



# Computational and experimental study of copper–gold nitride formation



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## ABSTRACT

This work investigates the formation of a Cu<sub>3</sub>Au-nitride alloy using experimental and computational methods. For this purpose, we prepared a custom-made Cu–Au target and then hit it with argon ions in the presence of molecular nitrogen that produced a film on Corning glass. This film was analyzed using spectroscopic and diffraction techniques. The four-point-probe method and Tauc plots were applied to determine the electrical and optical properties of this thin film. Using first principle calculations a structural model was constructed that validated our observations. The crystalline system that we used was cubic (*Pm3m* space group) with half the sites filled with Au randomly. The composition was close to Cu<sub>3</sub>Au<sub>0.5</sub>N. In agreement with the electrical measurements and calculations, the Cu<sub>3</sub>Au<sub>0.5</sub>N band structure was highly affected by the Au incorporation since the electrical resistance and carrier density were in the 10<sup>−3</sup> Ω cm and 10<sup>22</sup> cm<sup>−3</sup> ranges, respectively, and the optical gap decreased 0.61 eV with respect to the Cu<sub>3</sub>N. The material was a pseudo-gap conductor with conductance as good as a heavily-doped semiconductor at room temperature; this should give it great potential for use in the optoelectronics industry.

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## 1. Introduction

The intermetallic compounds are comparable to ceramics in several aspects. Both are stoichiometric with a limited composition range. They are mechanically brittle and the crystal structures and properties often differ markedly from those of their constituents. The relative sizes of the atoms and the ratio of the total number of valence electrons dictate the properties of both types of compounds. The copper–gold system is typical of intermetallic compounds and has been intensively studied as a model for ordered binary alloys [1]. Several compositions of the copper–gold system may produce a wide ranged order. While intermetallic alloys are intentionally developed to obtain better properties than those of the individual atoms, it has also been observed that metallic thin films (including alloys) exhibit, in some cases, unusual properties different from those of the thermally prepared bulk alloys [2,3]. The intermetallic formations have been thoroughly investigated and are reasonably understood; In contrast, studies of the formation of intermetallic-nitrides are relatively scarce. The purpose of this research was to focus on the intermetallic Cu<sub>3</sub>Au, which was nitrated in an attempt to form the ternary Cu<sub>3</sub>AuN compound.

When we use the Cu<sub>3</sub>Au intermetallic structure represented in the *Pm3m* (221) space group, the Wyckoff 3c positions is occupied by copper, and the Wyckoff 1a position is occupied by gold atoms. Whereas with the structure of copper nitride (Cu<sub>3</sub>N) the nitrogen atoms occupy the Wyckoff 1b position; this was described in detail in a previous paper [4]. Thus, if gold occupies the 1a sites in Cu<sub>3</sub>Au (221 space group), and nitrogen occupies 1b sites in Cu<sub>3</sub>N (the same space group), and copper keeps the 3c sites in both structures, it is possible to hypothesize that the formation of ordered Cu<sub>3</sub>AuN has no structural impediments. In addition, nitrogen has chemical affinity with the two metals (copper and gold). Such chemical affinity has been confirmed with the formation of nitrides of these metals [5–7]. However, it should be noted that the affinity of nitrogen to these metals has a clear preference to copper [7]. The main question we want to answer is: does the incorporation of nitrogen into the Cu<sub>3</sub>Au lattice, to form Cu<sub>3</sub>AuN, break the wide range order of the intermetallic alloy? With the purpose answering our question, we aimed to produce Cu<sub>3</sub>Au and Cu<sub>3</sub>AuN thin films.

## 2. Materials and method

### 2.1. Experiment

All materials presented in this work were formed as thin films by the DC-magnetron sputtering method over Corning glass slides. The thin films were formed from two different targets. The first one was a 5 cm diameter disk made of 99.99% copper (provided by Kurt J. Lesker Company). The second target, with the same purity and supplier, was modified with gold inserts. The modification

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consisted of drilling holes in the copper where the track was formed by the sputtering gun. Then gold pellets ( $3.175 \times 3.175 \text{ mm}^2$  and purity of 99.99 at.%) were inserted into the holes by using pressure in such a way that they became part of the sputtering target. The number of gold pellet inserts were calculated to yield an estimated surface ratio at the eroded zone of 3-copper to 1-gold. This second target was used to grow copper–gold and copper–gold nitride samples.

The magnetron power (30 W), working distance (85 mm), deposition time (20 min) and argon flow (5 sccm,  $P_{\text{Ar}} = 0.157 \text{ Pa}$ ) were set constant for all deposits. The only variable consisted of increasing the nitrogen flow. The  $\text{Cu}_3\text{Au}$  film was free of nitrogen flow. There was no intentional heating, so the substrate rise in temperature was only due to the deposition process itself and the temperature never got higher than  $70^\circ\text{C}$ . Before the deposition, the glass substrates were cleaned by ultrasonic waves in acetone and dried by blowing air. Before each deposition, the target was pre-sputtered for 5 min not only to remove the oxidized surface layer, but also to remove the contaminated layer from the previous deposition and to maintain compositional stability during film growth.

Once the depositions were finished, they were analyzed *in situ* by XPS (X-ray Photoelectron Spectroscopy) using a cylindrical analyzer of double-pass, 255GAR from PHI-548. XPS data were collected using a non-monochromatic Al  $K\alpha$  line at 1486.6 eV. The energy scale was calibrated by means of the reference binding energy of  $\text{Cu}2p_{3/2}$  at 932.67 eV and  $\text{Cu}3p_{3/2}$  at 75.14 eV. X-ray diffractograms were taken from thin films using the Bragg–Brentano configuration, where the samples were scanned at  $2\theta$  from  $20^\circ$  to  $80^\circ$ , with a Cu  $K\alpha$  line (Philips X'Pert). Electrical properties were obtained using the Van der Pauw method [8], in an ECOPIA instrument, model HMS-5000. The optical properties of the films were determined by UV–VIS spectroscopy. The transmission spectra were recorded between the range of 400–2500 nm region using a Perkin Elmer Lambda 12 Spectrophotometer.

## 2.2. Calculations

The calculations were performed employing the full potential linearized augmented plane wave (FP-LAPW) method [9] as implemented in the WIEN2k code [10] using the density functional theory (DFT) [11,12]. With this method, the unit cell is divided into non-overlapping muffin-tin spheres and interstitial regions. The Kohn–Sham wave functions and crystal potentials are expanded in spherical harmonics inside muffin-tin spheres and with the interstitial region as a plane wave expansion. The exchange and correlations of the electronic energies were calculated with the generalized gradient approximation (GGA) of Perdew et al. [13]. The parameters and corresponding values that we used were; the separation energy between the valence and core states which was set at  $-6.0 \text{ Ry}$ , the angular momentum to expand the wave function inside the atomic spheres and the plane wave expansion in the interstitial region which was set at  $l_{\text{max}} = 10$ , the plane wave cut-off defined by the product of the smallest atomic sphere radius times the magnitude of the largest reciprocal-lattice vector in the modified plane wave expansion which was set at  $\text{RKmax} = 7.0$ . The energy convergence criterion was set to  $0.1 \text{ mRy}$ , with a parameter of densities mixture of 0.2. We have chosen the muffin-tin radii values as 1.4, 2.0 and 2.0 bohr for nitrogen, copper and gold respectively. We used the special k-point sampling scheme that has  $10 \times 10 \times 10$  grid. Additionally, we studied the stabilities of the  $\text{Cu}_3\text{Au}_{0.5}\text{N}_x$  and  $\text{Cu}_3\text{AuN}_x$  systems. These calculations were done for a  $2 \times 2 \times 2$  supercell formed by  $\text{Cu}_{24}\text{Au}_4\text{N}_{x=0-8}$  and  $\text{Cu}_{24}\text{Au}_8\text{N}_{x=0-8}$  that were eight times the original cell. The space group was P-43m (215), which is a reduced-symmetry subgroup of Pm3m (Table 1). For these calculations, we introduced 1–8 nitrogen atoms per cell of the  $\text{Cu}_{24}\text{Au}_8$  and  $\text{Cu}_{24}\text{Au}_4$  alloys. We calculated the formation energy according to the following formula as defined in Refs. [9,14].

$$E^f = \left( E_{\text{Cu}_3\text{Au}_{0.5}\text{N}_x}^{\text{tot}} - nE_{\text{Cu-bulk}}^{\text{tot}} - oE_{\text{Au-bulk}}^{\text{tot}} - m \frac{1}{2} E_{\text{N}_2}^{\text{tot}} \right) / (n + o + m) \quad (1)$$

$$E^f = \left( E_{\text{Cu}_3\text{AuN}_x}^{\text{tot}} - nE_{\text{Cu-bulk}}^{\text{tot}} - oE_{\text{Au-bulk}}^{\text{tot}} - m \frac{1}{2} E_{\text{N}_2}^{\text{tot}} \right) / (n + o + m) \quad (2)$$

where  $n$  and  $o$  are the number of metal atoms and  $m$  is the number of nonmetal atoms used in the supercell made up of  $\text{Cu}_3\text{Au}_{0.5}\text{N}_x$ ,  $\text{Cu}_3\text{AuN}_x$ ,  $E_{\text{Cu}_3\text{Au}_{0.5}\text{N}_x}^{\text{tot}}$ ,  $E_{\text{Cu}_3\text{AuN}_x}^{\text{tot}}$  = energies for copper gold nitride compounds,  $E_{\text{Au-bulk}}^{\text{tot}}$  = bulk gold cell,  $E_{\text{Cu-bulk}}^{\text{tot}}$  = bulk copper cell, and  $E_{\text{N}_2}^{\text{tot}}$  = free nitrogen molecule.

## 3. Results and discussion

The aim of this research was to study the formation of copper–gold nitrides in an effort to produce an ordered  $\text{Cu}_3\text{AuN}$  compound. For this purpose, we divided the study in three stages. The first was focused on the formation of stoichiometric copper nitride ( $\text{Cu}_3\text{N}$ ). The second on the formation of stoichiometric  $\text{Cu}_3\text{Au}$ ; for this stage the variable was the number of gold pellets in the copper target at the eroded zone. The third stage was the formation of the  $\text{Cu}_3\text{AuN}$  compound as a function of nitrogen partial pressure in the growth

chamber. The results of quantitative XPS for all stages are listed in Table 2 and the binding energies in Table 3.

### 3.1. Deposition of $\text{Cu}_3\text{N}$ films

The formation of  $\text{Cu}_3\text{N}$  by magnetron sputtering has been thoroughly investigated by several researchers [6,15–17]. This subsection will briefly describe the conditions for  $\text{Cu}_3\text{N}$  growth in our setup. At 4 sccm of nitrogen flow, and total pressure of 20 mTorr, the quantitative XPS analysis gave  $\text{Cu}_{2.99}\text{N}_{1.01}$  (Table 2), which is within the experimental uncertainty to the ideal  $\text{Cu}_3\text{N}$  stoichiometry. Fig. 1(c) and (d) (middle panels) shows the  $\text{Cu}2p_{3/2}$  and  $\text{N}1s$  photoemission peaks of copper nitride. These peaks were centered at 934.2 eV and 398.7 eV for  $\text{Cu}2p_{3/2}$  and  $\text{N}1s$  respectively, and are attributed to Cu–N bonds in  $\text{Cu}_3\text{N}$ , which correspond to the reported values for  $\text{Cu}_3\text{N}$  [7,18–20]. Fig. 2(b) shows the XRD pattern of the  $\text{Cu}_3\text{N}$  film. The main peak position agrees with the Powder Diffraction File (PDF) #47-1088. From the XRD and XPS data we conclude that  $\text{Cu}_3\text{N}$  was deposited with [1 1 1] preferential orientation. This is in agreement with previous works which state that films grow along the preferential direction [1 1 1] for low  $\text{N}_2$  flow rates or low  $\text{N}_2$  partial pressure [21–26].

### 3.2. Deposition of $\text{Cu}_3\text{Au}$ films

The formation of  $\text{Cu}_3\text{Au}$  has also been thoroughly investigated in bulk samples [27,28]; however, for thin films the method presented here seems to be unusual. In a first attempt, the target was modified to a 3:1 copper to gold area at the eroded zone. The quantitative XPS analysis gave exactly  $\text{Cu}_3\text{Au}$ , (Table 2). The binding energies of  $\text{Cu}2p_{3/2}$  and  $\text{Au}4f_{7/2}$  were 932.5 and 84.5 eV, respectively, which were in the range of metallic alloy. Both peaks exhibit a symmetric shape, suggesting the absence of agglomerations of Cu or Au atoms (see Fig. 1(a) and (b)). Fig. 2(a) shows the XRD pattern of the  $\text{Cu}_3\text{Au}$  film. This film showed the same pattern of the  $\text{Cu}_3\text{Au}$  phase, according to PDF #35-1357. Its diffraction peaks come from the (2 2 0), (2 0 0) and (1 1 1) reflections. No secondary phases of Cu, Au,  $\text{CuAu}$  or  $\text{CuAu}_3$  were identified in that sample. The preferential orientation of the  $\text{Cu}_3\text{Au}$  thin film was in the [1 1 1] direction. The evidence showed the formation of the  $\text{Cu}_3\text{Au}$  alloys: the target had the correct composition so it was utilizable to test the preparation of a ternary  $\text{Cu}_3\text{AuN}$  compound.

### 3.3. Deposition of $\text{Cu}_3\text{Au}_x\text{N}_y$ films

This subsection describes the results of the thin films produced by sputtering in an atmosphere of molecular nitrogen using the modified Cu–Au target. It was projected that nitrogen would be integrated into the film by reactive sputtering, while the ratio between Cu and Au would be maintained. This series (Sample a to d) was prepared with the Ar flow rate fixed at 5 sccm, while the  $\text{N}_2$  flow was varied between 3 and 6 sccm. Table 2 lists the composition determined by XPS of this series. The Cu concentration is close to 60 at.%, Au varies from 14.3 up to 16.5 at.%, and N goes from 23.0 to 25.3 at.%. Clearly, the initial guess was not correct: the Cu/Au ratio was affected by nitrogen incorporation. However, nitrogen flow and composition showed no obvious correlation. Quantitative analysis revealed that although nitrogen flow changes, the concentration was similar for the samples. Similarly, the core-level binding energies determined by XPS (Table 3) remained virtually unaffected by variations in the nitrogen flow. The reason for this may be that the film was being grown in the saturation region of nitrogen. A detailed understanding of chemical bonding can be obtained by adjusting the XPS peaks with Gaussian functions, as it is seen in Fig. 1. The upper panel corresponds to  $\text{Cu}_3\text{Au}$ ; with  $\text{Cu}2p_{3/2}$  at 932.5 eV, and  $\text{Au}4f_{7/2}$  at 84.5 eV. The

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