

Article

# AACVD of Cu<sub>3</sub>N on Al<sub>2</sub>O<sub>3</sub> Using CuCl<sub>2</sub> and NH<sub>3</sub>

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**Abstract:** Cu<sub>3</sub>N has been grown on m-Al<sub>2</sub>O<sub>3</sub> by aerosol-assisted chemical vapor deposition using 0.1 M CuCl<sub>2</sub> in CH<sub>3</sub>CH<sub>2</sub>OH under an excess of NH<sub>3</sub> at 600 °C, which led to the deposition of Cu that was subsequently converted into Cu<sub>3</sub>N under NH<sub>3</sub>: O<sub>2</sub> at 400 °C in a two-step process without exposure to the ambient. The reaction of CuCl<sub>2</sub> with an excess of NH<sub>3</sub> did not lead to the growth of Cu<sub>3</sub>N, which is different to the case of halide vapor phase epitaxy of III-V semiconductors. The Cu<sub>3</sub>N layers obtained in this way had an anti-ReO<sub>3</sub> cubic crystal structure with a lattice constant of 3.8 Å and were found to be persistently n-type, with a room temperature carrier density of  $n = 2 \times 10^{16} \text{ cm}^{-3}$  and mobility of  $\mu_n = 32 \text{ cm}^2/\text{Vs}$ . The surface depletion, calculated in the effective mass approximation, was found to extend over  $\sim 0.15 \mu\text{m}$  by considering a surface barrier height of  $\phi_B = 0.4 \text{ eV}$  related to the formation of native Cu<sub>2</sub>O.

**Keywords:** copper nitride; chemical vapor deposition; structural; electrical properties

## 1. Introduction

Cu<sub>3</sub>N is a novel semiconductor in which crystal imperfections such as Cu interstitials (Cu<sub>i</sub>) and nitrogen vacancies (V<sub>N</sub>) give rise to states that are energetically located inside or very close to the conduction and valence bands, respectively [1], but do not give rise to any mid-gap states. Consequently, it has been suggested to be suitable as a solar cell absorber in view of the fact that it has an indirect energy band gap of  $\sim 1.0 \text{ eV}$  [2], but also due to the fact that n- and p-type doping are possible. However, despite the fact that Cu<sub>3</sub>N has been described as a defect-tolerant semiconductor, so far no one has fabricated a working p-n junction solar cell using Cu<sub>3</sub>N. In the past, Chen et al. [3] fabricated a Cu<sub>3</sub>N p-n homojunction on indium tin oxide, and Yee et al. [1] fabricated an Al: ZnO/ZnS/Cu<sub>3</sub>N p-n heterojunction, both of which exhibited rectifying behavior but no photogenerated current. This has been attributed to the large concentration of Cu<sub>i</sub> defects, which capture electrons and result into substantial Shockley–Read–Hall recombination and quenching of the steady-state minority carrier concentration under illumination. In other words, crystal imperfections such as V<sub>N</sub> and Cu<sub>i</sub> can still reduce the minority carrier lifetime and prevent the extraction of photogenerated electron–hole pairs in Cu<sub>3</sub>N. Nevertheless, Cu<sub>3</sub>N has been used successfully for energy storage as it has a cubic anti-ReO<sub>3</sub> crystal structure, belonging to the Pm3m space group (number 221) with a lattice constant of 3.8 Å [4], and a vacant body center that can readily act as a host for Li ions in batteries [5]. Cu<sub>3</sub>N has been obtained by many different methods including reactive sputtering [6], molecular beam epitaxy [7], atomic layer deposition [8,9] and pulsed laser deposition [10,11]. Recently, we converted Cu into Cu<sub>3</sub>N under NH<sub>3</sub>: O<sub>2</sub> between 400 °C and 600 °C, and observed distinct spectral features and maxima in differential transmission at 500 nm ( $\equiv 2.48 \text{ eV}$ ), 550 nm ( $\equiv 2.25 \text{ eV}$ ), 630 nm ( $\equiv 1.97 \text{ eV}$ ) and 670 nm ( $\equiv 1.85 \text{ eV}$ ) on a ps time scale by ultrafast pump–probe spectroscopy (UPPS) [12]. These correspond to the M and R direct energy band gaps of bulk-relaxed and strained Cu<sub>3</sub>N in excellent agreement with density functional theory (DFT) calculations of the electronic band structure [12]. This observation of the M and R direct energy band gaps in fact confirmed that Cu<sub>3</sub>N has a clean energy band gap. More recently, we also showed that iodine-doped Cu<sub>3</sub>N, i.e., I: Cu<sub>3</sub>N, is a p-type semiconductor and that



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the extensive incorporation of I in  $\text{Cu}_3\text{N}$  can be used to convert  $\text{Cu}_3\text{N}$  into  $\gamma\text{-CuI}$ , which is a p-type transparent semiconductor that was used in conjunction with n-type  $\text{Cu}_3\text{N}$ , for the fabrication of a  $\gamma\text{-CuI/TiO}_2/\text{Cu}_3\text{N}$  p-n heterojunction that exhibited rectifying current–voltage characteristics [13]. In the past, most have focused on n-type doping of  $\text{Cu}_3\text{N}$ , such as Gao et al. [14], who showed that the incorporation of Zn resulted into n-type  $\text{Cu}_3\text{N}$  and increased the carrier density from  $n = 10^{17}$  to  $10^{21} \text{ cm}^{-3}$  with a resistivity of  $10^{-3} \Omega \text{ cm}$ . In contrast, only a few have considered p-type doping of  $\text{Cu}_3\text{N}$ , such as Matsuzaki et al. [15], who used  $\text{NF}_3$  for the growth of F-doped p-type  $\text{Cu}_3\text{N}$ . The ability to obtain p-type  $\text{Cu}_3\text{N}$  is important, of course, for the realization of p-n junctions, but it should be noted that I-VII  $\gamma$ -cuprous halides such as  $\gamma\text{-CuCl}$ ,  $\text{CuBr}$  and  $\text{CuI}$  are p-type transparent semiconductors with a zinc blende crystal structure and direct energy band-gaps of 3.3, 2.9 and 2.95 eV, respectively. In addition, they have lattice constants close to that of Si [16] and may be readily combined with  $\text{Cu}_3\text{N}$  for the realization of novel cuprous electronic and optoelectronic devices.

Here  $\text{Cu}_3\text{N}$  has been obtained by aerosol-assisted chemical vapor deposition (AACVD) using  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{NH}_3$ . AACVD is a low-cost growth method [17] that has been used for the growth of a broad range of semiconductors [18] including III-V semiconductors such as  $\text{InN}$ ,  $\text{GaN}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  [19]. The growth of these III-Vs is carried out using anhydrous  $\text{N}_2$  and  $\text{NH}_3$ , i.e.,  $\text{O}_2$  and  $\text{H}_2\text{O}$  are generally avoided and eliminated. In the past, McInnes et al. [19] used 0.1M  $\text{GaCl}_3$  and 0.1M  $\text{InCl}_3$  in acetonitrile ( $\text{CH}_3\text{CN}$ ),  $\text{N}_2$  as carrier gas and anhydrous  $\text{NH}_3$  to grow  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . The total flow rate through the 0.1 M  $\text{GaCl}_3$  and 0.1 M  $\text{InCl}_3$  solutions was maintained at  $529 \text{ mL min}^{-1}$ , and anhydrous  $\text{NH}_3$  was used at a high flow rate of  $862 \text{ mL min}^{-1}$ , which assisted in promoting the formation of smaller droplets whilst also ensuring an excess of  $\text{NH}_3$  for the deposition of  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . The deposition was carried out at  $600 \text{ }^\circ\text{C}$ , which exceeds the melting point of both  $\text{GaCl}_3$  and  $\text{InCl}_3$  and gave layers with a thickness of  $\sim 2 \mu\text{m}$ . Both  $\text{GaCl}_3$  and  $\text{InCl}_3$  react directly with  $\text{NH}_3$ , leading to the deposition of  $\text{GaN}$  and  $\text{InN}$ , respectively, while  $\text{CH}_3\text{CN}$  [20] breaks into  $\text{HCN}$  and  $\text{CH}_4$  at elevated temperatures [21,22].

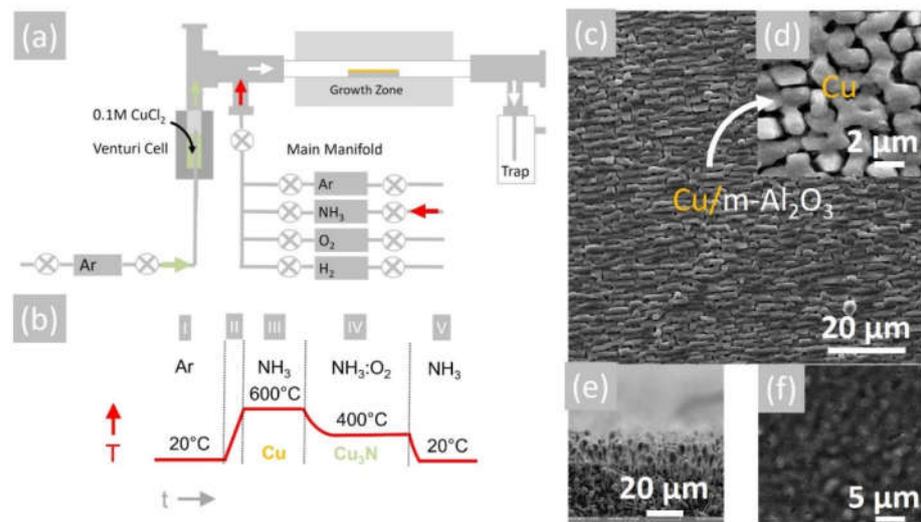
AACVD has also been used for the growth of  $\text{Cu}_3\text{N}$  by Yamaguchi et al. [23], who obtained  $\text{Cu}_3\text{N}$  on  $\alpha\text{-Al}_2\text{O}_3$  by AACVD at  $300 \text{ }^\circ\text{C}$  using copper (II) acetylacetonate  $\text{Cu}(\text{O}_2\text{C}_5\text{H}_7)_2$  that was dissolved in aqueous  $\text{NH}_3$ . No  $\text{CuO}$  or  $\text{Cu}_2\text{O}$  was detected in the  $\text{Cu}_3\text{N}$  despite the fact that  $\text{Cu}(\text{O}_2\text{C}_5\text{H}_7)_2$  was used in aqueous  $\text{NH}_3$ . Others such as Park et al. [8] used metal organic sources of copper such as  $\text{C}_{14}\text{H}_{32}\text{CuN}_2\text{O}_2$ , which contains oxygen in conjunction with  $\text{NH}_3$  for the atomic layer deposition of  $\text{Cu}_3\text{N}$ , but metal organic sources are expensive [9].

No one has previously attempted to grow  $\text{Cu}_3\text{N}$  using  $\text{CuCl}_2$  and  $\text{NH}_3$  by AACVD or tried to grow  $\text{Cu}_3\text{N}$  on  $m\text{-Al}_2\text{O}_3$ , which is ideally suited for the growth of cubic and tetragonal crystals. It is found that the reaction of  $\text{CuCl}_2$  with  $\text{NH}_3$  will not give  $\text{Cu}_3\text{N}$  as in the case of halide vapor phase epitaxy (HVPE) of III-V semiconductors such as  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . In contrast, the reaction of  $\text{CuCl}_2$  with an excess of  $\text{NH}_3$  resulted into the deposition of polycrystalline Cu layers consisting of oriented grains on  $m\text{-Al}_2\text{O}_3$ , which have a higher crystal quality compared to Cu obtained by sputtering [12] or electron beam evaporation [15] used previously to obtain  $\text{Cu}_3\text{N}$  under  $\text{NH}_3: \text{O}_2$ . Consequently, the Cu layers on  $m\text{-Al}_2\text{O}_3$  obtained via the reduction of  $\text{CuCl}_2$  under  $\text{NH}_3$  at elevated temperatures were converted into cubic  $\text{Cu}_3\text{N}$  under  $\text{NH}_3: \text{O}_2$  at a lower temperature without exposure of the Cu to the ambient. The  $\text{Cu}_3\text{N}$  layers on  $m\text{-Al}_2\text{O}_3$  have an anti- $\text{ReO}_3$  cubic crystal structure with a lattice constant of  $3.8 \text{ \AA}$  and are n-type with carrier density  $n = 2 \times 10^{16} \text{ cm}^{-3}$  and mobility  $\mu_n = 32 \text{ cm}^2/\text{Vs}$  at room temperature. The electrical properties are described in conjunction with theoretical calculations of the conduction band potential profile, surface band bending and depletion in the effective mass approximation.

## 2. Materials and Methods

Initially, 1.34 mg of  $\text{CuCl}_2$  (Aldrich 99.999%,  $134.45 \text{ gmol}^{-1}$ ), which has a rusty-brown color, was dissolved in 100 mL ethanol  $\text{CH}_3\text{CH}_2\text{OH}$  and stirred at 1000 rpm for 10 min

at room temperature.  $\text{CuCl}_2$  is soluble in water (75 g/100 mL  $\text{H}_2\text{O}$  at 25 °C) and ethanol (53 g/100 mL  $\text{CH}_3\text{CH}_2\text{OH}$  at 25 °C) but less so in acetonitrile  $\text{CH}_3\text{CN}$  (1.6 g/100 mL at 20 °C). In contrast,  $\text{CuCl}$  has a considerably lesser solubility than that of  $\text{CuCl}_2$ . More specifically,  $\text{CuCl}$  is slightly soluble in water (0.0047 g/100 mL  $\text{H}_2\text{O}$  at 20 °C) and insoluble in ethanol  $\text{CH}_3\text{CH}_2\text{OH}$  and acetone  $(\text{CH}_3)_2\text{CO}$ . In order to obtain a satisfactory growth rate, a 0.1 M solution of  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  was prepared that has a dark green color due to the  $(\text{CuCl}_4)^{2-}$  ions that are yellow and  $\text{Cu}^{+2}$  ions that are blue. The 0.1 M  $\text{CuCl}_2$  liquid precursor was turned into a mist using a Venturi nebulizer and Ar as a carrier gas. Square samples of  $\sim 8 \text{ mm} \times 8 \text{ mm}$  m- $\text{Al}_2\text{O}_3$  with a thickness of  $\sim 0.3 \text{ mm}$  were cleaned sequentially in trichloroethylene, methanol, acetone and isopropanol at 80 °C, after which they were rinsed in deionized water at 20 °C and dried with nitrogen, followed by a dehydration bake at 120 °C. The clean m- $\text{Al}_2\text{O}_3$  was loaded in a quartz boat that was positioned at the center of a 1" hot wall, single zone AACVD reactor, capable of reaching 1100 °C that was fed by a manifold consisting of four mass flow controllers connected to Ar,  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{H}_2$  and a separate side manifold for controlling the flow of Ar through the Venturi nebulizer, as shown in Figure 1a. The reactor was purged with 1000 mL/min of Ar for 10 min from the main manifold, after which the temperature was ramped at 30 °C/min under a flow of 90 mL/min Ar: 10 mL/min  $\text{H}_2$  at one atmosphere. Upon reaching 600 °C, the flow of Ar:  $\text{H}_2$  was interrupted and a flow of 800 mL/min  $\text{NH}_3$  was initiated, while at the same time a flow of 1000 mL/min Ar was established through the nebulizer. A visible flow of the aerosol was observed on the upstream side that was maintained for 30 min. Subsequently, the flow of Ar through the Venturi nebulizer was interrupted and the reactor allowed to cool down to 400 °C under a flow of 300 mL  $\text{min}^{-1}$   $\text{NH}_3$ . Upon reaching 400 °C, the Cu was converted into  $\text{Cu}_3\text{N}$  under a flow of 300 mL  $\text{min}^{-1}$   $\text{NH}_3$  and 15 mL  $\text{min}^{-1}$   $\text{O}_2$  for 30 min. At the end of the growth period, cool down took place under a flow of 300 mL/min  $\text{NH}_3$  supplied from the main manifold until the temperature fell below 100 °C. A typical temperature–time profile is shown in Figure 1b. The  $\text{Cu}_3\text{N}$  layers were removed after purging with 1000 mL  $\text{min}^{-1}$  of Ar at room temperature and were stored in a desiccator under vacuum.



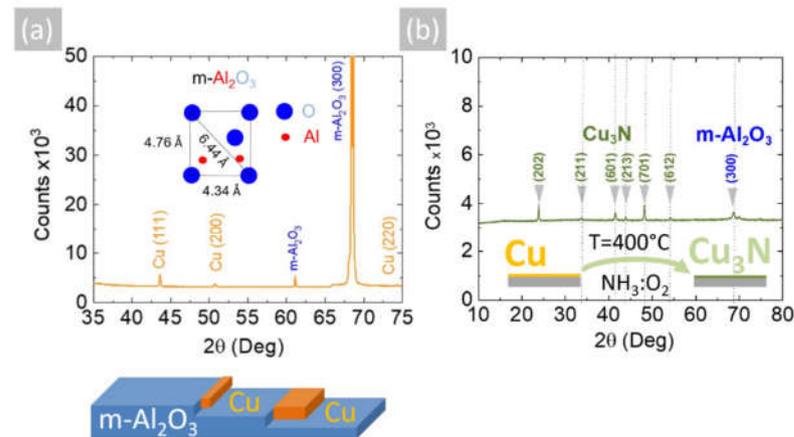
**Figure 1.** (a) Schematic of 1" AACVD hot wall-reactor; (b) temperature–time profile for the deposition of Cu and conversion to  $\text{Cu}_3\text{N}$  (c); (d) SEM image of Cu on m- $\text{Al}_2\text{O}_3$  obtained at 600 °C showing ordering of the grains; (e) side view of SEM image of Cu on m- $\text{Al}_2\text{O}_3$  obtained at 600 °C showing columnar growth; (f) SEM image of  $\text{Cu}_3\text{N}$  obtained from Cu under  $\text{NH}_3$ :  $\text{O}_2$  at 400 °C.

The morphology and crystal structure of the  $\text{Cu}_3\text{N}$  layers were determined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The carrier density and mobility of the  $\text{Cu}_3\text{N}$  layers were determined by the Hall effect in the van der Pauw configuration

by using a Keithley 2635A constant current source in conjunction with a Keithley 2182 voltmeter controlled by LabView.

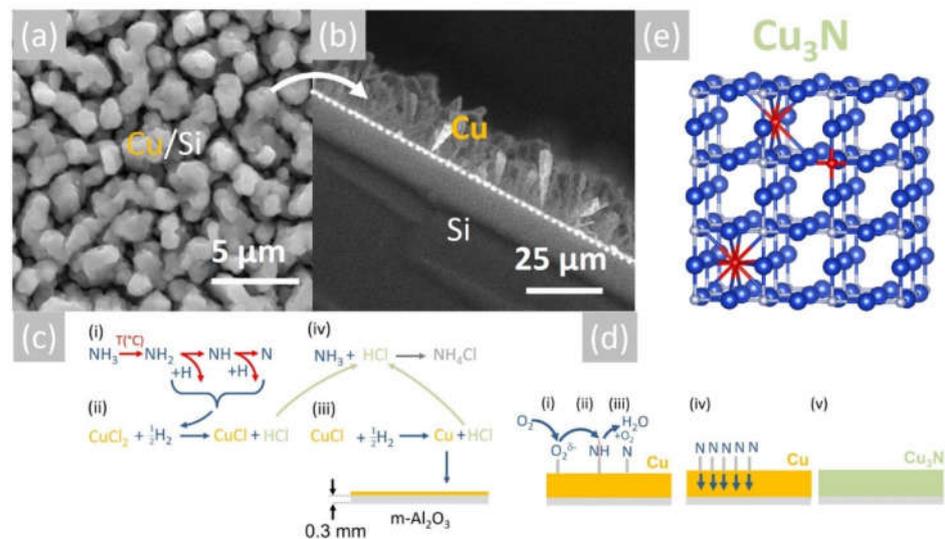
### 3. Results and Discussion

The reaction of  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  with an excess of  $\text{NH}_3$  did not lead to the direct deposition of  $\text{Cu}_3\text{N}$ , as in the case of HVPE of III-V semiconductors such as  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , but resulted into the deposition of metallic Cu on  $m\text{-Al}_2\text{O}_3$  that had a shiny, reflective surface and metallic conductivity. A typical SEM image of the Cu layer obtained on  $m\text{-Al}_2\text{O}_3$  at  $600^\circ\text{C}$  is shown in Figure 1c, from which one may observe that the Cu layer is polycrystalline and consists of grains oriented along a single direction. A higher magnification image is also shown in Figure 1d, from which it is evident that the grains have sizes of  $\sim 5\ \mu\text{m}$ , while a side view of the Cu on  $m\text{-Al}_2\text{O}_3$  is shown in Figure 1e, showing that columnar growth occurs. The epitaxial growth of Cu on  $c\text{-Al}_2\text{O}_3$  and  $a\text{-Al}_2\text{O}_3$  has been investigated extensively for the growth of high-quality graphene [24,25], but only a few have considered the growth of Cu on  $m\text{-Al}_2\text{O}_3$  [26]. The deposition of Cu on  $m\text{-Al}_2\text{O}_3$ , which contains grooves or steps along specific crystallographic directions, as shown in Figure 2a, will lead to instabilities and ruptures of the Cu layer at elevated temperatures [27]. These ruptures occur at high curvature sites, i.e., peaks and ridges, which act as retracting edges leading to a net flux of atoms away from the high positive curvature regions. For sufficiently thin layers, this process will lead to a self-assembly of the Cu grains along a specific direction [28].



**Figure 2.** (a) XRD of Cu on  $m\text{-Al}_2\text{O}_3$  obtained at  $600^\circ\text{C}$  showing peaks belonging to Cu and  $m\text{-Al}_2\text{O}_3$ ; inset shows the oxygen-terminated surface of  $m\text{-Al}_2\text{O}_3$ ; (b) XRD of  $\text{Cu}_3\text{N}$  obtained from Cu under  $\text{NH}_3:\text{O}_2$  at  $400^\circ\text{C}$  showing the peaks belonging to the anti- $\text{ReO}_3$  cubic crystal structure of  $\text{Cu}_3\text{N}$  and  $m\text{-Al}_2\text{O}_3$ .

The Cu layers exhibited clear peaks in the XRD, as shown in Figure 2a, corresponding to the face-centered cubic (fcc) crystal structure of Cu with a lattice constant of  $3.6\ \text{\AA}$ . No peaks belonging to  $\text{CuO}$ ,  $\text{Cu}_4\text{O}_3$  or  $\text{Cu}_2\text{O}$  are observed in Figure 2a. Likewise shown are the peaks corresponding to the underlying  $m\text{-Al}_2\text{O}_3$ , which has an oxygen-terminated surface with tetragonal crystal symmetry that is suitable for the epitaxial growth of semiconductors with a cubic crystal structure. It is worthwhile to point out that the deposition of Cu on  $n\text{-type Si (001)}$  resulted in columnar growth, as shown in Figure 3a,b. The Cu pillars have a height of  $\sim 20\ \mu\text{m}$ , but they are not ordered in any way. No  $\text{Cu}_3\text{N}$  was obtained under an excess of  $\text{NH}_3$  by varying the temperature between  $300^\circ\text{C}$  and  $800^\circ\text{C}$ . Instead, the reaction of  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  with  $\text{NH}_3$  always led to the deposition of Cu on  $m\text{-Al}_2\text{O}_3$ , which occurs via the reduction of  $\text{CuCl}_2$  to  $\text{CuCl}$  and then into Cu by the  $\text{H}_2$  evolving from  $\text{NH}_3$ .

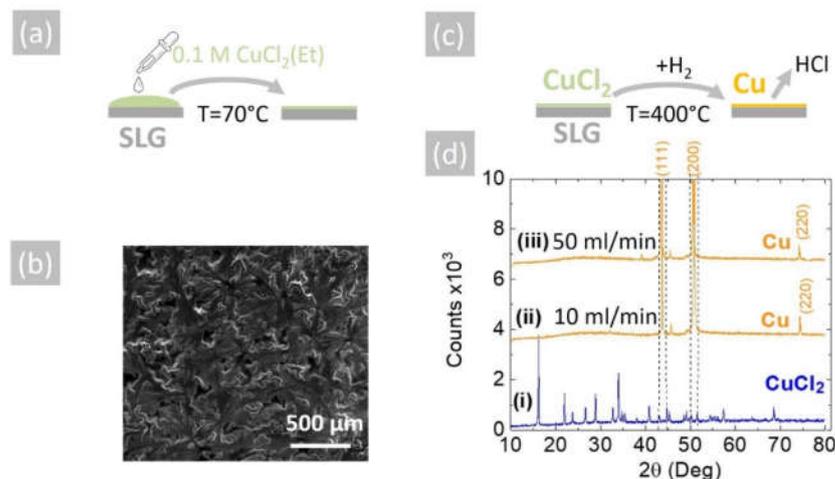


**Figure 3.** (a) SEM image of Cu on Si obtained at 600 °C and (b) section showing the formation of Cu rods on Si; (c) reaction mechanism for the deposition of Cu and (d) reaction mechanism for the conversion of Cu into  $\text{Cu}_3\text{N}$  obtained under  $\text{NH}_3$ :  $\text{O}_2$ ; (e) stick and ball model of the anti- $\text{ReO}_3$  cubic crystal structure of  $\text{Cu}_3\text{N}$ ; large blue spheres (Cu), small grey spheres (N) and red spheres (O).

More specifically, the 0.1 M solution of  $\text{CuCl}_2$  is initially converted into a mist of liquid drops and mixed with  $\text{NH}_3$ , which is soluble in  $\text{CH}_3\text{CH}_2\text{OH}$  [29]. Subsequently, the liquid drops are vaporized at an elevated temperature, and the  $\text{CH}_3\text{CH}_2\text{OH}$  gives  $\text{C}_2\text{H}_4$  and  $\text{H}_2\text{O}$  according to the reaction  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ . No carbon is released from the pyrolysis of  $\text{C}_2\text{H}_4$  between 500 °C and 800 °C [30]. Upon vaporization,  $\text{CuCl}_2$ , which has a melting point of 498 °C, will be reduced to  $\text{CuCl}$ , which has an even lower melting point of 423 °C [31], and finally into metallic Cu by the  $\text{H}_2$  evolving from the breakdown of  $\text{NH}_3$ . Before elaborating further, it is useful to note that the thermal breakdown of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$  was investigated as early as 1905 by White et al. [32], who showed that it depends on the gas flow, i.e., residence time as well as the temperature. In particular, White et al. [32] showed that a flow of 200 mL/min  $\text{NH}_3$  resulted in a dissociation of 5%  $\text{NH}_3$  at 600 °C and 10% at 700 °C. However, the breakdown of  $\text{NH}_3$  is also promoted catalytically by the deposited Cu at elevated temperatures [33]. In other words, the Cu deposited on the  $m\text{-Al}_2\text{O}_3$  will participate actively in the dissociation of  $\text{NH}_3$  near the surface, thereby further promoting the reduction of  $\text{CuCl}_2$  and deposition of Cu, which has a melting point of 1085 °C. A schematic representation of the proposed reaction mechanism is shown in Figure 3c. For completeness, it must also be pointed out that the  $\text{NH}_3$  will react with  $\text{CH}_3\text{CH}_2\text{OH}$  and give ethylamine ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ) and acetonitrile ( $\text{CH}_3\text{CN}$ ), which have boiling points of 20 °C and 82 °C, respectively.  $\text{CH}_3\text{CH}_2\text{NH}_2$  and  $\text{CH}_3\text{CN}$  will dissociate into  $\text{HCN}$  and  $\text{CH}_4$  depending on the temperature and residence time, but they are not expected to influence the overall reaction governing the deposition of Cu. It is also important to mention that the Cu will tend to react with  $\text{H}_2\text{O}$  supplied from the  $\text{CH}_3\text{CH}_2\text{OH}$  and give  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ . However, no oxides are detected in Figure 2a, so it is very likely that they are reduced to metallic Cu due to the  $\text{H}_2$  evolving from the  $\text{NH}_3$  over the Cu. This is consistent with the findings of Kim et al. [34], who showed that  $\text{CuO}$  is converted into metallic Cu under an excess of  $\text{H}_2$  without the formation of intermediate  $\text{Cu}_4\text{O}_3$  or  $\text{Cu}_2\text{O}$ .

In short,  $\text{CuCl}_2$  is reduced to  $\text{CuCl}$  and then into Cu by the  $\text{H}_2$  evolving from  $\text{NH}_3$ , according to:  $\text{CuCl}_2 + \text{H}_2 \rightarrow \text{CuCl} + 2\text{HCl}$  and  $2\text{CuCl} + \text{H}_2 \rightarrow 2\text{Cu} + 2\text{HCl}$ . The  $\text{HCl}$  reacted in turn with the excess  $\text{NH}_3$ , giving  $\text{NH}_4\text{Cl}$ , i.e.,  $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ , which solidified below its sublimation temperature, i.e., ~340 °C near the cool end of the reactor, very similar to what occurs during conventional HVPE of III-Vs.

The reduction of  $\text{CuCl}_2$  into Cu may also be achieved by using  $\text{H}_2$  as opposed to  $\text{NH}_3$ . In order to show this, the 0.1 M solution of  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  was used to deposit a layer of  $\text{CuCl}_2$  on 15 mm  $\times$  30 mm soda lime glass (SLG) slides by drop-casting, as shown in Figure 4a. The  $\text{CuCl}_2$  layer had a light green color and good uniformity, and a typical SEM image is shown in Figure 4b. This was converted into Cu under a flow of (i) 10 and (ii) 50 mL.min<sup>-1</sup> pure  $\text{H}_2$  at 400 °C for 30 min, as shown schematically in Figure 4c. The  $\text{CuCl}_2$  as-deposited on SLG displayed a crystalline structure and multiple peaks in the XRD, as shown in Figure 4d, but all the peaks were eliminated after the reduction of the  $\text{CuCl}_2$  into Cu.



**Figure 4.** (a) Schematic illustration of drop-casting a 0.1 M  $\text{CuCl}_2$  (Et) solution on SLG at 70 °C to aid the evaporation of the ethanol; (b) SEM image of the  $\text{CuCl}_2$  on SLG, which had a light green color; (c) schematic of conversion of  $\text{CuCl}_2$  into Cu under  $\text{H}_2$  at 400 °C; (d) XRD of (i)  $\text{CuCl}_2$  as-deposited on SLG, (ii) Cu obtained from  $\text{CuCl}_2$  under 10 mL/min  $\text{H}_2$  and (iii) 50 mL/min  $\text{H}_2$ . All of the  $\text{CuCl}_2$  peaks vanish, and the peaks belonging to Cu do not overlap with those of  $\text{CuCl}_2$ , as shown with the aid of the broken vertical lines.

The Cu deposited on  $m\text{-Al}_2\text{O}_3$  at 600 °C by AACVD using  $\text{CuCl}_2$  and  $\text{NH}_3$  has a higher crystal quality compared to the Cu obtained by sputtering, which was nonetheless successfully converted into crystalline  $\text{Cu}_3\text{N}$  under a flow of 300 mL/min  $\text{NH}_3$  and 15 mL/min  $\text{O}_2$  between 400 °C and 600 °C, as shown previously [12]. The  $\text{Cu}_3\text{N}$  obtained in this way had an anti- $\text{ReO}_3$  cubic crystal structure, and we observed the M and R direct energy band gaps of  $\text{Cu}_3\text{N}$  by UPPS in excellent agreement with DFT calculations of the electronic structure, confirming that it has a clean energy gap [12]. Consequently, the polycrystalline Cu layer that was obtained by AACVD on  $m\text{-Al}_2\text{O}_3$  at 600 °C was converted into  $\text{Cu}_3\text{N}$  under a flow of 300 mL/min  $\text{NH}_3$  and 15 mL/min  $\text{O}_2$  at 400 °C. The  $\text{Cu}_3\text{N}$  had an olive-green-like color, and a typical SEM image of the  $\text{Cu}_3\text{N}$  layer on  $m\text{-Al}_2\text{O}_3$  is shown in Figure 1f. This exhibited peaks in the XRD, as shown in Figure 2b, corresponding to the anti- $\text{ReO}_3$  cubic crystal structure of  $\text{Cu}_3\text{N}$  with a lattice constant of 3.8 Å.

The reaction of Cu with  $\text{NH}_3$  containing  $\text{O}_2$  and the formation of  $\text{Cu}_3\text{N}$  can be understood by considering the catalytic oxidation of  $\text{NH}_3$  by  $\text{O}_2$  in the presence of a catalyst, e.g., Cu, Pt, etc., at elevated temperatures, as described by Carley et al. [35], who investigated the catalytic reactivity of Cu (110) metal surfaces with coadsorbed  $\text{NH}_3$  and  $\text{O}_2$ . More specifically, Carley et al. [35] proposed that the oxidation of  $\text{NH}_3$  leads to the formation of a stabilized N monolayer on the Cu metal surface, which in turn is responsible for the conversion of the bulk Cu layer into  $\text{Cu}_3\text{N}$ . It should be noted that the reaction of  $\text{NH}_3$  with  $\text{O}_2$  also gives  $\text{H}_2\text{O}$  according to the reaction  $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$ , which was observed to condense near the cool end of the reactor upon increasing the gas flow of  $\text{O}_2$ . The reaction mechanism of the conversion of Cu into  $\text{Cu}_3\text{N}$  is depicted schematically in Figure 3d. No  $\text{Cu}_3\text{N}$  was obtained from Cu by using only  $\text{NH}_3$ , in accordance with

Matsuzaki et al. [15]. Moreover, no CuO or Cu<sub>2</sub>O peaks are detected in Figure 2b, but Cu<sub>2</sub>O will nevertheless form as native oxide on the surface of the Cu<sub>3</sub>N upon exposure to the ambient, as we have shown previously by using Raman spectroscopy [36]. Before considering the electrical properties of the Cu<sub>3</sub>N layers, it is useful to point out that the reaction of CuCl<sub>2</sub> with a smaller flow of 100 mL/min NH<sub>3</sub> at 600 °C mainly led to the deposition of Cu<sub>2</sub>O, not Cu<sub>3</sub>N.

In order to measure the Hall effect, Ag ohmic contacts were deposited at the four corners of the Cu<sub>3</sub>N layers on m-Al<sub>2</sub>O<sub>3</sub>. It has been shown that Au, Ag and Cu in Cu<sub>3</sub>N give rise to a semiconductor-to-metal transition and remarkably constant electrical resistivity over a very broad range of temperatures [37]. Consequently Ag, Au and Cu may be used for the formation of ohmic contacts on Cu<sub>3</sub>N, and in the past, we have shown that Au and Ag deposited on n-type Cu<sub>3</sub>N results in the formation of contacts with linear IVs [13]. The Cu<sub>3</sub>N layers on m-Al<sub>2</sub>O<sub>3</sub> were found to be n-type and had room temperature carrier densities of  $2 \times 10^{16} \text{ cm}^{-3}$  with a maximum mobility of 32 cm<sup>2</sup>/Vs. The Cu<sub>3</sub>N layers are n-type as they are Cu-rich, but also due to the fact that oxygen may be included in the Cu<sub>3</sub>N by the preferential formation of interstitial oxygen (O<sub>i</sub>) that acts as donors, not as acceptors [36]. Furthermore, the Cu<sub>3</sub>N layers obtained here were found to be persistently n-type, and the carrier density and mobility did not exhibit any changes upon illumination with light of  $\lambda = 450 \text{ nm}$  under ambient conditions. In other words, the n-type Cu<sub>3</sub>N layers did not exhibit any photoconductivity, which may be attributed to recombination via Cu<sub>i</sub> and V<sub>N</sub> states, in accordance with Yee et al. [1].

It is worthwhile pointing out here that Matsuzaki et al. [15] showed that epitaxial Cu<sub>3</sub>N layers with a thickness of 25 nm on SrTiO<sub>3</sub> were p-type, due to the upward surface band bending mediated by the chemisorption of O<sub>2</sub><sup>−</sup>, but switched to n-type upon exposure to ultraviolet (UV) light and reverted back to p-type after terminating the irradiation. In contrast, they observed that the Cu<sub>3</sub>N layers remained n-type after exposure to UV light under vacuum, confirming that the adsorbed O<sub>2</sub><sup>−</sup> is responsible for the surface inversion observed under ambient conditions in air. However, the epitaxial Cu<sub>3</sub>N layers of Matsuzaki et al. [15] were found to be persistently n-type under ambient conditions, with a carrier density of the order of  $10^{14} \text{ cm}^{-3}$  and mobility of 100 cm<sup>2</sup>/Vs after annealing under NH<sub>3</sub> between 125 and 350 °C, suggesting a change in the composition of the surface and overall band bending. The Cu<sub>3</sub>N layers obtained here were found to be persistently n-type and had a room temperature carrier density of  $2 \times 10^{16} \text{ cm}^{-3}$ , perhaps due to the fact that after the conversion of Cu into Cu<sub>3</sub>N under NH<sub>3</sub>: O<sub>2</sub>, the flow of NH<sub>3</sub> was maintained for at least 30 min until the temperature fell well below 100 °C.

However, the properties of Cu<sub>3</sub>N layers with a thickness of a few tens of nm will depend strongly on the properties of the surface but also the properties of the underlying substrate that is often overlooked. The Cu<sub>3</sub>N layers obtained here are persistently n-type with a carrier density of  $2 \times 10^{16} \text{ cm}^{-3}$ , most likely due to the fact that the thickness of the Cu<sub>3</sub>N layers is greater than 1 μm, so it is bulk-like and will not be strongly influenced by properties of the surface or underlying m-Al<sub>2</sub>O<sub>3</sub>. In thermodynamic equilibrium, the Fermi level ( $E_F$ ) with respect to the conduction band minimum ( $E_C$ ) away from the surface and deep in the bulk is determined from:

$$n = N_C e^{-\frac{E_C - E_F}{kT}},$$

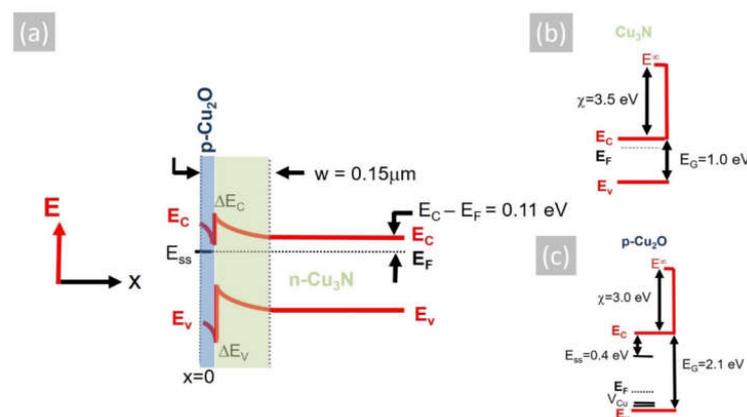
where  $N_C$  is the conduction band effective density of states,  $k$  is Boltzmann's constant and  $T$  the temperature taken to be equal  $T = 300 \text{ K}$ . The electron density is equal to  $n = 2 \times 10^{16} \text{ cm}^{-3}$ , and the conduction band effective density of states in Cu<sub>3</sub>N is given by:

$$N_C = 2 \left( \frac{2\pi m_n kT}{h^2} \right)^{\frac{3}{2}},$$

where  $m_n$  is the electron effective mass in  $\text{Cu}_3\text{N}$  taken to be  $m_n = 0.16 m_0$  [6],  $m_0$  is the free-electron mass and  $h$  is Planck's constant. This gives  $N_C = 1.6 \times 10^{24} \text{ m}^{-3}$  or  $1.6 \times 10^{18} \text{ cm}^{-3}$ , so  $E_C - E_F = 0.11 \text{ eV}$  in the bulk where a flat band condition exists. On the other hand, the energetic position of the Fermi level with respect to the conduction band edge, i.e.,  $E_C - E_F$ , at the surface is dependent on the local density and energetic position of any surface states that will be occupied by electrons, which in turn may pin the Fermi level at the surface. According to Navío et al. [38], the Fermi level at the surface of ultrathin  $\text{Cu}_3\text{N}$  layers is pinned at the middle of the gap, which will give rise to a barrier height of  $\phi_b = 0.5 \text{ eV}$ . The surface depletion region will extend into the  $\text{Cu}_3\text{N}$ , and the depletion width is:

$$w = \sqrt{\frac{2\epsilon_s \phi_b}{eN_D}},$$

where  $\epsilon_s = \epsilon_R \epsilon_0$ ,  $\epsilon_R$  is the static dielectric constant of  $\text{Cu}_3\text{N}$ ,  $\epsilon_0$  the permittivity of free space,  $e$  the electron charge and  $N_D$  the donor density taken to be equal to  $n = 2 \times 10^{16} \text{ cm}^{-3}$ . Considering that the static dielectric constant of  $\text{Cu}_3\text{N}$  is  $\epsilon_R \sim 10$  [39], the depletion width is found to be  $w = 0.16 \text{ }\mu\text{m}$ , taking into account that the Fermi level at the surface of  $\text{Cu}_3\text{N}$  layers is pinned at the middle of the gap, according to Navío et al. [38]. However, despite the fact that we did not detect any  $\text{CuO}$  or  $\text{Cu}_2\text{O}$  in the XRD, a thin layer of  $\text{Cu}_2\text{O}$  will exist on the surface of  $\text{Cu}_3\text{N}$ . According to Hodby et al. [40], the Fermi level at the surface of  $\text{Cu}_2\text{O}$  is pinned at states residing energetically in the upper half of the band gap  $\sim 0.4 \text{ eV}$  below the conduction band edge. The native  $\text{Cu}_2\text{O}$  layer of  $\text{Cu}_3\text{N}$  is expected to have a thickness of only a few nm and will be completely depleted, so the depletion width taking  $\phi_b = 0.4 \text{ eV}$  is found to be  $w = 0.15 \text{ }\mu\text{m}$ . The conduction band potential profile of the  $\text{Cu}_3\text{N}$  layer including the native  $\text{Cu}_2\text{O}$  layer at its surface is shown in Figure 5a, where the work function and electron affinity of  $\text{Cu}_3\text{N}$  i.e.,  $\phi(\text{Cu}_3\text{N}) = 5.0 \text{ eV}$  and  $\chi(\text{Cu}_3\text{N}) = 3.5 \text{ eV}$  [41] have been considered as well as the work function and electron affinity of  $\text{Cu}_2\text{O}$ , i.e.,  $\phi(\text{Cu}_2\text{O}) = 4.8 \text{ eV}$  and  $\chi(\text{Cu}_2\text{O}) = 3.2 \text{ eV}$  [42]. The formation of p-type  $\text{Cu}_2\text{O}$  over the n-type  $\text{Cu}_3\text{N}$  will lead to the confinement of photogenerated electron-hole pairs at the  $\text{Cu}_2\text{O}/\text{Cu}_3\text{N}$  heterojunction, which will inadvertently result into recombination via states at the interface, thereby suppressing the photoconductivity. This mechanism is different to that put forward by Yee et al. [1], who fabricated an Al:  $\text{ZnO}/\text{ZnS}/\text{Cu}_3\text{N}$  p-n heterojunction that exhibited rectifying behavior but no photogenerated current, which was attributed to the large concentration of  $\text{Cu}_i$  defects that capture electrons and result in substantial Shockley-Read-Hall recombination and quenching of the steady-state minority carrier concentration under illumination. While it is possible that both mechanisms are responsible for the suppression of the photocurrent and photoconductivity in  $\text{Cu}_3\text{N}$ , it is imperative that the surface recombination should be suppressed via the deposition of suitable layers that prevent the formation of  $\text{Cu}_2\text{O}$  that was originally suggested to act as a suitable passivation layer for  $\text{Cu}_3\text{N}$ , similar to that of  $\text{SiO}_2$  for Si p-n junction solar cells [2].



**Figure 5.** (a) Energy band potential profile of a  $\text{Cu}_2\text{O}/\text{Cu}_3\text{N}$  p-n heterojunction consisting of n-type  $\text{Cu}_3\text{N}$  and the native, surface p-type  $\text{Cu}_2\text{O}$ , where the Fermi level ( $E_F$ ) is pinned at the surface states

( $E_{ss}$ ) residing  $\sim 0.4$  eV below the conduction band edge of  $\text{Cu}_2\text{O}$ ; also shown are the conduction ( $\Delta E_C$ ) and valence ( $\Delta E_V$ ) band discontinuities as well as the surface depletion  $w$  that extends 0.15  $\mu\text{m}$  through the p-type  $\text{Cu}_2\text{O}$  and into the n-type  $\text{Cu}_3\text{N}$ . (b) Energy band diagram of n-type  $\text{Cu}_3\text{N}$  showing the conduction ( $E_C$ ) and valence ( $E_V$ ) bands as well as the Fermi level ( $E_F$ ) and electron affinity ( $\chi$ ) of  $\text{Cu}_3\text{N}$ , (c) same for  $\text{Cu}_2\text{O}$ ; also shown are the ( $V_{Cu}$ ) acceptor states, which reside above the top of the valence band, and the energetic position of the surface states ( $E_{ss}$ ).

#### 4. Conclusions

$\text{Cu}_3\text{N}$  layers have been grown on m- $\text{Al}_2\text{O}_3$  by aerosol-assisted chemical vapor deposition using 0.1 M  $\text{CuCl}_2$  in  $\text{CH}_3\text{CH}_2\text{OH}$  under an excess of  $\text{NH}_3$  at 600 °C, which resulted in the deposition of epitaxial Cu layers consisting of oriented grains with a face-centered cubic crystal structure that were subsequently converted into  $\text{Cu}_3\text{N}$  under  $\text{NH}_3$ :  $\text{O}_2$  at 400 °C in a two-step process without exposure to the ambient. The reaction of  $\text{CuCl}_2$  with an excess of  $\text{NH}_3$  did not give  $\text{Cu}_3\text{N}$ , which is different to halide vapor phase epitaxy of III-V semiconductors such as  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . The  $\text{Cu}_3\text{N}$  layers obtained in this way have an anti- $\text{ReO}_3$  cubic crystal structure and persistent room temperature carrier density of  $n = 2 \times 10^{16} \text{ cm}^{-3}$  and mobility of  $\mu_n = 32 \text{ cm}^2/\text{Vs}$ , but they did not exhibit any photoconductivity due to recombination via surface states in the  $\text{Cu}_2\text{O}$  or via indirect recombination via  $\text{Cu}_i$  defects, which capture electrons and result into substantial Shockley–Read–Hall recombination

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