c) the relief feature grows large, and branch off occurs due to the preferential orientation of the  $\{111\}$ -faceted  $\text{Cu}_3\text{N}$  nanocrystals [see Figs. 2(b) and 2(c)]. In processes (b) and (c), the crystallites have to be rearranged through glide against each other along the Cu-terminated  $\{111\}$  planes.

will make a glide motion against each other along the  $\{111\}$  planes, and conglomeration of a large quantity of such nanocrystals with facets joining at  $\alpha \approx 70.53^\circ$  results in fivefold symmetry at larger scales. Displayed in Fig. 4(b) is a piece of  $\text{Cu}_3\text{N}$  crystal in a specimen prepared with mechanical milling for transmission electron microscopic investigation—it is a pentagon with an edge length of 660 nm.

Now the picture becomes clear. An “orogenic movement” model can be formulated to illustrate the formation of relief rosettes in a growing  $\text{Cu}_3\text{N}$  thin film (Fig. 6). Copper nitride keeps decomposing while film growth proceeds. The reemitted nitrogen atoms recombine into molecules and together with entrapped nitrogen they agglomerate to form gas bubbles at the film-substrate interface by virtue of a large lateral mobility, since solubility of nitrogen in both Si and  $\text{Cu}_3\text{N}$  is low. Adhesion to the local substrate is undermined where a gas bubble forms, and detachment occurs [Fig. 6(b)]. By a delicate balance between expansion via nanocrystal glide and fast growth, the total area and the lateral dimension of the delaminated part grow in pace without cracking. As can be expected, at reduced growth rates a compact morphology of the film ensues. Gliding motion of the crystallites into ragged steps and terraces—similar to the movement of rocks in mountain building, i.e., orogenic movement—provides the path for a complete strain relaxation; this explains the negligible residual stress in the sample despite of the presence of the relief features, as concluded from the transmission electron microscopic and x-ray diffraction data about the lattice constant (Fig. 1). The possibility to glide along the Cu-terminated  $\{111\}$  planes for the pyramidal  $\text{Cu}_3\text{N}$  crystallines is prerequisite for the formation of the relief morphology; this also explains its absence in nearly stoichiometric films or heavily Cu-rich samples. As to the quintilobed structure of the rosettes that ramify at a branch-off angle of  $\sim 74^\circ$ , it is the consequence of the preferred packing and rearrangement driven by an anisotropic stress of about  $2 \times 10^6$ ,  $\{111\}$ -faceted  $\text{Cu}_3\text{N}$  nanocrystals. Unlike in the nanorods of cubic metals where the well-developed tetrahedral crystals textured along the  $[110]$  axis, so the fivefoldness of the symmetry has some rigidity, here the fivefold symmetry is quite “soft” in the sense that it occurs rather as an integral effect at large scales.

#### IV. CONCLUSIONS

We observed a rosettelike morphology in the copper nitride films and put forth an orogenic movement mechanism to illustrate the formation of such relief features based on the microscopic and spectrometric evidences. The fundamental rationale is the reemission of nitrogen from the compound during film growth which sets a limit on the crystallite size and strongly debilitates the bonding among the crystallites to facilitate the glide of nanocrystals along the Cu-terminated {111} planes. The occurrence of detachment without blistering is a problem of broad significance to the noble metal nitrides, which are generally unstable but are expected to find wide applications in electronics for the new era. This result reminds us that even in a film seemingly well adhered to the substrate and being applied at a temperature not too much over the room temperature, contact to the substrate may be gradually undercut by film decomposition.

#### ACKNOWLEDGMENT

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